

# **BASIC AND APPLIED THERMODYNAMICS**

**Second Edition**

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*Madhurima Basu Thakur  
and*

*Abhiroop Guha*

*with love and blessings*



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# Preface

The author feels greatly encouraged at the good response of the book *Engineering Thermodynamics*. The present book is a further updated and reorganized version, retaining the framework and style of presentation of the earlier book. The last four chapters of the book, viz., Statistical Thermodynamics, Irreversible Thermodynamics, Kinetic Theory of Gases and Transport Properties of Gases are of little relevance in undergraduate courses on Thermodynamics. Hence, the last four chapters of the book and also the topics not important for UG courses have been omitted in this edition and three new chapters on **Gas Compressors, Internal Combustion Engines** and **Gas Turbines and Propulsion Systems** have been included instead in this edition in conformity with the UG curricula of many colleges in Applied Thermodynamics and also the recommendation of the reviewers. In addition to contributing as a basic course, the book can be used for a further advanced course at a senior undergraduate or graduate level with topics selectively chosen.

The **first eight chapters** of the book are devoted to a thorough treatment of the basic principles and concepts of classical thermodynamics. The second law and entropy have been introduced using the concept of heat engine. **Chapters 9 and 10** present the properties of substances. **Chapter 11** gives the general thermodynamic relationships among properties. A detailed analysis of power and refrigeration cycles is given in **chapters 12 to 14**. **Chapter 15** deals with psychrometrics and air-conditioning systems, while reactive systems are analyzed in **Chapter 16**. **Chapters 17 and 18** deal with compressible fluid flow and heat transfer respectively. Gas compressors are discussed in **Chapter 19**. Internal combustion engines and their operating principles are explained in **Chapter 20**. **Chapter 21** is devoted to gas turbines and propulsion systems. Finally, **Chapter 22** discusses the transport processes in gases.

The style of presentation and inclusion of short questions, solved and exercise problems have been retained. Many illustrative examples are solved and many problems are provided in each chapter to aid comprehension and to stimulate the interest of the students. **Multiple Choice Questions** on the subject have been added at the end. Throughout the text, SI units have been used. Tables and charts given in the Appendices are also in SI units.

The book also has an accompanying website which can be accessed at <http://www.mhhe.com/nag/bat2e>.

The author hopes that the book will be useful to the students and teachers alike. The study on Steam like Steam Boilers, Steam Turbines and Condensers will be considered for inclusion in future depending on the demand after omitting and editing some of the existing material.

I am thankful to Ms Surabhi Shukla and Ms Devshree Lohchab for their arduous task of syllabi research and competitive analysis which helped me a great deal in preparing this revision. I would also like to thank Ms Sohini Mukherjee for her deft editorial services. Mr P L Pandita too deserves a special mention for his efficient handling of the production process. I am also indebted to the following reviewers for taking out time to review the book.

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Any constructive criticism as well as suggestions for improvement of the book will be welcome and gratefully acknowledged.

The present edition of the book is being dedicated to my grandchildren, Kumari Madhurima Basu Thakur and Sri Abhiroop Guha, with love and blessings.

# CONTENT HIGHLIGHTS

## New Chapters

New chapters on *Gas Compressors*, *Internal Combustion Engines* and *Gas Turbines and Propulsion Systems* included in the second edition would help engineers comprehend the role of compression processes, IC engines and propulsion systems in thermodynamics.

C H A P T E R

## 10 Gas Compressors

A gas compressor is a device in which work is done on the gas to raise its pressure, with an appreciable increase in its density. The compression of gases is an important process in many power plants, refrigeration plants, and industrial plants. Industrial uses occur in connection with compressed air motors for tools, pumps, and machinery.

C H A P T E R

## 20 Internal Combustion Engines

20.1 INTERNAL AND EXTERNAL COMBUSTION ENGINES

C H A P T E R

## 21 Gas Turbines and Propulsion Systems

The economics of power generation by gas turbines is now quite attractive due to low capital cost and its high reliability and flexibility in operation. Another outstanding feature is its capability of quick starting and using a wide variety of fuels from natural gas to residual oil or powdered coal. Its consumption of lubricating oil is quite low because of the absence of rubbing and reciprocating parts, and the balancing does not pose a major problem. Due to better materials being made available and with the use of adequate blade cooling, the inlet gas temperature to the gas turbine (GT) blades can now exceed 1200°C as a result of which the overall efficiency of a GT plant can be about 35%, almost the same as that of a conventional steam power plant.

Because of its low weight per unit power, gas turbine is exclusively used to drive aviation system of all kinds of aircraft. It is also being increasingly used in land vehicles like buses and trucks and also to drive locomotives and marine ships. In oil and gas industries, the gas turbine is widely employed to drive auxiliaries like compressors, blowers and pumps.

### 21.1 CLOSED CYCLE AND OPEN CYCLE PLANTS

The essential components of a gas turbine (GT) power plant are the compressor, combustion chamber and the turbine. The air standard cycle of a GT plant is the Brayton cycle.

A GT plant can either be open or closed. Figure 21.1 shows the arrangement of an open-cycle plant which is more common. The compressor takes in ambient air and raises its pressure. The temperature of air is increased when it flows through a combustion chamber where a fossil fuel is burned or a heat exchanger (nuclear fuel being used as a source of energy) is present. The high-pressure, high-temperature working fluid, mostly a gas, enters a turbine where it expands to a low-pressure (equal to or a little above the atmospheric pressure) fluid. In an open unit, the gas is released from the turbine to the surroundings and in a closed unit, the working fluid is cooled in a cooler after the exhaust from the turbine and is returned to the compressor.

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and blowers, fork lifts  
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### 14.3.5 Components in a Vapour Compression Plant

(a) **Condenser** It is in the condenser that heat is rejected in a vapour compression plant. Desuperheating of the vapour takes place in the discharge line and in the first few coils of the condenser. It is followed by the condensation of the vapour at the saturation temperature. Then, subcooling may take place near the bottom. However, the sensible heat of the desuperheating and subcooling processes is quite small compared to the latent heat of condensation.

The type of condenser is generally characterized by the cooling medium used. There are three types of condensers: (i) air-cooled condensers, (ii) water-cooled condensers, and (iii) evaporative condensers. An air-cooled condenser is used in small self-contained units below 5 TR because of high power consumption and large fan noise.

Water-cooled condensers can be of three types, viz., shell and tube, shell and coil and double tube. The shell-and-tube type with water flowing through tubes and the refrigerant condensing in the shell is the most commonly used condenser (Fig. 14.17).

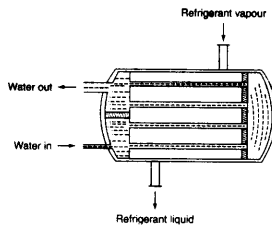


Fig. 14.17 Schematic representation of a two-pass water-cooled shell and tube condenser

(b) **Expansion Device** An expansion device in a refrigeration system normally serves two functions, viz., (i) it reduces the pressure from the evaporator to the condenser, and (ii) it regulates the flow of the refrigerant to the evaporator depending on the load. It is essentially a restriction offering resistance to flow so that the pressure drops.

### 14.3.7 Multi-Evaporator Systems

A situation often arises when varied types of cooling loads are connected to the same refrigeration system. Each load may need an evaporator working at a different refrigeration temperature. A two-evaporator single-compressor system with individual expansion valves for each evaporator and one compressor is shown in Fig. 14.22(a) and the corresponding  $p$ - $h$  diagram is shown in Fig. 14.22(b). The mass flow rates through evaporators 1 and 2 are

$$m_1 = \frac{Q_{e1}}{h_1 - h_4} \quad \text{and} \quad m_2 = \frac{Q_{e2}}{h_2 - h_4}$$

The enthalpy of liquid-vapour mixture entering the compressor is

$$h_3 = \frac{m_1 h_1 + m_2 h_2}{m_1 + m_2}$$

and the work input is

$$W = (m_1 + m_2) (h_2 - h_1)$$

### 14.3.8 Cascade

Two important of the two med To have reason

### 14.6 ELECTROLUX REFRIGERATOR

An electrolyx refrigerator works on three-fluid system. There is no circulation pump. The total pressure is the same throughout the system. The third fluid remains mainly in the evaporator, which reduces the partial pressure of refrigerant to enable it to evaporate at low pressure and hence low temperature.

The schematic diagram of an electrolyx refrigerator working on  $\text{NH}_3$ - $\text{H}_2\text{O}$  system with  $\text{H}_2$  as the third fluid is shown in Fig. 14.30. Liquid  $\text{NH}_3$  evaporates in the evaporator in the presence of  $\text{H}_2$ . Hydrogen is chosen because it is non-corrosive and insoluble in water. Thus a complete leakproof silent system is achieved.

A thermosiphon bubble pump is used to lift the weak aqua solution from the generator to the separator. The discharge tube from the generator is extended down below the liquid level in the generator. The bubbles rise and carry slugs of weak  $\text{NH}_3$ - $\text{H}_2\text{O}$  solution into the separator. Two U-bend constrictions are provided as vapour-locks or liquid-seal to prevent  $\text{H}_2$  from getting into the high side of the condenser.

The partial pressure of  $\text{H}_2$  provides the pressure difference of  $\text{NH}_3$  between the condenser and evaporator.

Accordingly, we have the following:

In the condenser, there is the pure  $\text{NH}_3$  vapour pressure which is the total pressure.

In the evaporator,  $\text{NH}_3$  vapour pressure = total pressure minus the partial pressure of  $\text{H}_2$ .

For example, let us consider the condenser temperature corresponding vapour pressure of  $\text{NH}_3$  are

Condenser,  $p_c = 20.33$  bar

Evaporator exit,  $p_e = 2.36$  bar

The approximate pressures in various parts of the

The vapours leaving the generator top are assumed to be 15.5 bar of  $\text{NH}_3$

Product	Heat of Respiration of Products in kJ/kg per 24 hours	
	Storage temperature 0°C	15.6°C
Apples	312-1500	2300-8215
Cabbage	1248	4265
Carrots	2183	8420
Cauliflower	4680	10,500
Grapes	416	2290
Lemon	520	2390
Orange	728	2495
Potato	1330	1960
Tomato	1040	5820

### 15.7 AIR-CONDITIONING SYSTEMS

Among many applications of air conditioning, the important ones are

- Cold storage
- Industrial air conditioning
- Comfort air conditioning

## New Topics

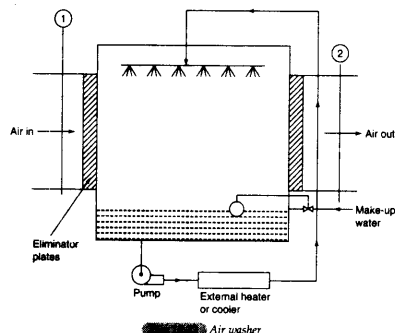
Coverage on Chapter 14 is enhanced by the insertion of the topics of Expansion Device, Multi-Evaporator Systems and Electrolux Refrigerator. Two essential topics on Air-Conditioning Systems and Air Washer are included in Chapter 15.

### 15.4.13 Air Washer

An air washer is shown schematically in Fig. 15.22. It involves the flow of air through a spray of water. During the course of flow, the air may be cooled or heated, humidified or dehumidified, or simply adiabatically saturated, depending on the mean surface temperature of water spray. The water is, accordingly, cooled or heated externally, or simply recirculated by a pump. Make-up water is added for any loss due to humidification. Eliminator plates are provided to minimise the loss of water droplets.

The thermodynamic changes of state of air along paths 1-2 in an air washer are shown in Fig. 15.23. The following processes are possible:

- Process 1-2A Heating and humidification ( $t_2 > t_1$ ).
- Process 1-2B Humidification ( $t_2 = t_1$ ).
- Process 1-2C Cooling and humidification ( $t_2' < t_1 < t_2$ ) where  $t_2'$  is the WBT and  $t_1$  the DBT.
- Process 1-2D Adiabatic saturation ( $t_2' = t_1$ ).
- Process 1-2E Cooling and humidification ( $t_2 < t_1 < t_2'$ ) where  $t_2$  is the DPT.





## Solved Examples

Solved examples in various chapters at the end of the theory portion help the students understand the applicability of engineering calculations for thermodynamic applications.

### Solved Examples

#### Example 2.1

Two mercury-in-glass thermometers are made of identical materials and are accurately calibrated at 0°C and 100°C. One has a tube of constant diameter, while the other has a tube of conical bore, ten per cent greater in diameter at 100°C than at 0°C. Both thermometers have the length between 0 and 100 subdivided uniformly. What will be the straight bore thermometer read in a place where the conical bore thermometer reads 50°C?

**Solution** The volume of mercury in the tube at  $t^\circ\text{C}$ ,  $V_t$ , is given by

$$V_t = V_0 [1 + \beta(t - t_0)]$$

where  $V_0$  is the volume of mercury at 0°C,  $\beta$  is the coefficient of volume expansion of mercury, and  $t_0$  is the ice point temperature which is 0°C. The volume change of glass is neglected.

Therefore  $V_t - V_0 = \beta V_0 t$

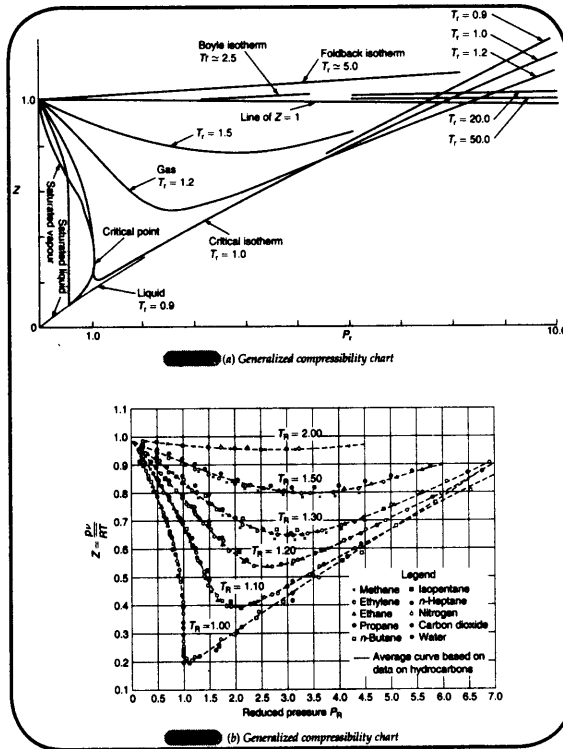
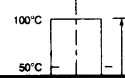
The temperature  $t$  is thus a linear function of volume change of mercury ( $V_t - V_0$ ).

Therefore  $\Delta V_{0-100} = \beta V_0 \cdot 100$

$$\Delta V_{0-50} = \beta V_0 \cdot 50$$

$$\frac{\Delta V_{0-50}}{\Delta V_{0-100}} = \frac{1}{2}$$

$$\therefore \frac{\Delta V_{0-50}}{\Delta V_{0-100}} = \frac{1}{2}$$



## Illustrations

Detailed illustrations are necessary for any book on engineering. Besides the existing ones, 133 new figures have been included in this edition to let students have a clear grasp of the contents.

## Review Questions

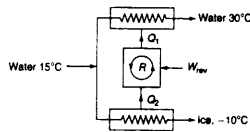
Review questions are provided at the end of each chapter. They cover the contents of the entire chapter. These review questions are very helpful to teachers in setting up examination papers and class work assignments.

### Review Questions

- What do you understand by high grade energy and low grade energy?
- What is available energy and unavailable energy?
- Who propounded the concept of availability?
- What is the available energy referred to a cycle?
- Show that there is a decrease in available energy when heat is transferred through a finite temperature difference.
- Deduce the expression for available energy from a finite energy source at temperature  $T$  when the environmental temperature is  $T_0$ .
- What do you understand by exergy and energy?
- What is meant by quality of energy?
- Why is exergy of a fluid at a higher temperature more than that at a lower temperature?
- How does the exergy value provide a useful measure of the quality of energy?
- Why is the second law called the law of degradation of energy?
- Energy is always conserved, but its quality is always degraded. Explain.
- What do you understand by the dead state?
- What is meant by availability?
- Give expressions for availabilities of a closed system and a steady flow open system.
- What are Helmholtz function and Gibbs function?
- What is the availability in a chemical reaction if the temperature before and after the reaction is the same and equal to the temperature of the surroundings?
- When is the availability of a chemical reaction equal to the decrease in the Gibbs function?
- Derive the expression for irreversibility or exergy loss in a process executed by: (a) a closed system, (b) a steady flow system, in a given environment.
- State and explain the Gouy-Stodola theorem.
- How is heat transfer through a finite temperature difference equivalent to the destruction of its availability?
- Considering the steady and adiabatic flow of an ideal gas through a pipe, show that the rate of decrease in availability or lost work is proportional to the pressure drop and the mass flow.

**Problems**

- 8.1 What is the maximum useful work which can be obtained when 100 kJ are abstracted from a heat reservoir at 675 K in an environment at 288 K? What is the loss of useful work if (a) a temperature drop of 50°C is introduced between the heat source and the heat engine, on the one hand, and the heat engine and the heat sink, on the other, (b) the source temperature drops by 50°C and the sink temperature rises by 50°C during the heat transfer process according to the linear law  $\frac{dQ}{dT} = \text{constant}$ ?  
*Ans.* 57.38 kJ, (a) 11.46 kJ, (b) 5.5 kJ
- 8.2 In a steam generator, water is evaporated at 260°C, while the combustion gas ( $c_p = 1.08$  kJ/kg K) is cooled from 1300°C to 320°C. The surroundings are at 30°C. Determine the loss in available energy due to the above heat transfer per kg of water evaporated. (Latent heat of vaporization of water at 260°C = 1662.5 kJ/kg.)  
*Ans.* 443.6 kJ
- 8.3 Exhaust gases leave an internal combustion engine at 800°C and 1 atm, after having done 1050 kJ of work per kg of gas in the engine ( $c_p$  of gas = 1.1 kJ/kg K). The temperature of the surroundings is 30°C. (a) How much available energy per kg of gas is lost by throwing away the exhaust gases? (b) What is the ratio of the lost available energy to the engine work? *Ans.* (a) 425.58 kJ, (b) 0.405
- 8.7 A lead storage battery used in an automobile is able to deliver 5.2 MJ of electrical energy. This energy is available for starting the car. Let compressed air be considered for doing an equivalent amount of work in starting the car. The compressed air is to be stored at 7 MPa, 25°C. What is the volume of the tank that would be required to let the compressed air have an availability of 5.2 MJ? For air,  $p \cdot v = 0.287 T$ , where  $T$  is in K,  $p$  in kPa, and  $v$  in  $\text{m}^3/\text{kg}$ .  
*Ans.* 0.228  $\text{m}^3$
- 8.8 Ice is to be made from water supplied at 15°C by the process shown in Fig. P 8.8. The final temperature of the ice is  $-10^\circ\text{C}$ , and the final temperature of the water that is used as cooling water in the condenser is 30°C. Determine the minimum work required to produce 1000 kg of ice. Take  $c_p$  for water = 4.187 kJ/kg K,  $c_p$  for ice = 2.093 kJ/kgK, and latent heat of fusion of ice = 334 kJ/kg.  
*Ans.* 31.92 MJ



**Problems with Answers**

A set of problems with answers is given in all the chapters. These help the students test their comprehension of the concepts.

**Appendices**

A total of 11 Appendices are given at the end of the book which contain relevant data, charts and tables related to thermodynamics.

**Appendix A**

TABLE A.1 STEAM TABLES\*

Saturated Steam: Temperature Table

Temp. $t$ , °C	Specific Volume $v$ , $\text{m}^3/\text{kg}$		Enthalpy $h$ , kJ/kg		Entropy $s$ , kJ/kg K	
	Sat. Liquid	Sat. Vapor	Sat. Liquid	Sat. Vapor	Sat. Liquid	Sat. Vapor
0.01	0.0113	0.001000	206.132	206.132	0.0000	0.0000
5	0.0113	0.001000	187.316	187.316	0.0000	0.0000
10	0.0113	0.001000	168.377	168.377	0.0000	0.0000
15	0.0113	0.001000	149.438	149.438	0.0000	0.0000
20	0.0113	0.001000	130.499	130.499	0.0000	0.0000
25	0.0113	0.001000	111.560	111.560	0.0000	0.0000
30	0.0113	0.001000	92.621	92.621	0.0000	0.0000
35	0.0113	0.001000	73.682	73.682	0.0000	0.0000
40	0.0113	0.001000	54.743	54.743	0.0000	0.0000
45	0.0113	0.001000	35.804	35.804	0.0000	0.0000

\* Adapted from Joseph H. Keenan, Frederick G. Keyes, Philip G. Hill, and Joun G. Moore, Steam Tables, John Wiley and Sons, New York, 1969.

## Multiple-Choice Questions

Over 60 MCQs have been added at the end of the book to let students have a quick revision of the fundamental concepts.

## Multiple-Choice Questions

- Lead compounds were earlier used to be added to gasoline in S.I. engines so as to
  - reduce hydrocarbon emissions
  - reduce knocking
  - reduce exhaust gas temperature
  - increase power output
- Decrease of air-fuel ratio in SI engines results in
  - an increase  $\text{NO}_x$
  - a decrease of CO and unburnt hydrocarbon
  - an increase of CO and unburnt hydrocarbon
  - none of the above
- If  $N$  is the rpm, the number of power strokes per minute in a four-stroke engine is
  - $2N$
  - $N/2$
  - $N$
  - $4N$
- Volumetric efficiency is a measure of
  - speed of the engine
  - power of the engine
  - breathing capacity of the engine
  - pressure rise in the cylinder
- If  $N$  is the rpm, the number of power strokes per minute in a two-stroke engine is
  - $N$
  - $N/2$
  - $2N$
  - $4N$
- The volumetric efficiency of a well-designed engine is in the range of
  - 30 to 40%
  - 40 to 60%
  - 60 to 70%
  - 75 to 90%
- If  $L$  is the stroke and  $N$  is the rpm, the mean piston speed of a two-stroke engine is
  - $LN$
  - $LN/2$
  - $2LN$
  - none of the above

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## Bibliography

A comprehensive list of references in the form of textbooks and journals with the title of the article is given at the end of the book.



# 1 Introduction

Thermodynamics is the science of energy transfer and its effect on the physical properties of substances. It is based upon observations of common experience which have been formulated into thermodynamic laws. These laws govern the principles of energy conversion. The applications of the thermodynamic laws and principles are found in all fields of energy technology, notably in steam and nuclear power plants, internal combustion engines, gas turbines, air conditioning, refrigeration, gas dynamics, jet propulsion, compressors, chemical process plants, and direct energy conversion devices.

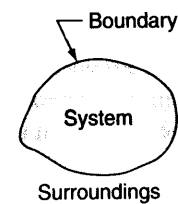
## 1.1 MACROSCOPIC VS MICROSCOPIC VIEWPOINT

There are two points of view from which the behaviour of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered, without the events occurring at the molecular level being taken into account. From the microscopic point of view, matter is composed of myriads of molecules. If it is a gas, each molecule at a given instant has a certain position, velocity, and energy, and for each molecule these change very frequently as a result of collisions. The behaviour of the gas is described by summing up the behaviour of each molecule. Such a study is made in *microscopic* or *statistical thermodynamics*. *Macroscopic thermodynamics* is only concerned with the effects of the action of many molecules, and these effects can be perceived by human senses. For example, the macroscopic quantity, pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit area. The effects of pressure can be felt. The macroscopic point of view is not concerned with the action of individual molecules, and the force on a given unit area can be measured by using, e.g. a pressure gauge. These macroscopic observations are completely independent of the assumptions regarding the nature of matter. All the results of classical or macroscopic thermodynamics can, however, be derived from the microscopic and statistical study of matter.

## 1.2 THERMODYNAMIC SYSTEM AND CONTROL VOLUME

A thermodynamic *system* is defined as a quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem. Everything external to the system is called the *surroundings* or the *environment*. The system is separated from the surroundings by the system boundary (Fig. 1.1). The boundary may be either *fixed* or *moving*. A system and its surroundings together comprise a *universe*.

There are three classes of systems: (a) closed system, (b) open system and (c) isolated system. The *closed system* (Fig. 1.2) is a system of fixed mass. There is no mass transfer across the system boundary. There may be energy transfer into or out of the system.



**Fig. 1.1** A thermodynamic system

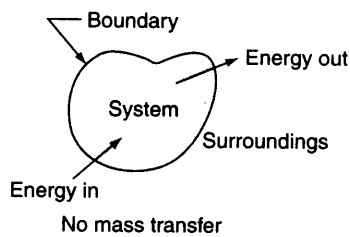


Fig. 1.2 A closed system

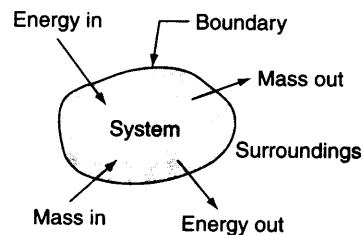


Fig. 1.3 An open system

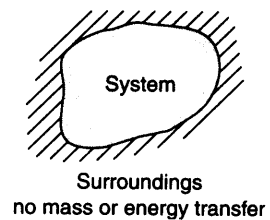


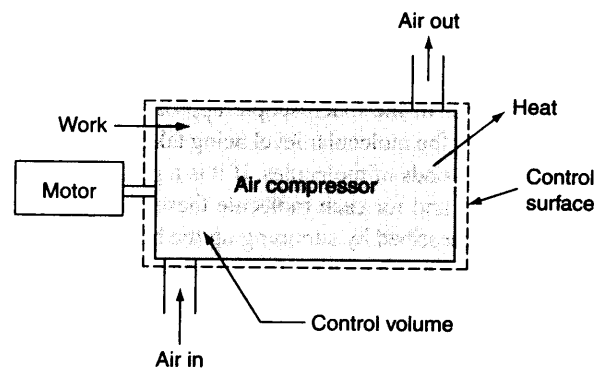
Fig. 1.4 An isolated system

A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system. The *open system* (Fig. 1.3) is one in which matter crosses the boundary of the system. There may be energy transfer also. Most of the engineering devices are generally open systems, e.g., an air compressor in which air enters at low pressure and leaves at high pressure and there are energy transfers across the system boundary. The *isolated system* (Fig. 1.4) is one in which there is no interaction between the system and the surroundings. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary.

If a system is defined as a certain quantity of matter, then the system contains the same matter and there can be no transfer of mass across its boundary. However, if a system is defined as a region of space within a prescribed boundary, then matter can cross the system boundary. While the former is called a closed system, the latter is an open system.

For thermodynamic analysis of an open system, such as an air compressor (Fig. 1.5), attention is focussed on a certain volume in space surrounding the compressor, known as the *control volume*, bounded by a surface called the *control surface*. Matter as well as energy crosses the control surface.

A closed system is a system closed to matter flow, though its volume can change against a flexible boundary. When there is matter flow, then the system is considered to be a volume of fixed identity, the control volume. There is thus no difference between an open system and a control volume.



Control volume and control surface

### 1.3 THERMODYNAMIC PROPERTIES, PROCESSES AND CYCLES

Every system has certain characteristics by which its physical condition may be described, e.g., volume, temperature, pressure, etc. Such characteristics are called *properties* of the system. These are all *macroscopic* in nature. When all the properties of a system have definite values, the system is said to exist at a definite *state*. Properties are the coordinates to describe the state of a system. They are the state variables of the system. Any operation in which one or more of the properties of a system changes is called a *change of state*. The succession of states passed through during a change of state is called the *path* of the change

of state. When the path is completely specified, the change of state is called a *process*, e.g., a constant pressure process. A thermodynamic *cycle* is defined as a series of state changes such that the final state is identical with the initial state (Fig. 1.6).

Properties may be of two types. *Intensive properties* are independent of the mass in the system, e.g. pressure, temperature, etc. *Extensive properties* are related to mass, e.g., volume, energy, etc. If mass is increased, the values of the extensive properties also increase. Specific extensive properties, i.e., extensive properties per unit mass, are intensive properties, e.g., specific volume, specific energy, density, etc.

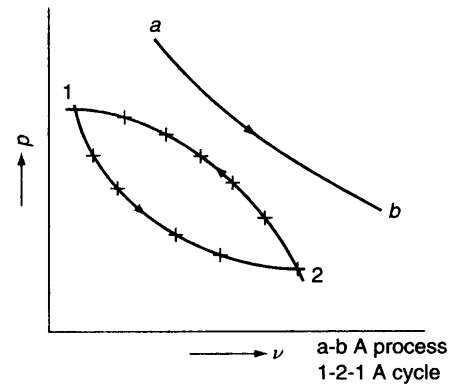


Fig. 1.6 A process and a cycle

#### 1.4 HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

A quantity of matter homogeneous throughout in chemical composition and physical structure is called a *phase*. Every substance can exist in any one of the three phases, viz., solid, liquid and gas. A system consisting of a single phase is called a *homogeneous system*, while a system consisting of more than one phase is known as a *heterogeneous system*.

#### 1.5 THERMODYNAMIC EQUILIBRIUM

A system is said to exist in a state of *thermodynamic equilibrium* when no change in any macroscopic property is registered, if the system is isolated from its surroundings.

An isolated system always reaches in course of time a state of thermodynamic equilibrium and *can never depart from it spontaneously*.

Therefore, there can be no *spontaneous change in any macroscopic property* if the system exists in an equilibrium state. Thermodynamics studies mainly the properties of physical systems that are found in equilibrium states.

A system will be in a state of thermodynamic equilibrium, if the conditions for the following three types of equilibrium are satisfied:

- (a) Mechanical equilibrium      (b) Chemical equilibrium      (c) Thermal equilibrium

In the absence of any unbalanced force within the system itself and also between the system and the surroundings, the system is said to be in a state of *mechanical equilibrium*. If an unbalanced force exists, either the system alone or both the system and the surroundings will undergo a change of state till mechanical equilibrium is attained.

If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to exist in a state of *chemical equilibrium*.

When a system existing in mechanical and chemical equilibrium is separated from its surroundings by a diathermic wall (diathermic means 'which allows heat to flow') and if there is no spontaneous change in any property of the system, the system is said to exist in a state of *thermal equilibrium*. When this is not satisfied, the system will undergo a change of state till thermal equilibrium is restored.

When the conditions for any one of the three types of equilibrium are not satisfied, a system is said to be in a *nonequilibrium state*. If the nonequilibrium of the state is due to an unbalanced force in the interior of a system or between the system and the surroundings, the pressure varies from one part of the system to another. There is no single pressure that refers to the system as a whole. Similarly, if the nonequilibrium is because of the temperature of the system being different from that of its surroundings, there is a nonuniform temperature distribution set up within the system and there is no single temperature that stands for the system as a whole. It can thus be inferred that when the conditions for thermodynamic equilibrium are not satisfied, the states passed through by a system cannot be described by thermodynamic properties which represent the system as a whole.

Thermodynamic properties are the macroscopic coordinates defined for, and significant to, only thermodynamic equilibrium states. Both classical and statistical thermodynamics study mainly the equilibrium states of a system.

## 1.6 QUASI-STATIC PROCESS

Let us consider a system of gas contained in a cylinder (Fig. 1.7). The system initially is in an equilibrium state, represented by the properties  $p_1$ ,  $v_1$ ,  $t_1$ . The weight on the piston just balances the upward force exerted by the gas. If the weight is removed, there will be an unbalanced force between the system and the surroundings, and under gas pressure, the piston will move up till it hits the stops. The system again comes to an equilibrium state, being described by the properties  $p_2$ ,  $v_2$ ,  $t_2$ . But the intermediate states passed through by the system are nonequilibrium states which cannot be described by thermodynamic coordinates. Figure 1.8 shows points 1 and 2 as the initial and final equilibrium states joined by a dotted line, which has got no meaning otherwise. Now if the single weight on the piston is made up of many very small pieces of weights (Fig. 1.9), and these weights are removed one by one very slowly from the top of the piston, at any instant of the upward travel of the piston, if the gas system is isolated, the departure of the state of the system from the thermodynamic equilibrium state will be infinitesimally small. So every state passed through by the system will be an equilibrium state. Such a process, which is but a locus of all the equilibrium points passed through by the system, is known as a *quasi-static process* (Fig. 1.10), 'quasi' meaning 'almost'. *Infinite slowness is the characteristic feature of a quasi-static process*. A quasi-static process is thus a succession of equilibrium states. A quasi-static process is also called a *reversible process*.

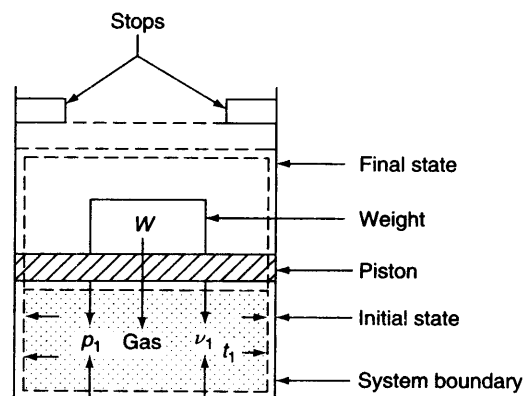


Fig. 1.7 Transition between two equilibrium states by an unbalanced force

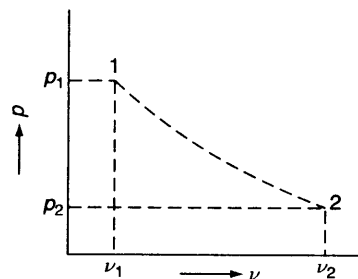


Fig. 1.8 Plot representing the transition between two equilibrium states



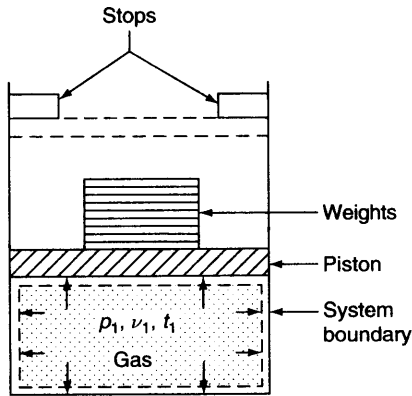


Fig. 1.9 Infinitely slow transition of a system by infinitesimal force

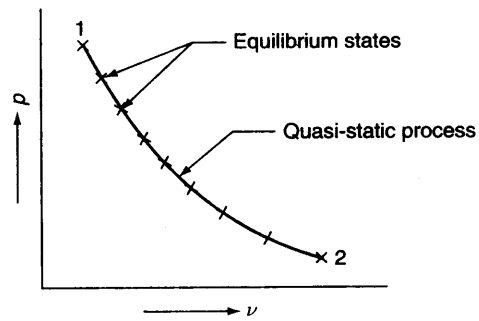


Fig. 1.10 A quasi-static process

### 1.7 PURE SUBSTANCE

A *pure substance* is defined as one that is homogeneous and invariable in chemical composition throughout its mass. The relative proportions of the chemical elements constituting the substance are also constant. Atmospheric air, steam-water mixture and combustion products of a fuel are regarded as pure substances. But the mixture of air and liquid air is not a pure substance, since the relative proportions of oxygen and nitrogen differ in the gas and liquid phases in equilibrium.

The state of a pure substance of given mass can be fixed by specifying two properties, provided the system is in equilibrium. This is known as the 'two-property rule'. The state can thus be represented as a point on thermodynamic property diagrams. Once any two properties of a pure substance are known, other properties can be determined from the available thermodynamic relations.

### 1.8 CONCEPT OF CONTINUUM

From the macroscopic viewpoint, we are always concerned with volumes which are very large compared to molecular dimensions. Even a very small volume of a system is assumed to contain a large number of molecules so that statistical averaging is meaningful and a property value can be assigned to it. Disregarding the behaviour of individual molecules, matter is here treated as continuous. Let us consider the mass  $\delta m$  in a volume  $\delta V$  surrounding the point  $P$  (Fig. 1.11). The ratio  $\delta m/\delta V$  is the average mass density of the system within the volume  $\delta V$ . We suppose that at first  $\delta V$  is rather large, and is subsequently shrunk about the point  $P$ . If we plot  $\delta m/\delta V$  against  $\delta V$ , the average density tends to approach an asymptote as  $\delta V$  increases (Fig. 1.12). However, when  $\delta V$  becomes so small as to contain relatively few molecules, the average density fluctuates substantially with time as molecules pass into and out of the volume in random motion, and so it is impossible to speak of a definite value of  $\delta m/\delta V$ . The smallest volume which may be regarded as continuous is  $\delta V'$ . The density  $\rho$  of the system at a point is thus defined as

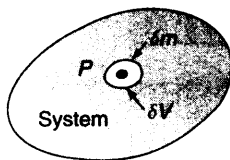


Fig. 1.11

$$\rho = \lim_{\delta V \rightarrow \delta V'} \frac{\delta m}{\delta V} \quad (1.1)$$

Similarly, the fluid velocity at a point P is defined as the instantaneous velocity of the centre of gravity of the smallest continuous volume  $\delta V'$ .

The concept of continuum loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel, as, for instance, in highly rarefied gases encountered in high vacuum technology, in rocket flights at high altitudes and in electron tubes. In most engineering applications, however, the assumption of a continuum is valid and convenient, and goes hand in hand with the macroscopic point of view.

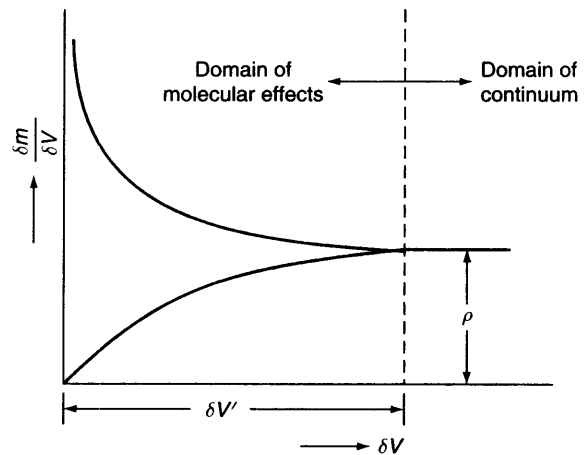


Fig.1.12 Definition of the macroscopic property, density

### 1.9 THERMOSTATICS

The science of thermodynamics deals with systems existing in thermodynamic equilibrium states which are specified by properties. Infinitely slow quasi-static processes executed by systems are only meaningful in thermodynamic plots. The name 'thermodynamics' is thus said to be a misnomer, since it does not deal with the dynamics of heat, which is nonquasi-static. The name 'thermostatitics' then seems to be more appropriate. However, most of the real processes are dynamic and nonquasi-static, although the initial and final states of the system might be in equilibrium. Such processes can be successfully dealt with by the subject. Hence, the term 'thermodynamics' is not inappropriate.

### 1.10 UNITS AND DIMENSIONS

In the present text, the SI (System International) system of units has been used. The basic units in this system are given in Table 1.1.

Table 1.1 System: Basic Units		
Quantity	Unit	Symbol
Length (L)	Metre	m
Mass (M)	Kilogramme	kg
Time (t)	Second	s
Amount of substance	Mole	mol
Temperature (T)	Kelvin	K
Electric current	Ampere	A
Luminous intensity	Candela	cd
Plane angle	Radian	rad
Solid angle	Steradian	sr

The dimensions of all other quantities are derived from these basic units which are given in Table 1.2.

Quantity	Unit	Symbol	Alternative unit	In basic units
Force (F)	Newton	N		kg m/s <sup>2</sup>
Energy (E)	Joule	J	Nm	kg m <sup>2</sup> /s <sup>2</sup>
Power	Watt	W	J/s	kg m <sup>2</sup> /s <sup>3</sup>
Pressure	Pascal	Pa	N/m <sup>2</sup>	kg/(m s <sup>2</sup> )
Frequency	Hertz	Hz		s <sup>-1</sup>
Electric charge	Coulomb	C		As
Electric potential	Volt	V	W/A = J/C	kg m <sup>2</sup> /(s <sup>3</sup> A)
Capacitance	Farad	F	C/V	s <sup>4</sup> A <sup>2</sup> /(kg m <sup>2</sup> )
Electrical resistance	Ohm	Ω	V/A	kg m <sup>2</sup> /(s <sup>3</sup> A <sup>2</sup> )
Magnetic flux	Weber	Wb	Vs	kg m <sup>2</sup> /(s <sup>2</sup> A)
Magnetic flux density	Tesla	T	Wb/m <sup>2</sup>	kg/(s <sup>2</sup> A)
Inductance	Henry	H	Wb/A	kg m <sup>2</sup> /(s <sup>2</sup> A <sup>2</sup> )

It is often convenient and desirable to use multiples of various units, the standard list of which is given in Table 1.3.

Factor	Prefix	Factor	Prefix
10 <sup>12</sup>	tera, T	10 <sup>-3</sup>	milli, m
10 <sup>9</sup>	giga, G	10 <sup>-6</sup>	micro, μ
10 <sup>6</sup>	mega, M	10 <sup>-9</sup>	nano, n
10 <sup>3</sup>	kilo, k	10 <sup>-12</sup>	pico, p

### 1.10.1 Force

The force acting on a body is defined by Newton's second law of motion. The unit of force is the newton (N). A force of one newton produces an acceleration of 1 ms<sup>-2</sup> when applied to a mass of 1 kg.

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

The weight of a body ( $W$ ) is the force with which the body is attracted to the centre of the earth. It is the product of its mass ( $m$ ) and the local gravitational acceleration ( $g$ ), i.e.  $W = mg$

The value of  $g$  at sea level is 9.80665 m/s<sup>2</sup>. The mass of a substance remains constant with elevation, but its weight varies with elevation.

### 1.10.2 Pressure

Pressure is the normal force exerted by a system against unit area of the bounding surface. If  $\delta A$  is a small area and  $\delta A'$  is the smallest area from continuum consideration, and  $\delta F_n$  is the component of force normal to  $\delta A$  (Fig. 1.13), the pressure  $p$  at a point on the wall is defined as

$$p = \lim_{\delta A \rightarrow \delta A'} \frac{\delta F_n}{\delta A}$$

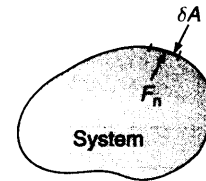


Fig. 1.13 Definition of pressure

The pressure  $p$  at a point in a fluid in equilibrium is the same in all directions.

The unit for pressure in the SI system is the *pascal* (Pa), which is the force of one newton acting on an area of  $1 \text{ m}^2$ .

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

The unit of pascal is very small. Very often kilo-pascal (kPa) or mega-pascal (MPa) is used.

Two other units, not within the SI system of units, continue to be widely used. These are the *bar*, where

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa} = 0.1 \text{ MPa}$$

and the standard atmosphere, where  $1 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$

Most instruments indicate pressure relative to the atmospheric pressure, whereas the pressure of a system is its pressure above zero, or relative to a perfect vacuum. The pressure relative to the atmosphere is called *gauge pressure*. The pressure relative to a perfect vacuum is called *absolute pressure*.

$$\text{Absolute pressure} = \text{Gauge pressure} + \text{Atmospheric pressure}$$

When the pressure in a system is less than atmospheric pressure, the gauge pressure becomes negative, but is frequently designated by a positive number and called *vacuum*. For example, 16 cm vacuum will be

$$\frac{76 - 16}{76} \times 1.013 = 0.80 \text{ bar}$$

Figure 1.14 shows a few pressure measuring devices. Figure (a) shows the Bourdon gauge which measures the difference between the system pressure inside the tube and atmospheric pressure. It relies on the deformation of a bent hollow tube of suitable material which, when subjected to the pressure to be measured on the inside (and atmospheric pressure on the outside), tends to unbend. This moves a pointer through a suitable gear-and-lever mechanism against a calibrated scale. Figure (b) shows an open U-tube indicating gauge pressure, and Fig. (c) shows an open U-tube indicating vacuum. Figure (d) shows a closed U-tube indicating absolute pressure. If  $p$  is atmospheric pressure, this is a *barometer*. These are called U-tube manometers.

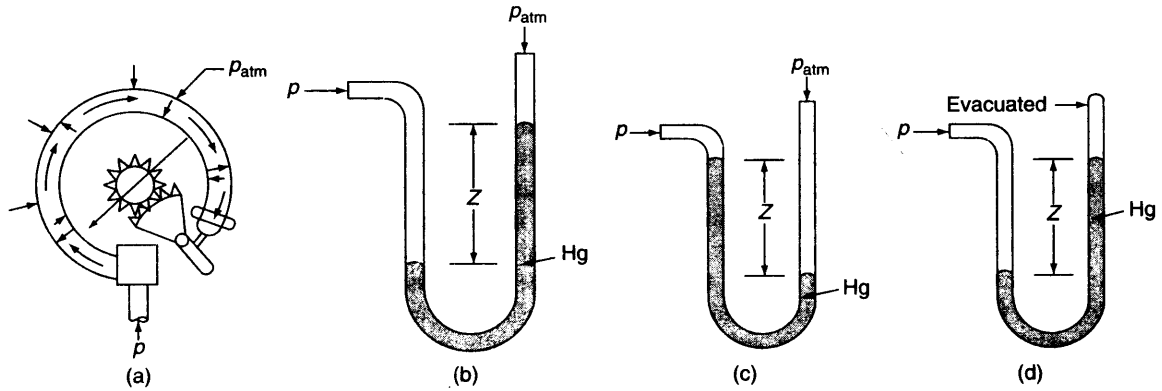
If  $Z$  is the difference in the heights of the fluid columns in the two limbs of the U-tube [Fig. (b) and Fig. (c)],  $\rho$  the density of the fluid and  $g$  the acceleration due to gravity, then from the elementary principle of hydrostatics, the gauge pressure  $p_g$  is given by

$$p_g = Z\rho g \left[ m \cdot \frac{\text{kg}}{\text{m}^3} \cdot \frac{\text{m}}{\text{s}^2} \right] = Z\rho g \text{ N/m}^2$$

If the fluid is mercury having  $\rho = 13,616 \text{ kg/m}^3$ , one metre head of mercury column is equivalent to a pressure of 1.3366 bar, as shown below

$$1 \text{ m Hg} = Z\rho g = 1 \times 13616 \times 9.81 = 1.3366 \times 10^5 \text{ N/m}^2 = 1.3366 \text{ bar}$$

The manometer is a sensitive, accurate and simple device, but it is limited to fairly small pressure differentials and, because of the inertia and friction of the liquid, is not suitable for fluctuating pressures, unless the rate of pressure change is small. A diaphragm-type pressure transducer along with a cathode ray oscilloscope can be used to measure rapidly fluctuating pressures.



**Fig. 1.14** Pressure gauges (a) bourdon gauge (b) open U-tube indicating gauge pressure (c) open U-tube indicating vacuum (d) closed U-tube indicating absolute pressure

### 1.10.3 Specific Volume and Density

Volume ( $V$ ) is the space occupied by a substance and is measured in  $\text{m}^3$ . The specific volume ( $v$ ) of a substance is defined as the volume per unit mass and is measured in  $\text{m}^3/\text{kg}$ . From continuum consideration the specific volume at a point is defined as  $v = \lim_{\delta V \rightarrow \delta V'} \frac{\delta V}{\delta m}$

where  $\delta V'$  is the smallest volume for which the system can be considered a continuum.

Density ( $\rho$ ) is the mass per unit volume of a substance, which has been discussed earlier, and is given in  $\text{kg}/\text{m}^3$ .

$$\rho = \frac{m}{v}$$

In addition to  $\text{m}^3$ , another commonly used unit of volume is the litre (l).

$$1\text{l} = 10^{-3} \text{m}^3$$

The specific volume or density may be given either on the basis of mass or in respect of mole. A *mole* of a substance has a mass numerically equal to the molecular weight of the substance. One g mol of oxygen has a mass of 32 g and 1 kg mol (or kmol) of nitrogen has a mass of 28 kg. The symbol  $\bar{v}$  is used for molar specific volume ( $\text{m}^3/\text{kmol}$ ).

### 1.10.4 Energy

Energy is the capacity to exert a force through a distance, and manifests itself in various forms. Engineering processes involve the conversion of energy from one form to another, the transfer of energy from place to place, and the storage of energy in various forms, utilizing a working substance.

The unit of energy in the SI system is Nm or J (joule). The energy per unit mass is the specific energy, the unit of which is J/kg.

### 1.10.5 Power

The rate of energy transfer or storage is called power. The unit of power is watt (W), kilowatt (kW) or megawatt (MW).

$$1 \text{ W} = 1 \text{ J/s} = 1 \text{ Nm/s}$$

$$1 \text{ kW} = 1000 \text{ W}$$

### 1.11 HISTORY OF THERMODYNAMICS

The latter half of the eighteenth century ushered man into the modern world of machinery and manufacture, and brought about cataclysmic changes in the social, economic and political life of the people. The historians have called it the *Industrial Revolution*. It began in England due to a fortuitous combination of many factors. There was bustling creative activity in science and technology during this period in England, with the appearance of a galaxy of some brilliant individuals. The invention of the steam engine gave an impetus to this activity, and for the first time made man free from the forces of nature. The name of Savery, Newcomen and notably James Watt are associated with this invention. Watt brought about considerable improvement in the performance of the steam engine, which began to be widely used in coal mines, iron metallurgy and textile mills. George Stephenson introduced steam engine for rail transport, and Robert Fulton used it in steam boats. A variety of industries grew up, and man gradually entered into the modern machine age. The advent of steam engine also gave stimulus to the birth of thermodynamics. Thermodynamics is said to be the “daughter” of the steam engine. [D. Bradley, “Thermodynamics – the Daughter of Steam”, Engineering Heritage, Vol. 2, I.Mech.E., London, 1966.]

There was once a young inventor who thought that he could produce energy out of nothing. “It is well known”, said he, “that an electrical motor converts electrical energy into mechanical energy and that an electric generator converts mechanical energy into electrical energy. Why not then, use the motor to run the generator and the generator to run the motor, and create thereby an endless supply of energy”? But this is never to happen. A hypothetical device which creates energy from nothing is called a perpetual motion machine of the first kind, a PPMI. Like the proverbial touchstone which changes all metals into gold, man attempted to find such a PPMI for long long years, but it turned out to be a wild goose chase. In fact, the development of the principle of conservation of energy has been one of the most significant achievements in the evolution of physical science. The first recognition of this principle was made by Leibnitz in 1693, when he referred to the sum of kinetic energy and potential energy in a gravitational force field. Energy is neither created nor destroyed. Energy manifests in various forms and gets transformed from one form to another. Through gentle metabolic processes, a day labourer gradually transforms the chemical energy of the food he eats and the oxygen he breathes into heat, sound and useful work. Work was always considered a form of energy. The concept of heat was, however a very actively debated scientific topic. Until the middle of the nineteenth century, heat was regarded as an invisible colourless, weightless, odourless fluid that flowed from a body of higher calorie to a body of lower calorie. This was known as the caloric theory of heat, first proposed in 1789 by Antoine Lavoisier (1743–1794), the father of modern chemistry. When an object became full of caloric, it was then said to be saturated with it. This was the origin of the terms “saturated liquid”, “saturated vapour” etc, that we use in thermodynamics today. The caloric was said to be conserved and it was indestructible. The caloric theory was, however, refuted and heat was confirmed as a form of energy in the middle of the nineteenth century leading to the formulation of the first law of thermodynamics. The names which stand out in the establishment of the first law were Benjamin Thompson (1753–1814), James Prescott Joule (1818–1889) and Julius Robert Mayer (1814–1878).

Benjamin Thompson, an American born in Massachusetts, did not support the revolt against the British during the American war of independence, and in 1775 he left for England where he took up government service. On a trip to Germany, he met the prince of Bavaria who offered him a job. He introduced many reforms in the government for which the title of Count von Rumford was conferred on him. While boring brass cannon hole, Count Rumford noticed that there was a continuous heat release. How could the caloric fluid be conserved, when it was being produced continuously by mechanical friction? From the established principle of conservation of mass, a true fluid can be neither created nor destroyed, so heat could not be a fluid if it could be continuously created in an object by mechanical friction. Rumford conceived that heat was “a kind of motion” and the hotness of an object was due to the vibrating motion of the particles in the objects. On his return to England, he

became a member of the Royal Society, and later founded the Royal Institution for the Advancement of Science. Rumford married the widow of Lavoisier and lived in Paris for the rest of his eventful life.

In the early forties of the nineteenth century, James P. Joule and Julius R. Mayer almost simultaneously set forth the idea that heat transfer and mechanical work were simply different forms of the same quantity, which we now recognize as energy in transit. In some modern treatments of engineering thermodynamics, Joule's name alone is attached to the establishment of the equivalence of "heat" and "work". The published record, however, shows that the idea of convertibility of heat into work was published independently by Mayer in May, 1842 and Joule in August, 1843. For an important aspect in the history of the first law, is the fact that both Mayer and Joule had difficulty in getting their papers published and in being taken seriously by their established contemporaries.

Robert Mayer was a doctor in a ship in the East Indies and from physiological observations, he believed in a principle of conservation of energy. He derived theoretically, the mechanical heat equivalent based on the calorimetric data of Joseph Black of Glasgow University. Mayer tried to publish his paper but remained unsuccessful for a long time. His despair was so great that he attempted suicide by jumping from a window, but he only broke his two legs. He was placed in an asylum for some time. In later years, however, he was given some measure or recognition and honoured equally with Joule in establishing the mechanical theory of heat.

Mayer argued that an amount of gas needs to be heated more at constant pressure than at constant volume, because at constant pressure it is free to dilate and do work against the atmosphere, which in today's notations becomes

$$mc_p\Delta T - mc_v\Delta T = P_{\text{atm}}\Delta V \quad (1.2)$$

Using the  $c_p$  and  $c_p/c_v$  constants that were known in his time, he estimated the left-hand side of the equation in calories, while the right-hand side was known in mechanical units. He thus established numerically the equivalence between these units. If the relation

$$Pv = RT \quad (1.3)$$

is used in Eq. (1.2), Mayer's argument reduces to

$$c_p - c_v = R \quad (1.4)$$

This classic relationship between the specific heats of an ideal gas is called Mayer's equation: while the ideal gas equation of state, Eq. (1.3), was first derived by Clapeyron [Bejan, 1988]\*.

Joule was the ultimate experimentalist. His experiments seem to be the direct continuation of those of Rumford and the gap of some forty years between the two investigations appeared puzzling to some authors. Joule's first discovery from his measurements was that the flow of current in a resistance, is accompanied by the development of heat proportional to the resistance. He concluded that caloric was indeed created by the flow of current. He was firmly convinced that there existed some conservation law of a general nature and hence set out to investigate whether the conversion of the various forms of energy is governed by definite conversion factors. He considered the conversion of chemical, electric, caloric, and mechanical energy forms in all combinations. The determination of the mechanical equivalent of heat forms the central part of his experiments, the results of which can be summed up in the general relation:

$$W = JQ \quad (1.5)$$

where  $J$  is the mechanical equivalent of heat. Joule's experiments suggested that this relation may have universal validity with the same numerical value of  $J$  under all conditions.

Joule communicated the results of his experiments to the British Association for the Advancement of Science in 1843. It was received with entire incredulity and general silence. In 1844 a paper by Joule on the same subject was rejected by the Royal Society. To convince the skeptics, he produced a series of nakedly simple experiments whose message proved impossible to refute. From the point of view of mechanical engineers, the most memorable among these experiments was the heating of a pool of water by an array of paddle wheels driven by falling weights. He discussed in 1847, before the British Association at Oxford, his

\* Adrian Bejan, "Research into the Origins of Engineering Thermodynamics", *Int. Comm. Heat Mass Transfer*, Vol. 15, No. 5, 1988, pp 571-580.

experimental results in which he suggested that the water at the bottom of the Niagara waterfall (160 feet high) should be warmer than at the top (by  $0.2^{\circ}\text{F}$ ). From the thermal expansion of gases Joule deduced that there should be a “zero of temperature”,  $480^{\circ}\text{F}$  below the freezing point of ice. This was the first suggestion of absolute zero. Although these results failed to provoke further discussion, it created interest in a young man who only two year ago had passed from the University of Cambridge with the highest honour. The young man was William Thomson, who later became Lord Kelvin. He somewhere stated that it was one of the most valuable recollections of his life. Michael Faraday was also present in the 1844 Oxford meeting, and he communicated Joule’s paper “On the Mechanical Equivalent of Heat” to the Royal Society in 1849.

The paper ultimately appeared in its Philosophical Transactions in 1850.

Even while Joule was perfecting the experimental basis of the energy law now called the Mayer-Joule principle, Herman Ludwig von Helmholtz (1821–1894) published in 1847, his famous essay on the conservation of force. In this work, he advanced the conservation of energy as a unifying principle extending over all branches of physics. Helmholtz, like Mayer, was a physician by profession and self-taught in Physics and Mathematics. He also faced great difficulties in getting his paper published in professional journals.

In the history of classical thermodynamics, one thinks of only the closed system formulations of the first law which were deliberated by the pioneers as stated above. In engineering thermodynamics, however, open system formulations are of prime interest. The first law for open systems was first stated by Gustave Zeuner, as part of the analysis of flow systems that operate in the steady state. Zeuner’s formula for the heat transfer rate to a stream  $m$  in steady flow and without shaft work in present notations is given to be:

$$d\dot{Q} / \dot{m} = d(u + Pv + V^2 / 2 + gz) \quad (1.6)$$

The reference of this formula is found in Stodola’s classic treatise on steam turbines, first published in the German language in 1903.

The first person to invent a theory simultaneously involving the ideas of conservation and conversion of energy was the young French military engineer Nicolas Leonard Sadi Carnot (1796–1832). The strikingly original ideas of Carnot’s work make it among the most brilliant new departures in theoretical physics. Sadi Carnot was the son of Napoleon’s general, Lazare Carnot, and was educated at the famous Ecole Polytechnique in Paris. Between 1794 and 1830, Ecole Polytechnique had such famous teachers as Lagrange, Fourier, Laplace, Ampere, Cauchy, Coriolis, Poisson. Gay-Lussac, and Poiseuille. After his formal education Carnot chose a career as an army officer. Britain was then a powerful military force, primarily as a result of the industrial revolution brought about by the steam engine. French technology was not developing as fast as Britain’s. Carnot was convinced that France’s inadequate utilization of steam power had made it militarily inferior. He began to study the fundamentals of steam engine technology, and in 1824 he published the results of his study in the form of a brochure “Reflection on the Motive Power of Heat and on Machines Fitted to Develop that Power”. Carnot was trained in the basic principles of hydraulics, pumps and water wheels at the Ecole Polytechnique. During Carnot’s time, caloric theory of heat was still persisting, and the water wheel as the major source of mechanical power was gradually getting replaced by the steam engine. Carnot conceived that the power of a steam engine was released, as the heat fluid or caloric fell from the high temperature of the boiler to the lower temperature of the condenser, in much the same way that water falls through a water wheel to produce mechanical shaft work output. Carnot stated, “The motive power of a water wheel depends on its height and the quantity of liquid. The motive power of heat also depends on the quantity of caloric used and on the height of its fall, i.e., the difference of temperatures of the bodies between which the exchange of caloric is made”.

Till Carnot’s time thermodynamics was developed primarily on an empirical basis provided by chemistry. Carnot approached an engineering problem, the efficiency of heat engines, in terms of entirely new concepts with the steam engine serving as the stimulus. Carnot observed that the existence of temperature differences is a necessary condition for producing mechanical work by means of a heat engine. He simplified the problem to its bare essentials and stipulates, that this system, consisting essentially of a working substance, should



exchange heat with its surroundings only at two fixed temperatures. In order to conceptualize such a situation, he introduces the idea of heat reservoirs. Two important conclusions emerged from Carnot's work.

1. No one could build a water wheel that would produce a continuous work output unless water actually entered and exited the wheel. If water with a certain kinetic and potential energy entered the wheel, then the same amount of water with a lower energy must also exit the wheel. It is thus impossible to make a water wheel that converts all the energy of the inlet water into shaft work output. There must be an outflow of water from the wheel.

If this idea is extended to a steam engine by replacing the water by heat fluid caloric, it can be concluded that when caloric at a certain energy level (temperature) enters a work producing heat engine, it must also exit the heat engine at a low energy level (temperature). Thus a continuously operating heat engine that converts all of its caloric (heat) input directly into work output is not possible. This is very close to the Kelvin-Planck statement of second law as it is known today.

2. The maximum efficiency of a water wheel was independent of the type of the liquid and depended only on the inlet and outlet flow energies. The maximum efficiency of the steam engine (or any heat engine) depends only on the temperatures of the high and low temperature thermal reservoirs of the engine and is independent of the working fluid. To achieve the maximum efficiency there must not be any mechanical friction or other losses of any kind.

Only at the age of 36, Sadi Carnot died of cholera following an attack of scarlet fever. The significance of Carnot's work was not recognized until 1850, when Rudolf Clausius (1822–1888) and William Thomson (1824–1907) worked out a clear formulation of the conservation of energy principle. Carnot's first conclusion was then called the second law of thermodynamics by Clausius, and Thomson used Carnot's second conclusion to develop the concept of absolute temperature scale. Thermodynamics is thus said to have originated from the "clumsy puffing of the early steam engines" and is often called "the daughter of steam engine".

Carnot's ideas were so revolutionary that they were largely ignored. Soon after Carnot's death, Emile Clapeyron (1799–1864), a French mining engineer, strengthened Carnot's ideas by using more precise mathematical derivation. Clapeyron constructed its thermodynamic cycle by deducing that it must be composed of two reversible isothermal processes and two reversible adiabatic processes. It is now known as Carnot's cycle. It was the first heat engine cycle to be conceptualized. No other heat engine can equal its efficiency.

Clapeyron was later able to derive a relation for the enthalpy change of the liquid to vapour phase ( $h_{fg}$ ) in terms of pressure, temperature and specific volume. This provided the first equation, now called the Clausius-Clapeyron equation, representing the first order phase transition, which could be used to estimate a property that is not directly measurable in terms of properties that are directly measurable. Clapeyron's equation is now most easily derived from one of Maxwell's equations.

William Thomson (1824–1907), who became a professor of natural philosophy at the University of Glasgow in 1848 at the age of 24 only, rejected the caloric theory of heat and for the first time used the terms "thermodynamics" and "mechanical energy". Apart from the deduction of the absolute temperature scale, Thomson worked with Joule from 1852 to 1862 in a series of experiments to measure the temperature of gas in a controlled expansion and propounded the Joule-Thomson effect for real gases.

Rudolf Julius Emanuel Clausius (1822–1888) realized that there were two distinct laws at work, the first law due to Joule and Mayer and the second law as expounded by Carnot. He defined the internal energy  $U$ . Although both Kelvin and Clausius used the function  $Q_{rev}/T$  for some years, Clausius recognized the value of this function and to describe it he coined the word "entropy" from the Greek work "tropee" meaning "transformation" and assigned it the symbol  $S$ . Clausius in 1865, summarized the first and second laws of thermodynamics in the following words:

"Die Energie der Welt ist konstant.

Die Entropie der Welt strebt einem Maximum zu"

which is translated as

"The energy of the world is constant.

The entropy of the world tends toward a maximum”

The world here means the universe, the system and the surroundings together.

These statements made a strong impression upon a young student, Max Karl Ernst Ludwig Planck (1858–1947). He was educated at the universities of Munich and Berlin. In his autobiography he stated, “One day I happened to come across the treatises of Rudolf Clausius, whose lucid style and enlightening clarity of reasoning made an enormous impression on me, and I became deeply absorbed in his articles, with an ever increasing enthusiasm. I appreciated especially his exact formulation of the two laws of thermodynamics, and the sharp distinction, which he was the first to establish between them”. In 1897, Planck<sup>1</sup> demonstrated the close connection between the second law and the concept of reversibility. He stated the second law as the impossibility of a cyclic device which produces positive work and exchanges heat with a single reservoir. Similar statement was also made by Kelvin, and is now recognized as Kelvin-Planck statement of second law. Poincare<sup>2</sup> in 1908, extended the work of Planck and prescribed a complete structure of classical thermodynamics.

The property, entropy, plays a stellar role in thermodynamics. It was introduced via the concept of heat engines. In 1909, the Greek mathematician Caratheodory proved the existence of entropy function mathematically without the aid of Carnot engines and refrigerators. Caratheodory’s statement of second law may be stated as: “In the neighbourhood of any arbitrary state  $P_0$  of a physical system, there exist neighbouring states which are not accessible from  $P_0$  along quasi-static adiabatic paths”. From the standpoint of the engineer and physicist it is entirely mathematical in form and devoid of physical insight.

William John Macquorn Rankine (1820–1872) defined the thermodynamic efficiency of a heat engine and showed the usefulness of  $p$ - $v$  diagrams as related to work. He wrote the first text book on thermodynamics<sup>3</sup>, and was the first to work out the thermodynamic cycle for the adiabatic cylinder steam engine, now known as Rankine cycle for a vapour power cycle.

In 1862, the cycle used in modern gasoline-powered I.C. engines was proposed in a patent issued to Alphonse Beau de Rochas (1815–1893). The first practical engine was, however, built by Nikolous August Otto (1832–1891) which was demonstrated at the Paris Exposition in 1878. Otto fought many legal battles with Beau de Rochas for production of these engines, but finally lost to him.

Captain John Ericsson (1803–1889) was a Swedish engineer who marketed small solar-powered and coal-fired hot air engines. Rev. Robert Stirling (1790–1879), an English parish minister, patented a practical heat engine in 1816 that used air as the working fluid. In theory, the cycle used the Stirling engine approaches the ideal cycle later proposed by Carnot (1824).

George Bailey Brayton (1830–1892), an American engineer, marketed an I.C. engine with a separate combustion chamber, where combustion of fuel occurred at about constant pressure. This cycle later formed the basis for modern gas turbine plants.

Gottlieb Daimler (1834–1900) obtained a patent in 1879 for a multicylinder automotive engine, which was commercially successful. Dr. Rudolf Christian Karl Diesel (1858–1913) studied at Technische Hochschule in Munich. He designed large steam engines and boilers. He later developed in 1897 an I.C. engine with fuel injection which resembled the modern diesel engine. Failing health, continuing criticism and serious financial setbacks beset Diesel who in 1913 disappeared from a boat crossing the English channel in a moonlit night. Josiah Willard Gibbs (1839–1903) is often regarded as the most brilliant thermodynamicist produced in the USA. He received the first doctorate degree in engineering in the USA (Yale University). He contributed significantly in many areas of thermodynamics like heterogeneous systems, phase rule, physical chemistry and statistical thermodynamics. Some of his very important papers were published in obscure journals like Connecticut Academy of Sciences, and remained unknown to most scientists. Only after his death, these were discovered.

<sup>1</sup> M. Planck, *Treatise on Thermodynamics* (1897), translated by A. Ogg, Longman and Green; London, 1927.

<sup>2</sup> H. Poincare, *Thermodynamique*, Gauthier-Villars, Paris, 1908.

<sup>3</sup> W.J.M. Rankine, “*Manual of the Steam Engine and other Prime Movers*”, 1859 going through 17 editions, as mentioned by Robert Balmer in “*Thermodynamics*”, West Publishing Co., 1990, page 399.

## Solved Examples

## Example 1.1

The pressure of gas in a pipe line is measured with a mercury manometer having one limb open to the atmosphere (Fig. Ex. 1.1). If the difference in the height of mercury in the two limbs is 562 mm, calculate the gas pressure. The barometer reads 761 mm Hg, the acceleration due to gravity is  $9.79 \text{ m/s}^2$ , and the density of mercury is  $13,640 \text{ kg/m}^3$ .

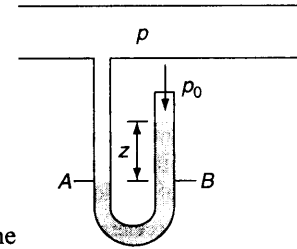


Fig. Ex. 1.1

**Solution** At the plane AB, we have  $p = p_0 + \rho gz$

$$\text{Now } p_0 = \rho g z_0$$

where  $z_0$  is the barometric height,  $\rho$  the density of mercury and  $p_0$  the atmospheric pressure.

$$\text{Therefore } p = \rho g (z + z_0)$$

$$= 13,640 \text{ kg/m}^3 \times 9.79 \text{ m/s}^2 (0.562 + 0.761) \text{ m}$$

$$= 177 \times 10^3 \text{ N/m}^2 = 177 \text{ kPa}$$

$$= 1.77 \text{ bar} = 1.746 \text{ atm}$$

Ans.

## Example 1.2

A turbine is supplied with steam at a gauge pressure of 1.4 MPa. After expansion in the turbine the steam flows into a condenser which is maintained at a vacuum of 710 mm Hg. The barometric pressure is 772 mm Hg. Express the inlet and exhaust steam pressure in pascals (absolute). Take the density of mercury as  $13.6 \times 10^3 \text{ kg/m}^3$ .

**Solution** The atmospheric pressure  $p_0 = \rho g z_0 = 13.6 \times 10^3 \text{ kg/m}^3 \times 9.81 \text{ m/s}^2 \times 0.772 \text{ m}$   
 $= 1.03 \times 10^5 \text{ Pa}$

$$\text{Inlet steam pressure} = [(1.4 \times 10^6) + (1.03 \times 10^5)] \text{ Pa}$$

$$= 15.03 \times 10^5 \text{ Pa} = 1.503 \text{ MPa}$$

Ans.

$$\text{Condenser pressure} = (0.772 - 0.710) \text{ m} \times 9.81 \text{ m/s}^2 \times 13.6 \times 10^3 \text{ kg/m}^3$$

$$= 0.827 \times 10^4 \text{ Pa} = 8.27 \text{ kPa}$$

Ans.

## Review Questions

- |   |   |
|---|---|
| 1.1 What do you understand by macroscopic and microscopic viewpoints?                       | 1.8 Define an isolated system.  |
| 1.2 Is thermodynamics a misnomer for the subject?   | 1.9 Distinguish between the terms 'change of state', 'path', and 'process'. |
| 1.3 How does the subject of thermodynamics differ from the concept of heat transfer?        | 1.10 What is a thermodynamic cycle?   |
| 1.4 What is the scope of classical thermodynamics?  | 1.11 What are intensive and extensive properties?                           |
| 1.5 What is a thermodynamic system?   | 1.12 What do you mean by homogeneous and heterogeneous systems?             |
| 1.6 What is the difference between a closed system and an open system?                      | 1.13 Explain what you understand by thermodynamic equilibrium.              |
| 1.7 An open system defined for a fixed region and a control volume are synonymous. Explain. | 1.14 Explain mechanical, chemical and thermal equilibrium.                  |

- 1.15 What is a quasi-static process/What is its characteristic feature?
- 1.16 What is the concept of continuum? How will you define density and pressure using this concept?

### Problems

- 1.1 A pump discharges liquid into a drum at the rate of  $0.0032 \text{ m}^3/\text{s}$ . The drum, 1.50 m in diameter and 4.20 m in length, can hold 3000 kg of the liquid. Find the density of the liquid and the mass flow rate of the liquid handled by the pump.
- 1.2 The acceleration of gravity is given as a function of elevation above sea level by

$$g = 980.6 - 3.086 \times 10^{-6} H$$

where  $g$  is in  $\text{cm}/\text{s}^2$ , and  $H$  is in cm. If an aeroplane weighs 90,000 N at sea level, what is the gravity force upon it at 10,000 m elevation? What is the percentage difference from the sea-level weight?

- 1.3 Prove that the weight of a body at an elevation  $H$  above sea-level is given by

$$W = \frac{mg}{g_0} \left( \frac{d}{d + 2H} \right)^2$$

where  $d$  is the diameter of the earth.

- 1.4 The first artificial earth satellite is reported to have encircled the earth at a speed of 28,840 km/h and its maximum height above the earth's surface was stated to be 916 km. Taking the mean diameter of the earth to be 12,680 km, and assuming the orbit to be circular, evaluate the value of the gravitational acceleration at this height.

The mass of the satellite is reported to have been 86 kg at sea-level. Estimate the gravitational force acting on the satellite at the operational altitude.

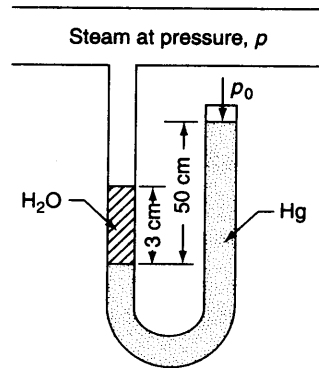
*Ans.*  $8.9 \text{ m}/\text{s}^2$ ; 765 N

- 1.5 Convert the following readings of pressure to kPa, assuming that the barometer reads 760 mm Hg:
- (a) 90 cm Hg gauge, (b) 40 cm Hg vacuum, (c) 1.2 m  $\text{H}_2\text{O}$  gauge, (d) 3.1 bar.
- 1.6 A 30 m high vertical column of a fluid of density  $1878 \text{ kg}/\text{m}^3$  exists in a place where  $g = 9.65 \text{ m}/\text{s}^2$ . What is the pressure at the base of the column.

*Ans.* 544 kPa

- 1.17 What is vacuum? How can it be measured?
- 1.18 What is a pressure transducer?

- 1.7 Assume that the pressure  $p$  and the specific volume  $v$  of the atmosphere are related according to the equation  $pv^{1.4} = 2.3 \times 10^3$ , where  $p$  is in  $\text{N}/\text{m}^2$  abs and  $v$  is in  $\text{m}^3/\text{kg}$ . The acceleration due to gravity is constant at  $9.81 \text{ m}/\text{s}^2$ . What is the depth of atmosphere necessary to produce a pressure of 1.0132 bar at the earth's surface? Consider the atmosphere as a fluid column. *Ans.* 64.8 km
- 1.8 The pressure of steam flowing in a pipe line is measured with a mercury manometer, shown in Fig. P. 1.8. Some steam condenses into water. Estimate the steam pressure in kPa. Take the density of mercury as  $13.6 \times 10^3 \text{ kg}/\text{m}^3$ , density of water as  $10^3 \text{ kg}/\text{m}^3$ , the barometer reading as 76.1 cm Hg, and  $g$  as  $9.806 \text{ m}/\text{s}^2$ .



**Fig. P.1.8**

- 1.9 A vacuum gauge mounted on a condenser reads 0.66 m Hg. What is the absolute pressure in the condenser in kPa when the atmospheric pressure is 101.3 kPa? *Ans.* 8.8 kPa
- 1.10 The basis barometer can be used to measure the height of a building. If the barometric readings at the top and at the bottom of a building are 730 and 760 mm Hg, respectively, determine the height of the building. Assume an average air density of  $1.18 \text{ kg}/\text{m}^3$ .

# 2 Temperature

## 2.1 ZEROTH LAW OF THERMODYNAMICS

The property which distinguishes thermodynamics from other sciences is temperature. One might say that temperature bears as important a relation to thermodynamics as force does to statics or velocity does to dynamics. Temperature is associated with the ability to distinguish hot from cold. When two bodies at different temperatures are brought into contact, after some time they attain a common temperature and are then said to exist in thermal equilibrium.

*When a body A is in thermal equilibrium with a body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.*

This is known as the *zeroth law of thermodynamics*. It is the basis of temperature measurement.

In order to obtain a quantitative measure of temperature, a reference body is used, and a certain physical characteristic of this body which changes with temperature is selected. The changes in the selected characteristic may be taken as an indication of change in temperature. The selected characteristic is called the *thermometric property*, and the reference body which is used in the determination of temperature is called the *thermometer*. A very common thermometer consists of a small amount of mercury in an evacuated capillary tube. In this case the extension of the mercury in the tube is used as the thermometric property.

There are five different kinds of thermometer, each with its own thermometric property, as shown in Table 2.1.

<i>Thermometer</i>	<i>Thermometric property</i>	<i>Symbol</i>
1. Constant volume gas thermometer	Pressure	$p$
2. Constant pressure gas thermometer	Volume	$V$
3. Electrical resistance thermometer	Resistance	$R$
4. Thermocouple	Thermal e.m.f.	$\epsilon$
5. Mercury-in-glass thermometer	Length	$L$

## 2.2 MEASUREMENT OF TEMPERATURE—THE REFERENCE POINTS

The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems. If a body is at, say,  $70^{\circ}\text{C}$ , it will be  $70^{\circ}\text{C}$ , whether measured by a mercury-in-glass thermometer, resistance thermometer or constant volume gas thermometer. If  $X$  is the thermometric property, let

us arbitrarily choose for the temperature common to the thermometer and to all systems in thermal equilibrium with it the following linear function of  $X$ :

$$\theta(X) = aX, \text{ where } a \text{ is an arbitrary constant.}$$

If  $X_1$  corresponds to  $\theta(X_1)$ , then  $X_2$  will correspond to  $\frac{\theta(X_1)}{X_1} \cdot X_2$

that is 
$$\theta(X_2) = \frac{\theta(X_1)}{X_1} \cdot X_2 \quad (2.1)$$

Two temperatures on the linear  $X$  scale are to each other as the ratio of the corresponding  $X$ 's.

### 2.2.1 Method Used Before 1954

The thermometer is first placed in contact with the system whose temperature  $\theta(X)$  is to be measured, and then in contact with an arbitrarily chosen standard system in an easily reproducible state where the temperature is  $\theta(X_1)$ . Thus

$$\frac{\theta(X_1)}{\theta(X)} = \frac{X_1}{X} \quad (2.2)$$

Then the thermometer at the temperature  $\theta(X)$  is placed in contact with another arbitrarily chosen standard system in another easily reproducible state where the temperature is  $\theta(X_2)$ . It gives

$$\frac{\theta(X_2)}{\theta(X)} = \frac{X_2}{X} \quad (2.3)$$

From Eqs (2.2) and (2.3) 
$$\frac{\theta(X_1) - \theta(X_2)}{\theta(X)} = \frac{X_1 - X_2}{X}$$

or 
$$\theta(X) = \frac{\theta(X_1) - \theta(X_2)}{X_1 - X_2} \cdot X \quad (2.4)$$

If we assign an arbitrary number of degrees to the temperature interval  $\theta(X_1) - \theta(X_2)$ , then  $\theta(X)$  can be calculated from the measurements of  $X$ ,  $X_1$  and  $X_2$ .

An easily reproducible state of an arbitrarily chosen standard system is called a fixed point. Before 1954, there were two fixed points: (a) *the ice point*, the temperature at which pure ice coexisted in equilibrium with air-saturated water at one atmosphere pressure, and (b) *the steam point*, the temperature of equilibrium between pure water and pure steam at one atmosphere pressure. The temperature interval,  $\theta(X_1) - \theta(X_2)$ , between these two fixed points was chosen to be 100 degrees.

The use of two fixed points was found unsatisfactory and later abandoned, because of (a) the difficulty of achieving equilibrium between pure ice and air-saturated water (since when ice melts, it surrounds itself only with pure water and prevents intimate contact with air-saturated water), and (b) extreme sensitiveness of the steam point to the change in pressure.

### 2.2.2 Method in Use After 1954

Since 1954 only one fixed point has been in use, viz., *the triple point of water*, the state at which ice, liquid water and water vapour coexist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value of 273.16 degrees Kelvin, or 273.16 K (the reason for using Kelvin's name will be explained later). Designating the triple point of water by  $\theta_t$ , and with  $X_t$  being the value of the thermometric property when

the body, whose temperature  $\theta$  is to be measured, is placed in contact with water at its triple point, it follows that

$$\theta_t = aX_t$$

$\therefore$

$$a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t}$$

Therefore

$$\begin{aligned}\theta &= aX \\ &= \frac{273.16}{X_t} \cdot X\end{aligned}$$

or

$$\theta = 273.16 \frac{X}{X_t} \quad (2.5)$$

The temperature of the triple point of water, which is an easily reproducible state, is now the *standard fixed point of thermometry*.

### 2.3 COMPARISON OF THERMOMETERS

Applying the above principle to the five thermometers listed in Table 2.1, the temperatures are given as:

- |                                       |  |
|---------------------------------------|--|
| (a) Constant volume gas thermometer   | $\theta(P) = 273.16 \frac{P}{P_t}$                               |
| (b) Constant pressure gas thermometer | $\theta(V) = 273.16 \frac{V}{V_t}$                               |
| (c) Electric resistance thermometer   | $\theta(R) = 273.16 \frac{R}{R_t}$                               |
| (d) Thermocouple                      | $\theta(\varepsilon) = 273.16 \frac{\varepsilon}{\varepsilon_t}$ |
| (e) Liquid-in-glass thermometer       | $\theta(L) = 273.16 \frac{L}{L_t}$                               |

If the temperature of a given system is measured simultaneously with each of the five thermometers, it is found that there is considerable difference among the readings. The smallest variation is, however, observed among different gas thermometers. That is why a gas is chosen as the standard thermometric substance.

### 2.4 IDEAL GAS

It has been established from experimental observations that the  $p - v - T$  behaviour of gases at a low pressure is closely given by the following relation

$$p\bar{v} = \bar{R}T \quad (2.6)$$

where  $\bar{R}$  is the universal gas constant, 8.3143 J/mol K and  $\bar{v}$  is the molar specific volume,  $\text{m}^3/\text{gmol}$ . (see Sec. 10.3.). Dividing Eq. (2.6) by the molecular weight  $\mu$ ,

$$pv = RT \quad (2.7)$$

where  $v$  is specific volume, in  $\text{m}^3/\text{kg}$ , and  $R$  is the characteristic gas constant. Substituting  $R = \bar{R} / \mu$  J/kg K, we get in terms of the total volume  $V$  of gas,

$$PV = n\bar{R}T$$

$$PV = mRT \quad (2.8)$$

where  $n$  is the number of moles and  $m$  is the mass of the gas. Equation (2.8) can be written for two states of the gas,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad (2.9)$$

Equation (2.6), (2.7) or (2.8) is called the *ideal gas equation of state*. At very low pressure or density, all gases and vapour approach ideal gas behaviour.

## 2.5 GAS THERMOMETERS

A schematic diagram of a constant volume gas thermometer is given in Fig. 2.1. A small amount of gas is enclosed in bulb  $B$  which is in communication via the capillary tube  $C$  with one limb of the mercury manometer  $M$ . The other limb of the mercury manometer is open to the atmosphere and can be moved vertically to adjust the mercury levels so that the mercury just touches lip  $L$  of the capillary. The pressure in the bulb is used as a thermometric property and is given by

$$p = p_0 + \rho_M Zg$$

where  $p_0$  is the atmospheric pressure  $\rho_M$  is the density of mercury.

When the bulb is brought in contact with the system whose temperature is to be measured, the bulb, in course of time, comes in thermal equilibrium with the system. The gas in the bulb expands, on being heated, pushing the mercury downward. The flexible limb of the manometer is then adjusted so that the mercury again touches the lip  $L$ . The difference in mercury level  $Z$  is recorded and the pressure  $p$  of the gas in the bulb is estimated. Since the volume of the trapped gas is constant, from the ideal gas equation,

$$\Delta T = \frac{V}{R} \Delta p \quad (2.10)$$

i.e. the temperature increase is proportional to the pressure increase.

In a constant pressure gas thermometer, the mercury levels have to be adjusted to keep  $Z$  constant, and the volume of gas  $V$ , which would vary with the temperature of the system, becomes the thermometric property.

$$\Delta T = \frac{p}{R} \Delta V \quad (2.11)$$

i.e. the temperature increase is proportional to the observed volume increase. The constant volume gas thermometer is, however, mostly in use, since it is simpler in construction and easier to operate.

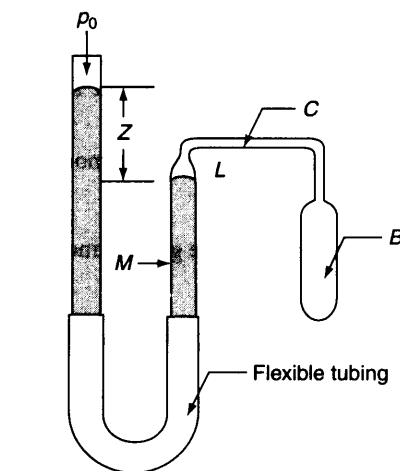


Fig. 2.1 Constant volume gas thermometer



## 2.6 IDEAL GAS TEMPERATURE

Let us suppose that the bulb of a constant volume gas thermometer contains an amount of gas such that when the bulb is surrounded by water at its triple point, the pressure  $p_t$  is 1000 mm Hg. Keeping the volume  $V$  constant, let the following procedure be conducted:

- (a) Surround the bulb with steam condensing at 1 atm, determine the gas pressure  $p$  and calculate

$$\theta = 273.16 \frac{p}{1000}$$

- (b) Remove some gas from the bulb so that when it is surrounded by water at its triple point, the pressure  $p_t$  is 500 mm Hg. Determine the new values of  $p$  and then  $\theta$  for steam condensing at 1 atm.

$$\theta = 273.16 \frac{p}{500}$$

- (c) Continue reducing the amount of gas in the bulb so that  $p_t$  and  $p$  have smaller and smaller values, e.g.  $p_t$  having, say, 250 mm Hg, 100 mm Hg, and so on. At each value of  $p_t$  calculate the corresponding  $\theta$ .
- (d) Plot  $\theta$  vs.  $p_t$  and extrapolate the curve to the axis where  $p_t = 0$ . Read from the graph

$$\lim_{p_t \rightarrow 0} \theta$$

The graph, as shown in Fig. 2.2, indicates that although the readings of a constant volume gas thermometer depend upon the nature of the gas, *all gases indicate the same temperature as  $p_t$  is lowered and made to approach zero.*

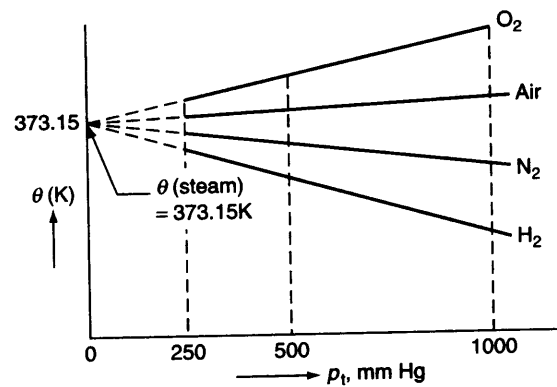
A similar series of tests may be conducted with a constant pressure gas thermometer. The constant pressure may first be taken to be 1000 mm Hg, then 500 mm Hg, etc. and at each value of  $p$ , the volumes of gas  $V$  and  $V_t$  may be recorded when the bulb is surrounded by steam condensing at 1 atm and the triple point of water, respectively. The corresponding value of  $\theta$  may be calculated from  $\theta = 273.16 \frac{V}{V_t}$

and  $\theta$  vs.  $p$  may be plotted, similar to Fig. 2.2. It is found from the experiments that all gases indicate the same value of  $\theta$  as  $p$  approaches zero.

Since a real gas, as used in the bulb, behaves as an ideal gas as pressure approaches zero (which would be explained later in Chapter 10), the *ideal gas temperature*  $T$  is defined by either of the two equations

$$\begin{aligned} T &= 273.16 \lim_{p_t \rightarrow 0} \frac{p}{p_t} \\ &= 273.16 \lim_{p \rightarrow 0} \frac{V}{V_t} \end{aligned}$$

where  $\theta$  has been replaced by  $T$  to denote this particular temperature scale, the *ideal gas temperature scale*.



## 2.7 CELSIUS TEMPERATURE SCALE

The Celsius temperature scale employs a degree of the same magnitude as that of the ideal gas scale, but its zero point is shifted, so that the Celsius temperature of the triple point of water is 0.01 degree Celsius or 0.01°C. If  $t$  denotes the Celsius temperature, then  $t = T - 273.15$

Thus the Celsius temperature  $t_s$  at which steam condenses at 1 atm. pressure

$$\begin{aligned} t_s &= T_s - 273.15 \\ &= 373.15 - 273.15 = 100.00^\circ\text{C} \end{aligned}$$

Similar measurements for ice points show this temperature on the Celsius scale to be 0.00°C. The only Celsius temperature which is fixed by definition is that of the triple point.

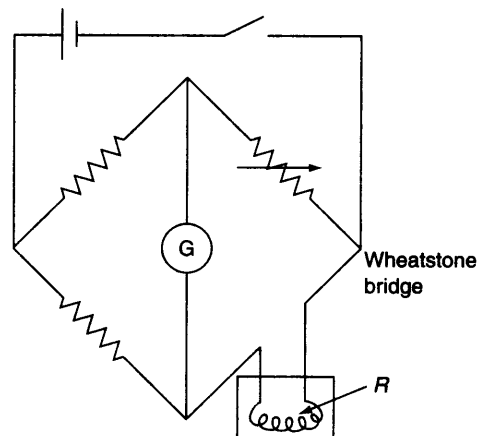
## 2.8 ELECTRICAL RESISTANCE THERMOMETER

In the resistance thermometer (Fig. 2.3) the change in resistance of a metal wire due to its change in temperature is the thermometric property. The wire, frequently platinum, may be incorporated in a Wheatstone bridge circuit. The platinum resistance thermometer measures temperature to a high degree of accuracy and sensitivity, which makes it suitable as a standard for the calibration of other thermometers.

In a restricted range, the following quadratic equation is often used

$$R = R_0 (1 + At + Bt^2)$$

where  $R_0$  is the resistance of the platinum wire when it is surrounded by melting ice and  $A$  and  $B$  are constants.



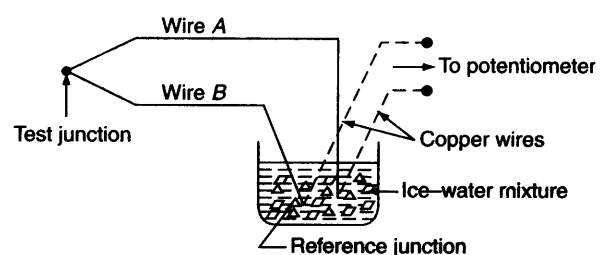
Resistance thermometer

## 2.9 THERMOCOUPLE

A thermocouple circuit made up from joining two wires  $A$  and  $B$  made of dissimilar metals is shown in Fig. 2.4. Due to the Seebeck effect, a net e.m.f. is generated in the circuit which depends on the difference in temperature between the hot and cold junctions and is, therefore, a thermometric property of the circuit. This e.m.f. can be measured by a microvoltmeter to a high degree of accuracy. The choice of metals depends largely on the temperature range to be investigated, and copper-constantan, chromel-alumel and platinum-platinum-rhodium are typical combinations in use.

A thermocouple is calibrated by measuring the thermal e.m.f. at various known temperatures, the reference junction being kept at 0°C. The results of such measurements on most thermocouples can usually be represented by a cubic equation of the form  $\varepsilon = a + bt + ct^2 + dt^3$

where  $\varepsilon$  is the thermal e.m.f. and the constants  $a$ ,  $b$ ,  $c$  and  $d$  are different for each thermocouple.



Thermocouple

The advantage of a thermocouple is that it comes to thermal equilibrium with the system, whose temperature is to be measured, quite rapidly, because its mass is small.

## 2.10 INTERNATIONAL PRACTICAL TEMPERATURE SCALE

An international temperature scale was adopted at the Seventh General Conference on Weights and Measures held in 1927. It was not to replace the Celsius or ideal gas scales, but to provide a scale that could be easily and rapidly used to calibrate scientific and industrial instruments. Slight refinements were incorporated into the scale in revisions adopted in 1948, 1954, 1960 and 1968. The international practical scale agrees with the Celsius scale at the defining fixed points listed in Table 2.2. The temperature interval from the oxygen point to the gold point is divided into three main parts, as given below.

(a) **From 0 to 660°C** A platinum resistance thermometer with a platinum wire whose diameter must lie between 0.05 and 0.20 mm is used, and the temperature is given by the equation

$$R = R_0 (1 + At + Bt^2)$$

where the constants  $R_0$ ,  $A$ , and  $B$  are computed by measurements at the ice point, steam point, and sulphur point.

(b) **From -190 to 0°C** The same platinum resistance thermometer is used, and the temperature is given by

$$R = R_0 [1 + At + Bt^2 + C(t - 100)t^3]$$

where  $R_0$ ,  $A$  and  $B$  are the same as before, and  $C$  is determined from a measurement at the oxygen point.

(c) **From 660 to 1063°C** A thermocouple, one wire of which is made of platinum and the other of an alloy of 90% platinum and 10% rhodium, is used with one junction at 0°C. The temperature is given by the formula

$$\varepsilon = a + bt + ct^2$$

where  $a$ ,  $b$ , and  $c$  are computed from measurements at the antimony point, silver point, and gold point. The diameter of each wire of the thermocouple must lie between 0.35 and 0.65 mm.

An optical method is adopted for measuring temperatures higher than the gold point. The intensity of radiation of any convenient wavelength is compared with the intensity of radiation of the same wavelength emitted by a black body at the gold point. The temperature is then determined with the help of Planck's law of thermal radiation.

<i>Temperatures of Fixed Points</i>	
	<i>Temperature °C</i>
Normal boiling point of oxygen	-182.97
<b>Triple point of water (standard)</b>	<b>+0.01</b>
Normal boiling point of water	100.00
<b>Normal boiling point of sulphur</b>	<b>444.60</b>
(Normal melting point of zinc-suggested as an alternative to the sulphur point)	419.50
<b>Normal melting point of antimony</b>	<b>630.50</b>
Normal melting point of silver	960.80
<b>Normal melting point of gold</b>	<b>1063.00</b>

## Solved Examples

## Example 2.1

Two mercury-in-glass thermometers are made of identical materials and are accurately calibrated at  $0^\circ\text{C}$  and  $100^\circ\text{C}$ . One has a tube of constant diameter, while the other has a tube of conical bore, ten per cent greater in diameter at  $100^\circ\text{C}$  than at  $0^\circ\text{C}$ . Both thermometers have the length between 0 and 100 subdivided uniformly. What will be the straight bore thermometer read in a place where the conical bore thermometer reads  $50^\circ\text{C}$ ?

**Solution** The volume of mercury in the tube at  $t^\circ\text{C}$ ,  $V_t$ , is given by

$$V_t = V_0 [1 + \beta(t - t_0)]$$

where  $V_0$  is the volume of mercury at  $0^\circ\text{C}$ ,  $\beta$  is the coefficient of volume expansion of mercury, and  $t_0$  is the ice point temperature which is  $0^\circ\text{C}$ . The volume change of glass is neglected.

Therefore

$$V_t - V_0 = \beta V_0 t$$

The temperature  $t$  is thus a linear function of volume change of mercury ( $V_t - V_0$ ).

Therefore

$$\Delta V_{0-100} = \beta V_0 \cdot 100$$

$$\Delta V_{0-50} = \beta V_0 \cdot 50$$

$$\therefore \frac{\Delta V_{0-50}}{\Delta V_{0-100}} = \frac{1}{2}$$

i.e., at  $50^\circ\text{C}$ , the volume of mercury will be half of that at  $100^\circ\text{C}$ , for the straight bore thermometer [Fig. Ex.2.1a].

But if the bore is conical [Fig. Ex. 2.1b], mercury will fill up the volume  $ACDB$ , which is less than half of the mercury volume at  $100^\circ\text{C}$ , i.e. volume  $AEFB$ . Let  $t$  be the true temperature when mercury rises half the length of the conical tube (the apparent temperature being  $50^\circ\text{C}$ ). Let  $EA$  and  $FB$  be extended to meet at  $G$ . Let  $l$  represent the length of the thermometers and  $l'$  the vertical height of the cone  $ABG$ , as shown in the figure. Now,

$$\frac{l'}{l+l'} = \frac{d}{1.1d} = \frac{1}{1.1}$$

$$l' = 10$$

and 
$$\frac{l'}{l+l/2} = \frac{d}{CD}$$

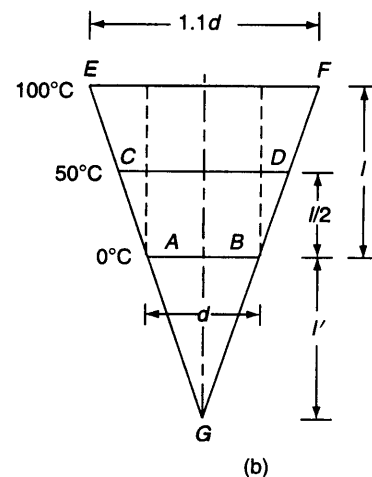
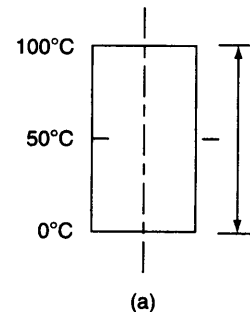
$$\therefore CD = \frac{10.5}{10}d = 1.05d$$

Again

$$\Delta V_{0-100} = V_0 \cdot \beta \cdot 100$$

$$\Delta V_{0-t} = V_0 \beta t$$

$$\frac{\Delta V_{0-t}}{\Delta V_{0-100}} = \frac{t}{100}$$



$$\begin{aligned} \text{or } \frac{\text{Volume } ACDB}{\text{Volume } AEFB} &= \frac{t}{100} \\ \text{or } \frac{\frac{1}{3} \pi (1.05d)^2 \times 10.5l - \frac{1}{3} \pi d^2 \cdot 10l}{\frac{1}{3} \pi (1.1d)^2 \times 11l - \frac{1}{3} \pi d^2 \cdot 10l} &= \frac{t}{100} \\ \text{or } \frac{1.05 \times 1.05 \times 10.5 - 10}{1.1 \times 1.1 \times 11 - 10} &= \frac{t}{100} \\ \therefore t &= \frac{1.58}{3.31} \times 100 = 47.7^\circ\text{C} \quad \text{Ans.} \end{aligned}$$

**Example 2.2**

The e.m.f. in a thermocouple with the test junction at  $t^\circ\text{C}$  on gas thermometer scale and reference junction at ice point is given by

$$e = 0.20t - 5 \times 10^{-4} t^2 \text{ mV}$$

The millivoltmeter is calibrated at ice and steam points. What will this thermometer read in a place where the gas thermometer reads  $50^\circ\text{C}$ ?

**Solution** At ice point, when  $t = 0^\circ\text{C}$ ,  $\varepsilon = 0 \text{ mV}$

At steam point, when  $t = 100^\circ\text{C}$ ,  $\varepsilon = 0.20 \times 100 - 5 \times 10^{-4} \times (100)^2 = 15 \text{ mV}$

At  $t = 50^\circ\text{C}$ ,  $\varepsilon = 0.20 \times 50 - 5 \times 10^{-4} (50)^2 = 8.75 \text{ mV}$

When the gas thermometer reads  $50^\circ\text{C}$ , the thermocouple will read

$$\frac{100}{15} \times 8.75, \text{ or } 58.33^\circ\text{C} \quad \text{Ans.}$$

**Review Questions**

- |  |   |
|--|---|
| 2.1 What is the zeroth law of thermodynamics?  | 2.10 What is a constant volume gas thermometer? Why is it preferred to a constant pressure gas thermometer? |
| 2.2 Define thermometric property.  | 2.11 What do you understand by the ideal gas temperature scale?   |
| 2.3 What is a thermometer?   | 2.12 How can the ideal gas temperature for the steam point be measured?                                     |
| 2.4 What is a fixed point?   | 2.13 What is the Celsius temperature scale?   |
| 2.5 How many fixed points were used prior to 1954? What are these?                               | 2.14 What is the advantage of a thermocouple in temperature measurement?                                    |
| 2.6 What is the standard fixed point in thermometry? Define it.                                  | 2.15 How does the resistance thermometer measure temperature?   |
| 2.7 Why is a gas chosen as the standard thermometric substance?                                  | 2.16 What is the need of the international practical temperature scale?                                     |
| 2.8 What is an ideal gas?  |   |
| 2.9 What is the difference between the universal gas constant and a characteristic gas constant? |   |

### Problems

- 2.1 The limiting value of the ratio of the pressure of gas at the steam point and at the triple point of water when the gas is kept at constant volume is found to be 1.36605. What is the ideal gas temperature of the steam point?
- 2.2 In a constant volume gas thermometer the following pairs of pressures readings were taken at the boiling point of water and the boiling point of sulphur, respectively:

Water b.p.	50.0	100	200	300
Sulphur b.p.	96.4	193	387	582

The numbers are the gas pressures, mm Hg, each pair being taken with the same amount of gas in the thermometer, but the successive pairs being taken with different amounts of gas in the thermometer. Plot the ratio of  $S_{b.p.} : H_2O_{b.p.}$  against the reading at the water boiling point, and extrapolate the plot to zero pressure at the water boiling point. This gives the ratio of  $S_{b.p.} : H_2O_{b.p.}$  on a gas thermometer operating at zero gas pressure, i.e., an ideal gas thermometer. What is the boiling point of sulphur on the gas scale, from your plot?

*Ans.* 445°C

- 2.3 The resistance of a platinum wire is found to be 11.000 ohms at the ice point, 15.247 ohms at the steam point, and 28.887 ohms at the sulphur point. Find the constants  $A$  and  $B$  in the equation

$$R = R_0 (1 + At + Bt^2)$$

and plot  $R$  against  $t$  in the range 0 to 660°C.

- 2.4 When the reference junction of a thermocouple is kept at the ice point and the test junction is at the Celsius temperature  $t$ , and e.m.f.  $\varepsilon$  of the thermocouple is given by the equation

$$\varepsilon = at + bt^2$$

where  $a = 0.20$  mV/deg, and  $b = -5.0 \times 10^{-4}$  mV/deg<sup>2</sup>

- (a) Compute the e.m.f. when  $t = -100^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ , and  $500^\circ\text{C}$ , and draw graph of  $\varepsilon$  against  $t$  in this range.
- (b) Suppose the e.m.f.  $\varepsilon$  is taken as a thermometric property and that a temperature scale  $t^*$  is defined by the linear equation.

$$t^* = a'\varepsilon + b'$$

and that  $t^* = 0$  at the ice point and  $t^* = 100$  at the steam point. Find the numerical values of  $a'$  and  $b'$  and draw a graph of  $\varepsilon$  against  $t^*$ .

- (c) Find the values of  $t^*$  when  $t = -100^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ , and  $500^\circ\text{C}$ , and draw a graph of  $t^*$  against  $t$ .
- (d) Compare the Celsius scale with the  $t^*$  scale.

- 2.5 The temperature  $t$  on a thermometric scale is defined in terms of a property  $K$  by the relation

$$t = a \ln K + b$$

where  $a$  and  $b$  are constants.

The values of  $K$  are found to be 1.83 and 6.78 at the ice point and the steam point, the temperatures of which are assigned the numbers 0 and 100 respectively. Determine the temperature corresponding to a reading of  $K$  equal to 2.42 on the thermometer.

*Ans.* 21.346°C

- 2.6 The resistance of the windings in a certain motor is found to be 80 ohms at room temperature ( $25^\circ\text{C}$ ). When operating at full load under steady state conditions, the motor is switched off and the resistance of the windings, immediately measured again, is found to be 93 ohms. The windings are made of copper whose resistance at temperature  $t^\circ\text{C}$  is given by

$$R_t = R_0 [1 + 0.00393 t]$$

where  $R_0$  is the resistance at  $0^\circ\text{C}$ . Find the temperature attained by the coil during full load.

*Ans.* 70.41°C

- 2.7 A new scale  $N$  of temperature is divided in such a way that the freezing point of ice is  $100^\circ\text{N}$  and the boiling point is  $400^\circ\text{N}$ . What is the temperature reading on this new scale when the temperature is  $150^\circ\text{C}$ ? At what temperature both the Celsius and the new temperature scale reading would be the same?

*Ans.*  $550^\circ\text{N}$ ,  $-50^\circ\text{C}$ .

- 2.8 A platinum wire is used as a resistance thermometer. The wire resistance was found to be 10 ohm and 16 ohm at ice point and steam point respectively, and 30 ohm at sulphur boiling point of  $444.6^\circ\text{C}$ . Find the resistance of the wire at  $500^\circ\text{C}$ , if the resistance varies with temperature by the relation.

$$R = R_0 (1 + \alpha t + \beta t^2) \quad \text{Ans. } 31.3 \text{ ohm}$$

# 3 Work and Heat Transfer

A closed system and its surroundings can interact in two ways: (a) by work transfer, and (b) by heat transfer. These may be called *energy interactions* and these bring about changes in the properties of the system. Thermodynamics mainly studies these energy interactions and the associated property changes of the system.

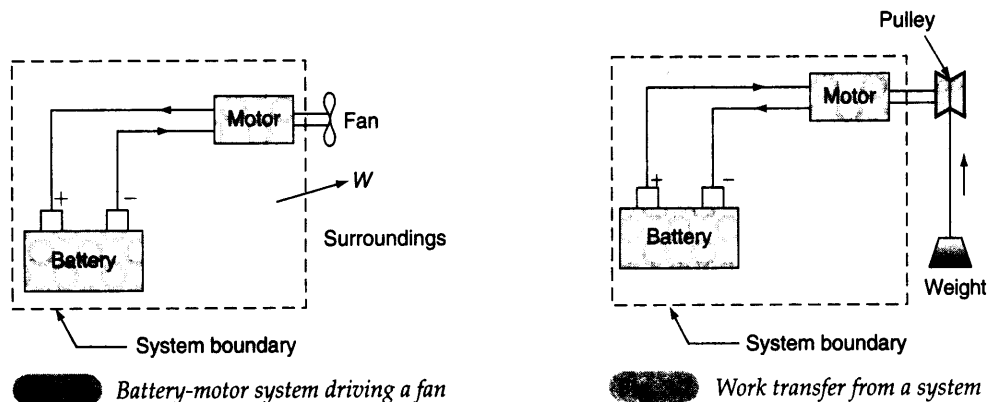
## 3.1 WORK TRANSFER

Work is one of the basic modes of energy transfer. In mechanics, the action of a force on a moving body is identified as work. A force is a means of transmitting an effect from one body to another. But a force itself never produces a physical effect except when coupled with motion and hence it is not a form of energy. An effect such as the raising of a weight through a certain distance can be performed by using a small force through a large distance or a large force through a small distance. The product of force and distance is the same to accomplish the same effect. In mechanics work is defined as:

*The work is done by a force as it acts upon a body moving in the direction of the force.*

The action of a force through a distance (or of a torque through an angle) is called *mechanical work* since other forms of work can be identified, as discussed later. The product of the force and the distance moved parallel to the force is the magnitude of mechanical work.

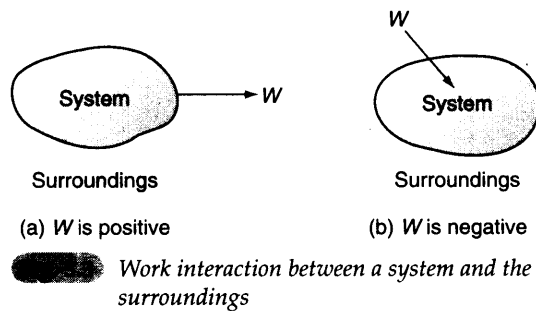
In thermodynamics, work transfer is considered as occurring between the system and the surroundings. *Work is said to be done by a system if the sole effect on things external to the system can be reduced to the raising of a weight.* The weight may not actually be raised, but the net effect external to the system would be the raising of a weight. Let us consider the battery and the motor in Fig. 3.1 as a system. The motor is driving a fan. The system is doing work upon the surroundings. When the fan is replaced by a pulley and a weight, as shown in Fig. 3.2, the weight may be raised with the pulley driven by the motor. The sole effect on things external to the system is then the raising of a weight.



When work is done by a system, it is arbitrarily taken to be positive, and when work is done on a system, it is taken to be negative (Fig. 3.3). The symbol  $W$  is used for work transfer.

The unit of work is N.m or Joule [1 Nm = 1 Joule]. The rate at which work is done by, or upon, the system is known as *power*. The unit of power is J/s or watt.

Work is one of the forms in which a system and its surroundings can interact with each other. There are various types of work transfer which can get involved between them.



### 3.2 pdV-WORK OR DISPLACEMENT WORK

Let the gas in the cylinder (Fig. 3.4) be a system having initially the pressure  $p_1$  and volume  $V_1$ . The system is in thermodynamic equilibrium, the state of which is described by the coordinates  $p_1, V_1$ . The piston is the only boundary which moves due to gas pressure. Let the piston move out to a new final position 2, which is also a thermodynamic equilibrium state specified by pressure  $p_2$  and volume  $V_2$ . At any intermediate point in the travel of the piston, let the pressure be  $p$  and the volume  $V$ . This must also be an equilibrium state, since macroscopic properties  $p$  and  $V$  are significant only for equilibrium states. When the piston moves an infinitesimal distance  $dl$ , and if 'a' be the area of the piston, the force  $F$  acting on the piston  $F = p.a$  and the infinitesimal amount of work done by the gas on the piston

$$\delta W = F \cdot dl = padl = pdV \quad (3.1)$$

where  $dV = a dl =$  infinitesimal displacement volume. The differential sign in  $dW$  with the line drawn at the top of it will be explained later.

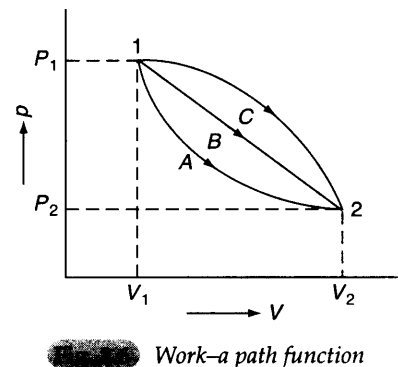
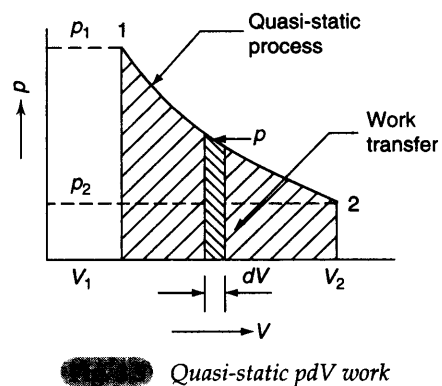
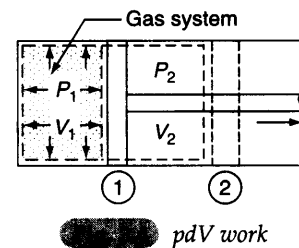
When the piston moves out from position 1 to position 2 with the volume changing from  $V_1$  to  $V_2$ , the amount of work  $W$  done by the system will be

$$W_{1-2} = \int_{V_1}^{V_2} pdV$$

The magnitude of the work done is given by the area under the path 1-2, as shown in Fig. 3.5. Since  $p$  is at all times a thermodynamic coordinate, all the states passed through by the system as the volume changes from  $V_1$  to  $V_2$  must be equilibrium states, and the path 1-2 must be *quasi-static*. The piston moves infinitely slowly so that every state passed through is an equilibrium state. The integration  $\int pdV$  can be performed only on a quasi-static path.

#### 3.2.1 Path Function and Point Function

With reference to Fig. 3.6, it is possible to take a system from state 1 to state 2 along many quasi-static paths, such as A, B or C. Since the





area under each curve represents the work for each process, the amount of work involved in each case is not a function of the end states of the process, and it depends on the path the system follows in going from state 1 to state 2. For this reason, work is called a *path function*, and  $\delta W$  is an *inexact or imperfect differential*.

Thermodynamic properties are *point functions*, since for a given state, there is a definite value for each property. The change in a thermodynamic property of a system in a change of state is independent of the path the system follows during the change of state, and depends only on the initial and final states of the system. The differentials of point functions are *exact or perfect differentials*, and the integration is simply

$$\int_{V_1}^{V_2} dV = V_2 - V_1$$

The change in volume thus depends only on the end states of the system irrespective of the path the system follows.

On the other hand, work done in a quasi-static process between two given states depends on the path followed.

$$\int_1^2 \delta W \neq W_2 - W_1$$

Rather,

$$\int_1^2 \delta W = W_{1-2} \text{ or } {}_1W_2$$

To distinguish an inexact differential  $\delta W$  from an exact differential  $dV$  or  $dp$  the differential sign is being cut by a line at its top.

From Eq. (3.1), 
$$dV = \frac{1}{p} \delta W \quad (3.2)$$

Here,  $1/p$  is called the *integrating factor*. Therefore, an inexact differential  $\delta W$  when multiplied by an integrating factor  $1/p$  becomes an exact differential  $dV$ .

For a cyclic process, the initial and final states of the system are the same, and hence, the change in any property is zero, i.e.

$$\oint dV = 0, \quad \oint dp = 0, \quad \oint dT = 0 \quad (3.3)$$

where the symbol  $\oint$  denotes the cyclic integral for the closed path. Therefore, *the cyclic integral of a property is always zero*.

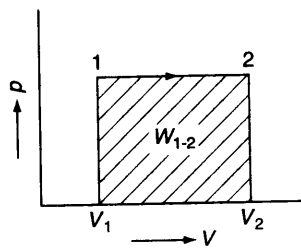
### 3.2.2 $pdV$ -Work in Various Quasi-Static Processes

(a) Constant pressure process (Fig. 3.7) (isobaric or isopiestic process)

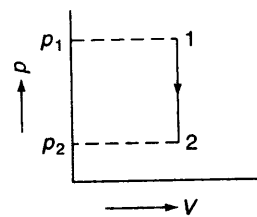
$$W_{1-2} = \int_{V_1}^{V_2} p dV = p(V_2 - V_1) \quad (3.4)$$

(b) Constant volume process (Fig. 3.8) (isochoric process)

$$W_{1-2} = \int p dV = 0 \quad (3.5)$$



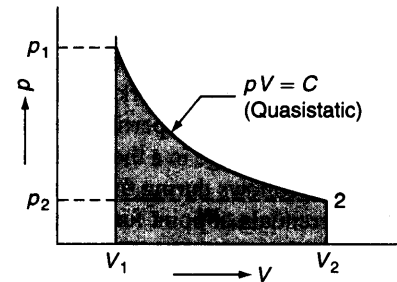
Constant pressure process



Constant volume process

(c) Process in which  $pV = C$  (Fig. 3.9)

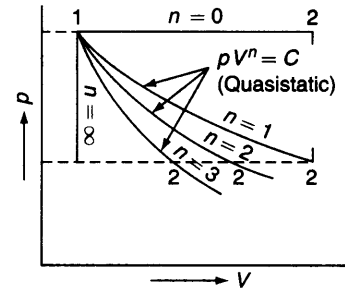
$$\begin{aligned} \therefore W_{1-2} &= \int_{V_1}^{V_2} p dV, \quad pV = p_1 V_1 = C \\ p &= \frac{(p_1 V_1)}{V} \\ W_{1-2} &= p_1 V_1 \int_{V_1}^{V_2} \frac{dV}{V} = p_1 V_1 \ln \frac{V_2}{V_1} \\ &= p_1 V_1 \ln \frac{p_1}{p_2} \end{aligned} \quad (3.6)$$



Process in which  $pV = \text{constant}$

(d) Process in which  $pV^n = C$ , where  $n$  is a constant (Fig. 3.10).

$$\begin{aligned} pV^n &= p_1 V_1^n = p_2 V_2^n = C \\ p &= \frac{(p_1 V_1^n)}{V^n} \\ \therefore W_{1-2} &= \int_{V_1}^{V_2} p dV \\ &= \int_{V_1}^{V_2} \frac{p_1 V_1^n}{V^n} \cdot dV \\ &= (p_1 V_1^n) \left[ \frac{V^{-n+1}}{-n+1} \right]_{V_1}^{V_2} \\ &= \frac{p_1 V_1^n}{1-n} (V_2^{1-n} - V_1^{1-n}) \\ &= \frac{p_2 V_2^n \times V_2^{1-n} - p_1 V_1^n \times V_1^{1-n}}{1-n} \\ &= \frac{p_1 V_1 - p_2 V_2}{n-1} = \frac{p_1 V_1}{n-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{n-1/n} \right] \end{aligned} \quad (3.7)$$

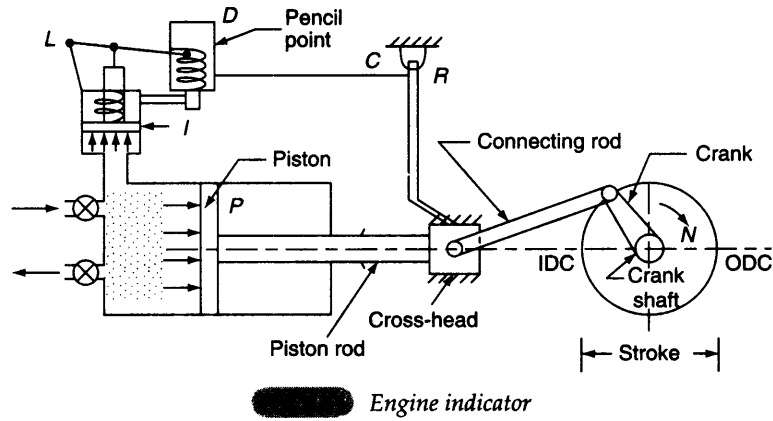


Process in which  $pV^n = \text{constant}$

### 3.3 INDICATOR DIAGRAM

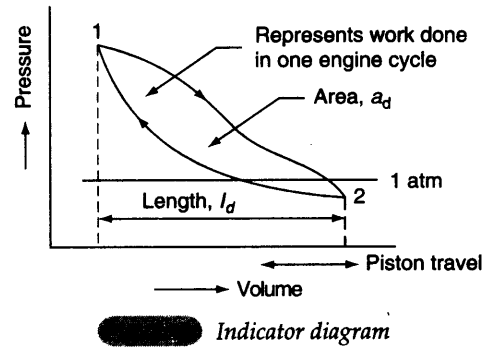
An indicator diagram is a trace made by a recording pressure gauge, called the indicator, attached to the cylinder of a reciprocating engine. This represents the work done in one engine cycle. Figure 3.11 shows a typical engine indicator.

The same gas pressure acts on both the engine piston  $P$  and the indicator piston  $I$ . The indicator piston is loaded by a spring and it moves in direct proportion to the change in pressure. The motion of the indicator piston causes a pencil held at the end of the linkage  $L$  to move upon a strip of paper wrapped around drum  $D$ . The drum is rotated about its axis by cord  $C$ , which is connected through a reducing motion  $R$  to the piston  $P$  of the engine. The surface of drum  $D$  moves horizontally under the pencil while the pencil moves vertically over the surface and a plot of pressure upon the piston vs. piston travel is obtained.



Before tracing the final indicator diagram, a pressure reference line is recorded by subjecting the indicator to the atmosphere and tracing a line at a constant pressure of one atmosphere.

The area of the indicator diagram represents the magnitude of the net work done by the system in one engine cycle. The area under the path 1–2 represents work done by the system and the area under the path 2–1 represents work done upon the system (Fig. 3.12). The area of the diagram,  $a_d$ , is measured by means of a planimeter, and the length of the diagram,  $l_d$ , is also measured. The *mean effective pressure* (m.e.p.)  $p_m$  is defined in the following way



$$p_m = \frac{a_d}{l_d} \times K$$

where  $K$  is the indicator spring constant ( $\text{N/cm}^2 \times \text{cm travel}$ ). Work done in one engine cycle

$$= (p_m \cdot A) L$$

where  $A = \text{cross-sectional area of the cylinder} = \frac{\pi}{4} D^2$ , where  $D$  is the cylinder diameter

and  $L = \text{stroke of piston, or length of cylinder}$ .

Let  $N$  be the revolutions per minute (r.p.m.) of the crankshaft. In a two stroke cycle, the engine cycle is completed in two strokes of the piston or in one revolution of the crankshaft. In a four-stroke cycle, the engine cycle is completed in four strokes of the piston or two revolutions of the crankshaft.

For a two-stroke engine, work done in one minute =  $p_m ALN$ , and for a four-stroke engine, work done in one minute =  $p_m ALN/2$ .

The power developed inside the cylinder of the engine is called *indicated power* (IP),

$$\therefore \text{IP} = \frac{p_m AL \left( N \text{ or } \frac{N}{2} \right) n}{60} \text{ kW} \tag{3.8}$$

where  $p_m$  is in kPa and  $n$  is the number of cylinders in the engine.

The power available at the crankshaft is always less than this value (IP) due to friction, etc. and is called the *brake power* (BP) or *shaft power* (SP). If  $\omega$  is the angular velocity of the crankshaft in radian/sec, then

$$\text{BP} = T \omega \quad (3.9)$$

where  $T$  is the torque transmitted to the crankshaft in mN.

$$\therefore \text{BP} = \frac{2\pi TN}{60} \quad (3.10)$$

where  $N$  is the number of revolutions per minute (rpm).

The mechanical efficiency of the engine,  $\eta_{\text{mech}}$ , is defined as

$$\eta_{\text{mech}} = \frac{\text{BP}}{\text{IP}} \quad (3.11)$$

An engine is said to be *double-acting*, if the working fluid is made to work on both sides of the piston. Such an engine theoretically develops twice the amount of work developed in a single-acting engine. Most reciprocating steam engines are double-acting, and so are many marine diesel engines. Internal combustion engines for road transport are always single-acting.

### 3.4 OTHER TYPES OF WORK TRANSFER

There are forms of work other than  $pdV$  or displacement work. The following are the additional types of work transfer which may get involved in system-surroundings interactions.

**(a) Electrical Work** When a current flows through a resistor (Fig. 3.13), taken as a system, there is work transfer into the system. This is because the current can drive a motor, the motor can drive a pulley and the pulley can raise a weight.

The current flow,  $I$ , in amperes, is given by  $I = \frac{dC}{d\tau}$

where  $C$  is the charge in coulombs and  $\tau$  is time in seconds. Thus  $dC$  is the charge crossing a boundary during time  $d\tau$ . If  $E$  is the voltage potential, the work is  $dW = E \cdot dC = EI d\tau$

$$\therefore W = \int_1^2 EI d\tau \quad (3.12)$$

The electrical power will be

$$\dot{W} = \lim_{d\tau \rightarrow 0} \frac{dW}{d\tau} = EI \quad (3.13)$$

This is the rate at which work is transferred.

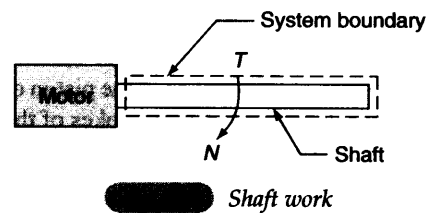
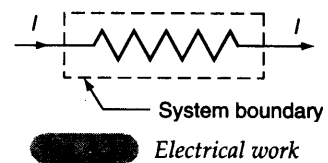
**(b) Shaft Work** When a shaft, taken as the system (Fig. 3.14), is rotated by a motor, there is work transfer into the system. This is because the shaft can rotate a pulley which can raise a weight. If  $T$  is the torque applied to the shaft and  $d\theta$  is the angular displacement of the shaft, the shaft work is

$$W = \int_1^2 T d\theta \quad (3.14)$$

and the shaft power is

$$\dot{W} = \int_1^2 T \frac{d\theta}{d\tau} = T \omega \quad (3.15)$$

where  $\omega$  is the angular velocity and  $T$  is considered a constant in this case.



(c) **Paddle-Wheel Work or Stirring Work** As the weight is lowered, and the paddle wheel turns (Fig. 3.15), there is work transfer into the fluid system which gets stirred. Since the volume of the system remains constant,  $\int p dV = 0$ . If  $m$  is the mass of the weight lowered through a distance  $dz$  and  $T$  is the torque transmitted by the shaft in rotating through an angle  $d\theta$ , the differential work transfer to the fluid is given by

$$dW = mgdz = Td\theta$$

and the total work transfer is

$$W = \int_1^2 mgdz = \int_1^2 W' dz = \int_1^2 Td\theta \tag{3.16}$$

where  $W'$  is the weight lowered.

(d) **Flow Work** The flow work, significant only in a flow process or an open system, represents the energy transferred across the system boundary as a result of the energy imparted to the fluid by a pump, blower or compressor to make the fluid flow across the control volume. Flow work is analogous to displacement work. Let  $p$  be the fluid pressure in the plane of the imaginary piston, which acts in a direction normal to it (Fig. 3.16). The work done on this imaginary piston by the external pressure as the piston moves forward is given by

$$\delta W_{\text{flow}} = pdV, \tag{3.17}$$

where  $dV$  is the volume of fluid element about to enter the system.

$$\therefore \delta W_{\text{flow}} = pv \, dm \tag{3.18}$$

where  $dV = v \, dm$

Therefore, flow work at inlet (Fig. 3.16),  $(dW_{\text{flow}})_{\text{in}} = p_1 v_1 \, dm_1 \tag{3.19}$

Equation (3.17) can also be derived in a slightly different manner. If the normal pressure  $p_1$  is exerted against the area  $A_1$ , giving a total force  $(p_1 A_1)$  against the piston, in time  $d\tau$ , this force moves a distance  $V_1 d\tau$ , where  $V_1$  is the velocity of flow (piston). The work in the time  $d\tau$  is  $p_1 A_1 V_1 d\tau$ , or the work per unit time is  $p_1 A_1 V_1$ . Since the flow rate

$$w_1 = \frac{A_1 V_1}{v_1} = \frac{dm_1}{d\tau}$$

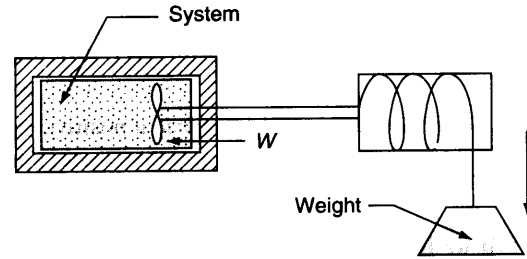
the work done in time  $d\tau$  becomes  $(\delta W_{\text{flow}})_{\text{in}} = p_1 v_1 \, dm_1$

Similarly, flow work of the fluid element leaving the system is

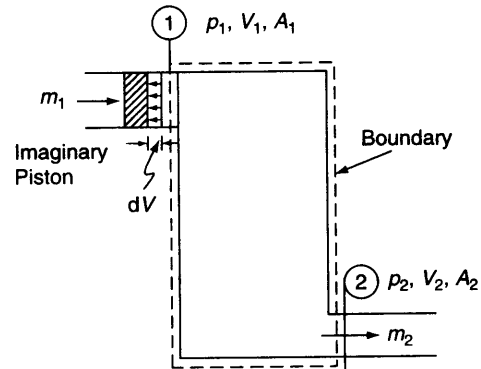
$$(\delta W_{\text{flow}})_{\text{out}} = p_2 v_2 \, dm_2 \tag{3.20}$$

The flow work per unit mass is thus  $W_{\text{flow}} = pv \tag{3.21}$

It is the displacement work done at the moving system boundary.



Paddle-wheel work



Flow work

**(e) Work Done in Stretching a Wire** Let us consider a wire as the system. If the length of the wire in which there is a tension  $\mathcal{F}$  is changed from  $L$  to  $L + dL$ , the infinitesimal amount of work that is done is equal to

$$\delta W = -\mathcal{F} dL$$

The minus sign is used because a positive value of  $dL$  means an expansion of the wire, for which work must be done on the wire, i.e. negative work. For a finite change of length,

$$W = -\int_1^2 \mathcal{F} dL \quad (3.22)$$

If we limit the problem to within the elastic limit, where  $E$  is the modulus of elasticity,  $s$  is the stress,  $\varepsilon$  is the strain, and  $A$  is the cross-sectional area, then

$$\mathcal{F} = sA = E\varepsilon A, \quad \text{since } \frac{s}{\varepsilon} = E$$

$$d\varepsilon = \frac{dL}{L}$$

$$\delta W = -\mathcal{F} dL = -E\varepsilon AL d\varepsilon$$

$$\therefore W = -AEL \int_1^2 \varepsilon d\varepsilon = -\frac{AEL}{2}(\varepsilon_2^2 - \varepsilon_1^2) \quad (3.23)$$

**(f) Work Done in Changing the Area of a Surface Film** A film on the surface of a liquid has a surface tension, which is a property of the liquid and the surroundings. The surface tension acts to make the surface area of the liquid a minimum. It has the unit of force per unit length. The work done on a homogeneous liquid film in changing its surface area by an infinitesimal amount  $dA$  is  $\delta W = -\sigma dA$

where  $\sigma$  is the surface tension (N/m).

$$\therefore W = -\int_1^2 \sigma dA \quad (3.24)$$

**(g) Magnetization of a Paramagnetic Solid** The work done per unit volume on a magnetic material through which the magnetic and magnetization fields are uniform is  $\delta W = -HdI$

and

$$W_{1-2} = -\int_{I_1}^{I_2} HdI \quad (3.25)$$

where  $H$  is the field strength, and  $I$  is the component of the magnetization field in the direction of the field. The minus sign provides that an increase in magnetization (positive  $dI$ ) involves negative work.

The following equations summarize the different forms of work transfer:

Displacement work

$$\text{(compressible fluid)} \quad W = \int_1^2 pdV$$

$$\text{Electrical work} \quad W = \int_1^2 E dC = \int_1^2 EI d\tau$$

$$\text{Shaft work} \quad W = \int_1^2 T d\theta$$

$$\text{Surface film} \quad W = -\int_1^2 \sigma dA \quad (3.26)$$

$$\text{Stretched wire} \quad W = -\int_1^2 \mathcal{F} dL$$

$$\text{Magnetised solid} \quad W = -\int_1^2 H dI$$

It may be noted in the above expressions that the work is equal to the integral of the product of an intensive property and the change in its related extensive property. These expressions are valid only for infinitesimally slow quasi-static processes.

There are some other forms of work which can be identified in processes that are not quasi-static, for example, the work done by shearing forces in a process involving friction in a viscous fluid.

### 3.5 FREE EXPANSION WITH ZERO WORK TRANSFER

Work transfer is identified only at the boundaries of a system. It is a boundary phenomenon, and a form of energy in transit crossing the boundary. Let us consider a gas separated from the vacuum by a partition (Fig. 3.17). Let the partition be removed. The gas rushes to fill the entire volume. The expansion of a gas against vacuum is called *free expansion*. If we neglect the work associated with the removal of partition, and consider the gas and vacuum together as our system (Fig. 3.17a), there is no work transfer involved here, since no work crosses the system boundary, and hence

$$\int_1^2 \delta W = 0, \quad \text{although} \quad \int_1^2 p dV \neq 0$$

If only the gas is taken as the system (Fig. 3.17b), when the partition is removed there is a change in the volume of the gas, and one is tempted to calculate the work from the expression  $\int_1^2 p dV$ . However, this is not a quasistatic process, although the initial and final end states are in equilibrium. Therefore, the work cannot be calculated from this relation. The two end states can be located on the  $p$ - $V$  diagram and these are joined by a dotted line (Fig. 3.17c) to indicate that the process had occurred. However, if the vacuum space is divided into a large number of small volumes by partitions and the partitions are removed one by one slowly (Fig. 3.17d), then every state passed through by the system is an equilibrium state and the work done can then be estimated from the relation  $\int_1^2 p dV$  (Fig. 3.17e). Yet, in free expansion of a gas, there is no resistance to the fluid at the system boundary as the volume of the gas increases to fill up the vacuum space. Work is done by a system to overcome some resistance. Since vacuum does not offer any resistance, there is no work transfer involved in free expansion.

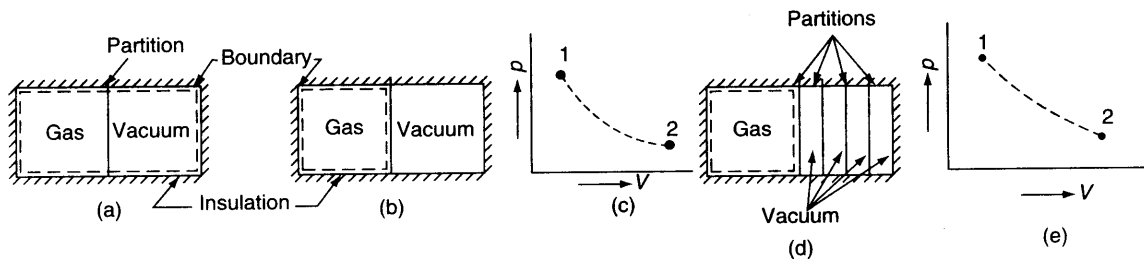


Fig. 3.17 Free expansion

### 3.6 NET WORK DONE BY A SYSTEM

Often different forms of a work transfer occur simultaneously during a process executed by a system. When all these work interactions have been evaluated, the total or net work done by the system would be equal to the algebraic sum of these as given below

$$W_{\text{total}} = W_{\text{displacement}} + W_{\text{shear}} + W_{\text{electrical}} + W_{\text{stirring}} + \dots$$

### 3.7 HEAT TRANSFER

Heat is defined as the form of energy that is transferred across a boundary *by virtue of a temperature difference*. The temperature difference is the 'potential' or 'force' and heat transfer is the 'flux'.

The transfer of heat between two bodies in direct contact is called *conduction*. Heat may be transferred between two bodies separated by empty space or gases by the mechanism of *radiation* through electromagnetic waves. A third method of heat transfer is *convection* which refers to the transfer of heat between a wall and a fluid system in motion.

The direction of heat transfer is taken from the high temperature system to the low temperature system. *Heat flow into a system is taken to be positive, and heat flow out of a system is taken as negative* (Fig. 3.18). The symbol  $Q$  is used for heat transfer, i.e. the quantity of heat transferred within a certain time.

Heat is a form of energy in transit (like work transfer). It is a boundary phenomenon, since it occurs only at the boundary of a system. Energy transfer by virtue of temperature difference only is called heat transfer. All other energy interactions may be termed as work transfer.

Heat is not that which inevitably causes a temperature rise. When heat is transferred to an ice-and-water mixture, the temperature does not rise until all the ice has melted. When a temperature rise in a system occurs, it may not be due to heat transfer, since a temperature rise may be caused by work transfer also. Heat, like work, is not a conserved quantity, and is not a property of a system.

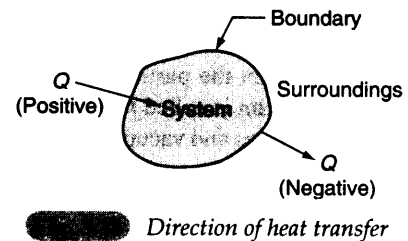
A process in which no heat crosses the boundary of the system is called an *adiabatic process*.

Thus, an adiabatic process is one in which there is only work interaction between the system and its surroundings.

A wall which is impermeable to the flow of heat is an *adiabatic wall*, whereas a wall which permits the flow of heat is a *diathermic wall*.

The unit of heat is Joule in S.I. units.

The rate of heat transfer or work transfer is given in kW or W.



### 3.8 HEAT TRANSFER—A PATH FUNCTION

Heat transfer is a *path function*, that is, the amount of heat transferred when a system changes from state 1 to state 2 depends on the intermediate states through which the system passes, i.e. its path. Therefore  $dQ$  is an inexact differential, and we write  $\int_1^2 \delta Q = Q_{1-2}$  or  ${}_1Q_2$

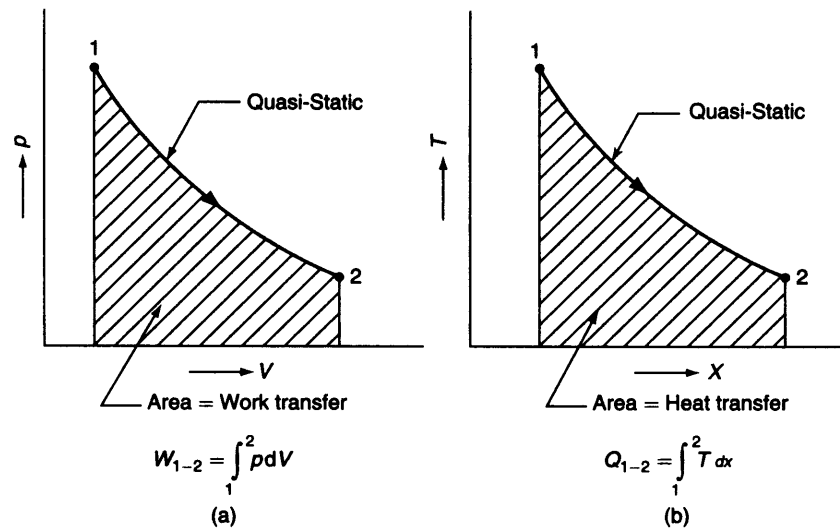
The displacement work is given by  $W_{1-2} = \int_1^2 \delta W = \int_1^2 p dV$

It is valid for a quasi-static process, and the work transfer involved is represented by the area under the path on  $p$ - $v$  diagram (Fig. 3.19a). Whenever there is a difference in pressure, there will be displacement work. The pressure difference is the cause and work transfer is the effect. The work transfer is equal to the integral of the product of the intensive property,  $p$  and the differential change in the extensive property,  $dV$ .

Likewise, whenever there is a difference in temperature, there will be heat flow. The temperature difference is the cause and heat transfer is the effect. Just like displacement work, the heat transfer can also be written as the integral of the product of the intensive property  $T$  and the differential change of an extensive property, say  $X$  (Fig. 3.19b).

$$Q_{1-2} = \int_1^2 \delta Q = \int_1^2 T dX \quad (3.27)$$





Representation of work transfer and heat transfer in quasi-static processes on  $p$ - $v$  and  $T$ - $x$  coordinates

It must also be valid for a quasi-static process only, and the heat transfer involved is represented by the area under the path 1–2 in  $T$ - $X$  plot (Fig. 3.19b). Heat transfer is, therefore, a path function, i.e. the amount of heat transferred when a system changes from a state 1 to a state 2 depends on the path the system follows (Fig. 3.19b). Therefore,  $\delta Q$  is an inexact differential. Now,  $\delta Q = T dX$  where  $X$  is an extensive property and  $dX$  is an exact differential.

$$\therefore dX = \frac{1}{T} \delta Q \quad (3.28)$$

To make  $\delta Q$  integrable, i.e., an exact differential, it must be multiplied by an integrating factor which is, in this case,  $1/T$ . The extensive property  $X$  is yet to be defined. It has been introduced in Chapter 7 and it is called 'entropy'.

### 3.9 SPECIFIC HEAT AND LATENT HEAT

The *specific heat* of a substance is defined as the amount of heat required to raise a unit mass of the substance through a unit rise in temperature. The symbol  $c$  will be used for specific heat.

$$\therefore c = \frac{Q}{m \cdot \Delta t} \text{ J/kg K}$$

where  $Q$  is the amount of heat transfer (J),  $m$ , the mass of the substance (kg), and  $\Delta t$ , the rise in temperature (K).

Since heat is not a property, as explained later, so the specific heat is qualified with the process through which exchange of heat is made. For gases, if the process is at constant pressure, it is  $c_p$ , and if the process is at constant volume, it is  $c_v$ . For solids and liquids, however, the specific heat does not depend on the process. An elegant manner of defining specific heats,  $c_v$  and  $c_p$ , in terms of properties is given in Secs 4.5 and 4.6.

The product of mass and specific heat ( $mc$ ) is called the *heat capacity* of the substance. The capital letter  $C$ ,  $C_p$  or  $C_v$  is used for heat capacity.

The latent heat is the amount of heat transfer required to cause a phase change in unit mass of a substance at a constant pressure and temperature. There are three phases in which matter can exist: solid, liquid, and

vapour or gas. The *latent heat of fusion* ( $l_{fu}$ ) is the amount of heat transferred to melt unit mass of solid into liquid, or to freeze unit mass of liquid to solid. The *latent heat of vaporization* ( $l_{vap}$ ) is the quantity of heat required to vaporize unit mass of liquid into vapour, or condense unit mass of vapour into liquid. The *latent heat of sublimation* ( $l_{sub}$ ) is the amount of heat transferred to convert unit mass of solid to vapour or vice versa.  $l_{fu}$  is not much affected by pressure, whereas  $l_{vap}$  is highly sensitive to pressure.

### 3.10 POINTS TO REMEMBER REGARDING HEAT TRANSFER AND WORK TRANSFER

- Heat transfer and work transfer are the *energy interactions*. A closed system and its surroundings can interact in two ways: by heat transfer and by work transfer. Thermodynamics studies how these interactions bring about property changes in a system.
- The same effect in a closed system can be brought about either by heat transfer or by work transfer. Whether heat transfer or work transfer has taken place depends on what constitutes the system.
- Both heat transfer and work transfer are boundary phenomena. Both are observed at the boundaries of the system, and both represent energy crossing the boundaries of the system.
- It is wrong to say 'total heat' or 'heat content' of a closed system, because heat or work is not a property of the system. Heat, like work, cannot be stored by the system. Both heat and work are the energy in transit.
- Heat transfer is the energy interaction due to temperature difference only. All other energy interactions may be termed as work transfer.
- Both heat and work are path functions and inexact differentials. The magnitude of heat transfer or work transfer depends upon the path the system follows during the change of state.

### Solved Examples

#### Example 3.1

Gas from a bottle of compressed helium is used to inflate an inelastic flexible balloon, originally folded completely flat to a volume of  $0.5 \text{ m}^3$ . If the barometer reads  $760 \text{ mm Hg}$ , what is the amount of work done upon the atmosphere by the balloon? Sketch the system before and after the process.

**Solution** The firm line  $P_1$  (Fig. Ex. 3.1) shows the boundary of the system before the process, and the dotted line  $P_2$  shows the boundary after the process. The displacement work

$$\begin{aligned} W_d &= \int_{\text{Balloon}} p dV + \int_{\text{Bottle}} p dV = p \Delta V + 0 \\ &= 101.325 \frac{\text{kN}}{\text{m}^2} \times 0.5 \text{ m}^3 = 50.66 \text{ kJ} \end{aligned}$$

This is positive because work is done by the system. Work done by the atmosphere is  $-50.66 \text{ kJ}$ . Since the wall of the bottle is rigid, there is no  $p dV$ -work involved in it.

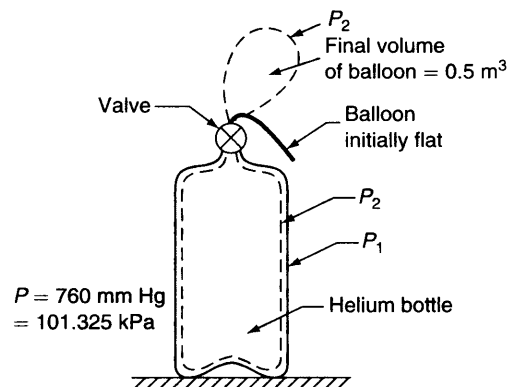


Fig. Ex. 3.1

It is assumed that the pressure in the balloon is atmospheric at all times, since the balloon fabric is light, inelastic and unstressed. If the balloon were elastic and stressed during the filling process, the work done by the gas would be greater than 50.66 kJ by an amount equal to the work done in stretching the balloon, although the displacement work done by the atmosphere is still  $-50.66$  kJ. However, if the system includes both the gas and the balloon, the displacement work would be 50.66 kJ, as estimated above.

### Example 3.2

When the valve of the evacuated bottle (Fig. Ex. 3.2) is opened, atmospheric air rushes into it. If the atmospheric pressure is 101.325 kPa, and  $0.6 \text{ m}^3$  of air (measured at atmospheric conditions) enters into the bottle, calculate the work done by air.

**Solution** The displacement work done by air

$$W_d = \int_{\text{Bottle}} p dV + \int_{\text{Free-air boundary}} p dV$$

$$= 0 + p \Delta V$$

$$= 101.325 \text{ kN/m}^2 \times 0.6 \text{ m}^3 = 60.8 \text{ kJ}$$

Since the free-air boundary is contracting, the work done by the system is negative ( $\Delta V$  being negative), and the surroundings do positive work upon the system.

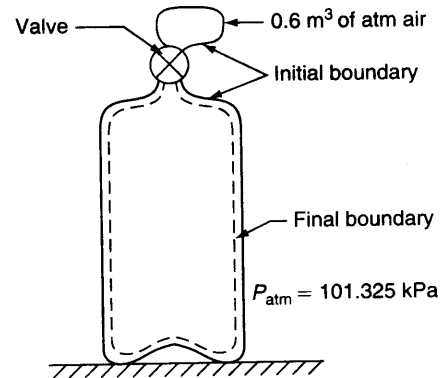
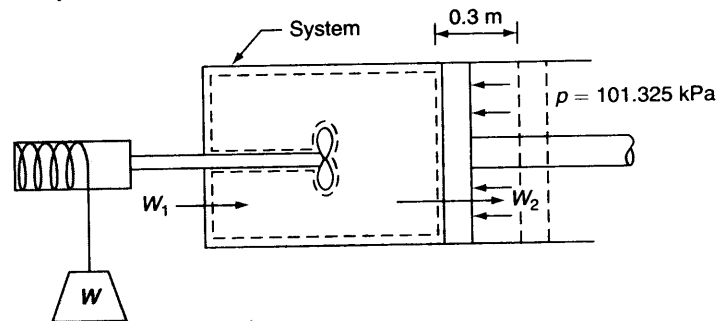


Fig. Ex. 3.2

### Example 3.3

A piston and cylinder machine containing a fluid system has a stirring device in the cylinder (Fig. Ex. 3.3). The piston is frictionless, and it is held down against the fluid due to the atmospheric pressure of 101.325 kPa. The stirring device is turned 10,000 revolutions with an average torque against the fluid of 1.275 mN. Meanwhile the piston of 0.6 m diameter moves out 0.8 m. Find the net work transfer for the system.



**Solution** Work done by the stirring device upon the system (Fig. Ex. 3.3).

$$W_1 = 2\pi TN$$

$$= 2\pi \times 1.275 \times 10,000 \text{ Nm} = 80 \text{ kJ}$$

This is negative work for the system.

Work done by the system upon the surroundings

$$\begin{aligned} W_2 &= (pA) \cdot L \\ &= 101.325 \frac{\text{kN}}{\text{m}^2} \times \frac{\pi}{4} (0.6)^2 \text{ m}^2 \times 0.80 \text{ m} = 22.9 \text{ kJ} \end{aligned}$$

This is positive work for the system. Hence, the net work transfer for the system

$$W = W_1 + W_2 = -80 + 22.9 = -57.1 \text{ kJ}$$

#### Example 3.4

The following data refer to a 12-cylinder, single-acting, two-stroke marine diesel engine:

Speed—150 rpm

Cylinder diameter—0.8 m

Stroke of piston—1.2 m

Area of indicator diagram— $5.5 \times 10^{-4} \text{ m}^2$

Length of diagram—0.06 m

Spring value—147 MPa per m

Find the net rate of work transfer from the gas to the pistons in kW.

**Solution** Mean effective pressure,  $p_m$ , is given by

$$\begin{aligned} p_m &= \frac{a_d}{l_d} \times \text{spring constant} \\ &= \frac{5.5 \times 10^{-4} \text{ m}^2}{0.06} \times 147 \frac{\text{MPa}}{\text{m}} = 1.35 \text{ MPa} \end{aligned}$$

One engine cycle is completed in two strokes of the piston or one revolution of the crank-shaft.

$\therefore$  Work done in one minute =  $p_m LAN$

$$= 1.35 \times \frac{\pi}{4} (0.8)^2 \times 1.2 \times 150 = 122 \text{ MJ}$$

Since the engine is single-acting, and it has 12 cylinders, each contributing an equal power, the rate of work transfer from the gas to the piston is given by

$$\begin{aligned} W &= 122 \times 12 \text{ MJ/min} = 24.4 \text{ MJ/s} \\ &= 24.4 \text{ MW} = 24,400 \text{ kW} \end{aligned}$$

*Ans.*

#### Example 3.5

It is required to melt 5 tonnes/h of iron from a charge at  $15^\circ\text{C}$  to molten metal at  $1650^\circ\text{C}$ . The melting point is  $1535^\circ\text{C}$ , and the latent heat is  $270 \text{ kJ/kg}$ . The specific heat in solid state is  $0.502$  and in liquid state ( $29.93/\text{atomic weight}$ )  $\text{kJ/kg K}$ . If an electric furnace has 70% efficiency, find the kW rating needed. If the density in molten state is  $6900 \text{ kg/m}^3$  and the bath volume is three times the hourly melting rate, find the dimensions of the cylindrical furnace if the length to diameter ratio is 2. The atomic weight of iron is 56.

**Solution** Heat required to melt 1 kg of iron at 15°C to molten metal at 1650°C  
 = Heat required to raise the temperature from 15°C to 1535°C + Latent heat  
 + Heat required to raise the temperature from 1535°C to 1650°C  
 = 0.502 (1535 – 15) + 270 + 29.93 (1650 – 1535)/56  
 = 763 + 270 + 61.5 = 1094.5 kJ/kg  
 Melting rate =  $5 \times 10^3$  kg/h  
 So, the rate of heat supply required =  $(5 \times 10^3 \times 1094.5)$  kJ/h  
 Since the furnace has 70% efficiency, the rating of the furnace would be

$$= \frac{\text{Rate of heat supply per second}}{\text{Furnace efficiency}}$$

$$= \frac{5 \times 10^3 \times 1094.5}{0.7 \times 3600} = 217 \times 10^3 \text{ kW}$$

Ans.

$$\text{Volume needed} = \frac{3 \times 5 \times 10^3}{6900} \text{ m}^3 = 2.18 \text{ m}^3$$

If  $d$  is the diameter and  $l$  the length of the furnace

$$\frac{\pi}{4} d^2 l = 2.18 \text{ m}^3$$

or  $\frac{\pi}{4} d^2 \times 2d = 2.18 \text{ m}^3$

$\therefore d = 1.15 \text{ m}$

and  $l = 2.30 \text{ m}$

Ans.

### Example 3.6

If it is desired to melt aluminium with solid state specific heat 0.9 kJ/kg K, latent heat 390 kJ/kg, atomic weight 27, density in molten state 2400 kg/m<sup>3</sup> and final temperature 700°C, find out how much metal can be melted per hour with the above kW rating. Other data are as in the above example. Also, find the mass of aluminium that the above furnace will hold. The melting point of aluminium is 660°C.

**Solution** Heat required per kg of aluminium

$$= 0.9 (660 - 15) + 390 + \frac{29.93}{27} (700 - 660)$$

$$= 580.5 + 390 + 44.3 = 1014.8 \text{ kJ}$$

$$\text{Heat to be supplied} = \frac{1014.8}{0.7} = 1449.7 \text{ kJ/kg}$$

With the given power, the rate at which aluminium can be melted

$$= \frac{2.17 \times 10^3 \times 3600}{1449.7} \text{ kg/h} = 5.39 \text{ tonnes/h}$$

Ans.

Mass of aluminium that can be held in the above furnace

$$= 2.18 \times 2400 \text{ kg} = 5.23 \text{ tonnes}$$

Ans.

### Review Questions

- 3.1 How can a closed system and its surroundings interact? What is the effect of such interactions on the system?
- 3.2 When is work said to be done by a system?
- 3.3 What are positive and negative work interactions?
- 3.4 What is displacement work?
- 3.5 Under what conditions is the work done equal to  $\int_1^2 p dV$ ?
- 3.6 What do you understand by path function and point function? What are exact and inexact differentials?
- 3.7 Show that work is a path function, and not a property.
- 3.8 What is an indicator diagram?
- 3.9 What is mean effective pressure? How is it measured?
- 3.10 What are the indicated power and the brake power of an engine?
- 3.11 How does the current flowing through a resistor represent work transfer?
- 3.12 What do you understand by flow work? Is it different from displacement work?
- 3.13 Why does free expansion have zero work transfer?
- 3.14 What is heat transfer? What are its positive and negative directions?
- 3.15 What are adiabatic and diathermic walls?
- 3.16 What is an integrating factor?
- 3.17 Show that heat is a path function and not a property.
- 3.18 What is the difference between work transfer and heat transfer?
- 3.19 Does heat transfer inevitably cause a temperature rise?

### Problems

- 3.1 (a) A pump forces  $1 \text{ m}^3/\text{min}$  of water horizontally from an open well to a closed tank where the pressure is  $0.9 \text{ MPa}$ . Compute the work the pump must do upon the water in an hour just to force the water into the tank against the pressure. Sketch the system upon which the work is done before and after the process.  
*Ans.*  $13.31 \text{ kJ}$
- (b) If the work done as above upon the water had been used solely to raise the same amount of water vertically against gravity without change of pressure, how many metres would the water have been elevated?
- (c) If the work done in (a) upon the water had been used solely to accelerate the water from zero velocity without change of pressure or elevation, what velocity would the water have reached? If the work had been used to accelerate the water from an initial velocity of  $10 \text{ m/s}$ , what would the final velocity have been?
- 3.2 The piston of an oil engine, of area  $0.0045 \text{ m}^2$ , moves downwards  $75 \text{ mm}$ , drawing in  $0.00028 \text{ m}^3$  of fresh air from the atmosphere. The pressure in the cylinder is uniform during the process at  $80 \text{ kPa}$ , while the atmospheric pressure is  $101.325 \text{ kPa}$ , the difference being due to the flow resistance in the induction pipe and the inlet valve. Estimate the displacement work done by the air finally in the cylinder.  
*Ans.*  $27 \text{ J}$
- 3.3 An engine cylinder has a piston of area  $0.12 \text{ m}^2$  and contains gas at a pressure of  $1.5 \text{ MPa}$ . The gas expands according to a process which is represented by a straight line on a pressure-volume diagram. The final pressure is  $0.15 \text{ MPa}$ . Calculate the work done by the gas on the piston if the stroke is  $0.30 \text{ m}$ .  
*Ans.*  $29.7 \text{ kJ}$
- 3.4 A mass of  $1.5 \text{ kg}$  of air is compressed in a quasi-static process from  $0.1 \text{ MPa}$  to  $0.7 \text{ MPa}$  for which  $p v = \text{constant}$ . The initial density of air is  $1.16 \text{ kg/m}^3$ . Find the work done by the piston to compress the air.  
*Ans.*  $251.62 \text{ kJ}$
- 3.5 A mass of gas is compressed in a quasi-static process from  $80 \text{ kPa}$ ,  $0.1 \text{ m}^3$  to  $0.4 \text{ MPa}$ ,  $0.03 \text{ m}^3$ . Assuming that the pressure and volume are related by  $p v^n = \text{constant}$ , find the work done by the gas system.  
*Ans.*  $-11.83 \text{ kJ}$

- 3.6 A single-cylinder, double-acting, reciprocating water pump has an indicator diagram which is a rectangle 0.075 m long and 0.05 m high. The indicator spring constant is 147 MPa per m. The pump runs at 50 rpm. The pump cylinder diameter is 0.15 m and the piston stroke is 0.20 m. Find the rate in kW at which the piston does work on the water. *Ans.* 43.3 kW
- 3.7 A single-cylinder, single-acting, 4 stroke engine of 0.15 m bore develops an indicated power of 4 kW when running at 216 rpm. Calculate the area of the indicator diagram that would be obtained with an indicator having a spring constant of  $25 \times 10^6$  N/m<sup>3</sup>. The length of the indicator diagram is 0.1 times the length of the stroke of the engine. *Ans.* 505 mm<sup>2</sup>
- 3.8 A six-cylinder, 4-stroke gasoline engine is run at a speed of 2520 RPM. The area of the indicator card of one cylinder is  $2.45 \times 10^3$  mm<sup>2</sup> and its length is 58.5 mm. The spring constant is  $20 \times 10^6$  N/m<sup>3</sup>. The bore of the cylinders is 140 mm and the piston stroke is 150 mm. Determine the indicated power, assuming that each cylinder contributes an equal power. *Ans.* 243.57 kW
- 3.9 A closed cylinder of 0.25 m diameter is fitted with a light frictionless piston. The piston is retained in position by a catch in the cylinder wall and the volume on one side of the piston contains air at a pressure of 750 kN/m<sup>2</sup>. The volume on the other side of the piston is evacuated. A helical spring is mounted coaxially with the cylinder in this evacuated space to give a force of 120 N on the piston in this position. The catch is released and the piston travels along the cylinder until it comes to rest after a stroke of 1.2 m. The piston is then held in its position of maximum travel by a ratchet mechanism. The spring force increases linearly with the piston displacement to a final value of 5 kN. Calculate the work done by the compressed air on the piston. *Ans.* 3.07 kJ
- 3.10 A steam turbine drives a ship's propeller through an 8 : 1 reduction gear. The average resisting torque imposed by the water on the propeller is  $750 \times 10^3$  N and the shaft power delivered by the turbine to the reduction gear is 15 MW. The turbine speed is 1450 rpm. Determine (a) the torque developed by the turbine, (b) the power delivered to the propeller shaft, and (c) the net rate of working of the reduction gear. *Ans.* (a)  $T = 98.84$  km N, (b) 14.235 MW, (c) 0.765 MW
- 3.11 A fluid, contained in a horizontal cylinder fitted with a frictionless leakproof piston, is continuously agitated by means of a stirrer passing through the cylinder cover. The cylinder diameter is 0.40 m. During the stirring process lasting 10 minutes, the piston slowly moves out a distance of 0.485 m against the atmosphere. The net work done by the fluid during the process is 2 kJ. The speed of the electric motor driving the stirrer is 840 rpm. Determine the torque in the shaft and the power output of the motor. *Ans.* 0.08 mN, 6.92 W
- 3.12 At the beginning of the compression stroke of a two-cylinder internal combustion engine the air is at a pressure of 101.325 kPa. Compression reduces the volume to 1/5 of its original volume, and the law of compression is given by  $pv^{1.2} = \text{constant}$ . If the bore and stroke of each cylinder is 0.15 m and 0.25 m, respectively, determine the power absorbed in kW by compression strokes when the engine speed is such that each cylinder undergoes 500 compression strokes per minute. *Ans.* 17.95 kW
- 3.13 Determine the total work done by a gas system following an expansion process as shown in Fig. P. 3.13. *Ans.* 2952 MJ

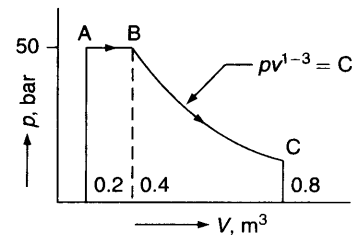


Fig. P. 3.13

- 3.14 A system of volume  $V$  contains a mass  $m$  of gas at pressure  $p$  and temperature  $T$ . The macroscopic properties of the system obey the following relationship:

$$\left(p + \frac{a}{V^2}\right)(V - b) = mRT$$

where  $a$ ,  $b$  and  $R$  constants.

- Obtain an expression for the displacement work done by the system during a constant-temperature expansion from volume  $V_1$  to volume  $V_2$ . Calculate the work done by a system which contains 10 kg of this gas expanding from  $1 \text{ m}^3$  to  $10 \text{ m}^3$  at a temperature of 293 K. Use the values  $a = 15.7 \times 10^4 \text{ Nm}^4$ ,  $b = 1.07 \times 10^{-2} \text{ m}^3$ , and  $R = 0.278 \text{ kJ/kg-K}$ . *Ans.* 1742.14 kJ
- 3.15 If a gas of volume  $6000 \text{ cm}^3$  and at pressure of 100 kPa is compressed quasistatically according to  $pV^2 = \text{constant}$  until the volume becomes  $2000 \text{ cm}^3$ , determine the final pressure and the work transfer. *Ans.* 900 kPa, 1.2 kJ
- 3.16 The flow energy of  $0.124 \text{ m}^3/\text{min}$  of a fluid crossing a boundary to a system is 18 kW. Find the pressure at this point. *Ans.* 764 kPa
- 3.17 A milk chilling unit can remove heat from the milk at the rate of 41.87 MJ/h. Heat leaks into the milk from the surroundings at an average rate of 4.187 MJ/h. Find the time required for cooling a batch of 500 kg of milk from  $45^\circ\text{C}$  to  $5^\circ\text{C}$ . Take the  $c_p$  of milk to be  $4.187 \text{ kJ/kgK}$ . *Ans.* 2h 13 min
- 3.18 680 kg of fish at  $5^\circ\text{C}$  are to be frozen and stored at  $-12^\circ\text{C}$ . The specific heat of fish above freezing point is  $3.182$ , and below freezing point is  $1.717 \text{ kJ/kgK}$ . The freezing point is  $-2^\circ\text{C}$ , and the latent heat of fusion is  $234.5 \text{ kJ/kg}$ . How much heat must be removed to cool the fish, and what per cent of this is latent heat? *Ans.* 186.28 MJ, 85.6%
- 3.19 A horizontal cylinder fitted with a sliding piston contains  $0.1 \text{ m}^3$  of a gas at a pressure of 1 atm. The piston is restrained by a linear spring. In the initial state, the gas pressure inside the cylinder just balances the atmospheric pressure of 1 atm of the outside of the piston and the spring exerts no force on the piston. The gas is then heated reversibly until its volume and pressure become  $0.16 \text{ m}^3$  and 2 atm, respectively. (a) Write the equation for the relation between the pressure and volume of the gas. (b) Calculate the work done by the gas. (c) Of the total work done by the gas, how much is done against the atmosphere? How much is done against the spring? *Ans.* (a)  $p(\text{N/m}^2) = 2.026 \times 10^6 V - 1.013 \times 10^5$   
(b) 7,598 J, (c) 5,065 J, 2,533 J
- 3.20 An elastic sphere initially has a diameter of 1 m and contains a gas at a pressure of 1 atm. Due to heat transfer the diameter of the sphere increases to 1.1 m. During the heating process the gas pressure inside the sphere is proportional to the sphere diameter. Calculate the work done by the gas. *Ans.* 18.4 kJ
- 3.21 A piston-cylinder device contains  $0.05 \text{ m}^3$  of a gas initially at 200 kPa. At this state, a linear spring having a spring constant of 150 kN/m is touching the piston but exerting no force on it. Now heat is transferred to the gas, causing the piston to rise and to compress the spring until the volume inside the cylinder doubles. If the cross-sectional area of the piston is  $0.25 \text{ m}^2$ , determine (a) the final pressure inside the cylinder, (b) the total work done by the gas, and (c) the fraction of this work done against the spring to compress it. *Ans.* (a) 320 kPa, (b) 13 kJ, (c) 3 kJ
- 3.22 A piston-cylinder device, whose piston is resting on a set of stops, initially contains 3 kg of air at 200 kPa and  $27^\circ\text{C}$ . The mass of the piston is such that a pressure of 400 kPa is required to move it. Heat is now transferred to the air until its volume doubles. Determine the work done by the air and the total heat transferred to the air. *Ans.* 516 kJ, 2674 kJ



# 4 First Law of Thermodynamics

Energy can be in two forms: (a) energy in *transit*, like heat and work transfer observed at the boundaries of a system, and (b) energy in *storage*, where energy is stored either *macroscopically* by virtue of motion, position or configuration of the system, or *microscopically* in the molecules or atoms constituting the system.

## 4.1 FIRST LAW FOR A CLOSED SYSTEM UNDERGOING A CYCLE

The transfer of heat and the performance of work may both cause the same effect in a system. Heat and work are different forms of the same entity, called energy, which is conserved. Energy which enters a system as heat may leave the system as work, or energy which enters the system as work may leave as heat.

Let us consider a closed system which consists of a known mass of water contained in an adiabatic vessel having a thermometer and a paddle wheel, as shown in Fig. 4.1. Let a certain amount of work  $W_{1-2}$  be done upon the system by the paddle wheel. The quantity of work can be measured by the fall of weight which drives the paddle wheel through a pulley. The system was initially at temperature  $t_1$ , the same as that of atmosphere, and after work transfer let the temperature rise to  $t_2$ . The pressure is always 1 atm. The process 1-2 undergone by the system is shown in Fig. 4.2 in generalized thermodynamic coordinates  $X, Y$ . Let the insulation now be removed. The system and the surroundings interact by heat transfer till the system returns to the original temperature  $t_1$ , attaining the condition of thermal equilibrium with the atmosphere. The amount of heat transfer  $Q_{2-1}$  from the system during this process, 2-1, shown in Fig. 4.2, can be estimated. The system thus executes a cycle, which consists of a definite amount of work input  $W_{1-2}$  to the system followed by the transfer of an amount of heat  $Q_{2-1}$  from the system. It has been found that this  $W_{1-2}$  is always proportional to the heat  $Q_{2-1}$ , and the constant of proportionality is called the Joule's equivalent or the *mechanical equivalent of heat*. In the simple example given here, there are only two energy transfer quantities as the system performs a thermodynamic cycle. If the cycle involves many more heat and work quantities, the same result will be found. Expressed algebraically.

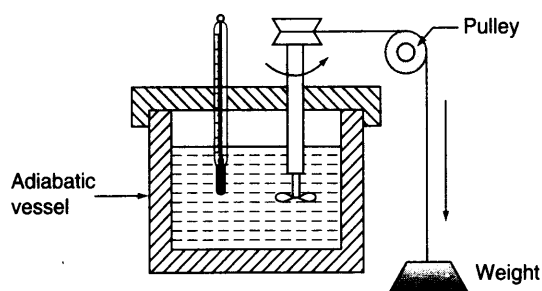


Fig. 4.1 Adiabatic work

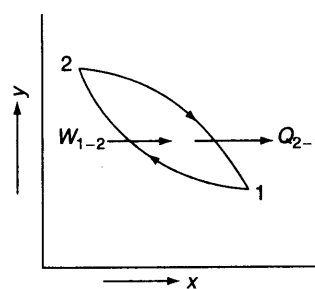


Fig. 4.2 Cycle completed by a system with two energy interactions: adiabatic work transfer  $W_{1-2}$  followed by heat transfer  $Q_{2-1}$

$$(\Sigma W)_{\text{cycle}} = J(\Sigma Q)_{\text{cycle}} \quad (4.1)$$

where  $J$  is the Joule's equivalent. This is also expressed in the form  $\oint dW = J \oint dQ$

where the symbol  $\oint$  denotes the cyclic integral for the closed path. This is the *first law for a closed system undergoing a cycle*. It is accepted as a *general law of nature*, since no violation of it has ever been demonstrated.

In the S.I. system of units, both heat and work are measured in the derived unit of energy, the Joule. The constant of proportionality,  $J$ , is therefore unity ( $J = 1 \text{ Nm/J}$ ).

The first law of thermodynamics owes much to J.P. Joule who, during the period 1840–1849, carried out a series of experiments to investigate the equivalence of work and heat. In one of these experiments, Joule used an apparatus similar to the one shown in Fig. 4.1. Work was transferred to the measured mass of water by means of paddle wheel driven by the falling weight. The rise in the temperature of water was recorded. Joule also used mercury as the fluid system, and later a solid system of metal blocks which absorbed work by friction when rubbed against each other. Other experiments involved the supplying of work in an electric current. In every case, he found the same ratio ( $J$ ) between the amount of work and the quantity of heat that would produce identical effects in the system.

Prior to Joule, heat was considered to be an invisible fluid flowing from a body of higher calorie to a body of lower calorie, and this was known as the *caloric theory of heat*. It was Joule who first established that heat is a form of energy, and thus laid the foundation of the first law of thermodynamics.

## 4.2

## FIRST LAW FOR A CLOSED SYSTEM UNDERGOING A CHANGE OF STATE

The expression  $(\Sigma W)_{\text{cycle}} = (\Sigma Q)_{\text{cycle}}$  applies only to systems undergoing cycles, and the algebraic summation of all energy transfer across system boundaries is zero. But if a system undergoes a change of state during which both heat transfer and work transfer are involved, the *net* energy transfer will be stored or accumulated within the system. If  $Q$  is the amount of heat transferred to the system and  $W$  is the amount of work transferred from the system during the process (Fig. 4.3), the net energy transfer ( $Q - W$ ) will be stored in the system. Energy in storage is neither heat nor work, and is given the name *internal energy* or simply, the *energy* of the system.

Therefore  $Q - W = \Delta E$

where  $\Delta E$  is the increase in the energy of the system

or  $Q = \Delta E + W$  (4.2)

Here  $Q$ ,  $W$ , and  $\Delta E$  are all expressed in the same units (in joules). Energy may be stored by a system in different modes, as explained in Article 4.4.

If there are more energy transfer quantities involved in the process, as shown in Fig. 4.4, the first law gives

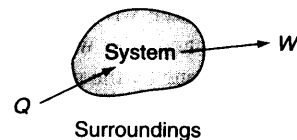


Fig. 4.3 Heat and work interactions of a system with its surroundings in a process

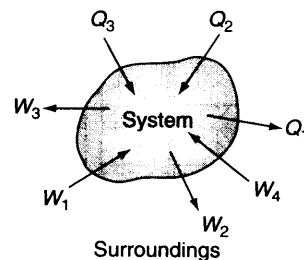


Fig. 4.4 System-surroundings interaction in a process involving many energy fluxes

$$(Q_2 + Q_3 - Q_1) = \Delta E + (W_2 + W_3 - W_1 - W_4)$$

Energy is thus conserved in the operation. The first law is a particular formulation of the principle of the conservation of energy. Equation (4.2) may also be considered as the definition of energy. This definition does not give an absolute value of energy  $E$ , but only the change of energy  $\Delta E$  for the process. It can, however, be shown that the energy has a definite value at every state of a system and is, therefore, a property of the system.

### 4.3 ENERGY—A PROPERTY OF THE SYSTEM

Consider a system which changes its state from state 1 to state 2 by following the path  $A$ , and returns from state 2 to state 1 by following the path  $B$  (Fig. 4.5). So the system undergoes a cycle.

Writing the first law for path  $A$   $Q_A = \Delta E_A + W_A$  (4.3)

and for path  $B$   $Q_B = \Delta E_B + W_B$  (4.4)

The processes  $A$  and  $B$  together constitute a cycle, for which

$$(\Sigma W)_{\text{cycle}} = (\Sigma Q)_{\text{cycle}}$$

or  $W_A + W_B = Q_A + Q_B$

or  $Q_A - W_A = W_B - Q_B$  (4.5)

From Eqs (4.3), (4.4), and (4.5), it yields  $\Delta E_A = -\Delta E_B$  (4.6)

Similarly, had the system returned from state 2 to state 1 by following the path  $C$  instead of path  $B$

$$\Delta E_A = -\Delta E_C$$
 (4.7)

From Eqs (4.6) and (4.7)  $\Delta E_B = \Delta E_C$  (4.8)

Therefore, it is seen that the change in energy between two states of a system is the same, whatever path the system may follow in undergoing that change of state. If some arbitrary value of energy is assigned to state 2, the value of energy at state 1 is fixed independent of the path the system follows. Therefore, energy has a definite value for every state of the system. Hence, it is a *point function and a property of the system*.

The energy  $E$  is an extensive property. The *specific energy*,  $e = E/m$  (J/kg), is an intensive property.

The cyclic integral of any property is zero, because the final state is identical with the initial state.  $\oint dE = 0$ ,  $\oint dV = 0$ , etc. So for a cycle, the Eq. (4.2) reduces to Eq. (4.1).

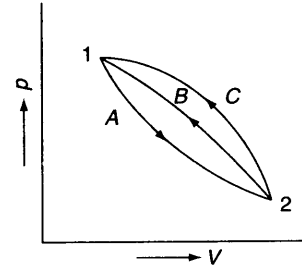


Fig. 4.5 Energy—a property of a system

### 4.4 DIFFERENT FORMS OF STORED ENERGY

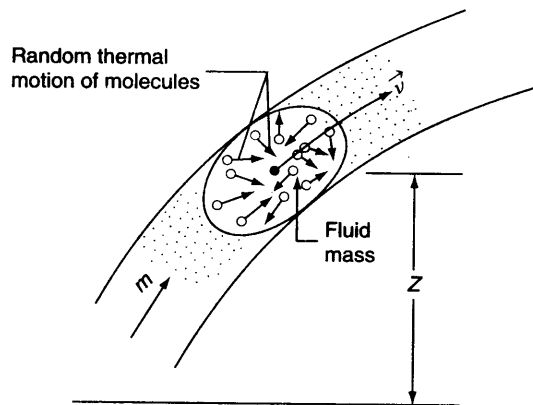
The symbol  $E$  refers to the total energy stored in a system. Basically there are two modes in which energy may be stored in a system:

- (a) Macroscopic energy mode
- (b) Microscopic energy mode

The macroscopic energy mode includes the macroscopic kinetic energy and potential energy of a system. Let us consider a fluid element of mass  $m$  having the centre of mass velocity  $\vec{V}$  (Fig. 4.6). The macroscopic kinetic energy  $E_K$  of the fluid element by virtue of its motion is given by  $E_K = \frac{m\vec{V}^2}{2}$

If the elevation of the fluid element from an arbitrary datum is  $z$ , then the macroscopic potential energy  $E_p$  by virtue of its position is given by  $E_p = mgz$

The microscopic energy mode refers to the energy stored in the molecular and atomic structure of the system, which is called the *molecular internal energy* or *simply internal energy*, customarily denoted by the symbol  $U$ . Matter is composed of molecules. Molecules are in random thermal motion (for a gas) with an average velocity  $\bar{v}$ , constantly colliding with one another and with the walls (Fig. 4.6). Due to a collision, the molecules may be subjected to rotation as well as vibration. They can have translational kinetic energy, rotational kinetic energy, vibrational energy, electronic energy, chemical energy and nuclear energy (Fig. 4.7). If  $\epsilon$  represents the energy of one molecule, then



Macroscopic and microscopic energy

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{chem}} + \epsilon_{\text{electronic}} + \epsilon_{\text{nuclear}} \quad (4.9)$$

If  $N$  is the total number of molecules in the system, then the total internal energy

$$U = N\epsilon \quad (4.10)$$

In an ideal gas there are no intermolecular forces of attraction and repulsion, and the internal energy depends only on temperature. Thus

$$U = f(T) \text{ only} \quad (4.11)$$

Other forms of energy which can also be possessed by a system are magnetic energy, electrical energy and surface (tension) energy. In the absence of these forms, the total energy  $E$  of a system is given by

$$E = \underbrace{E_K + E_P}_{\text{macro}} + \underbrace{U}_{\text{micro}} \quad (4.12)$$

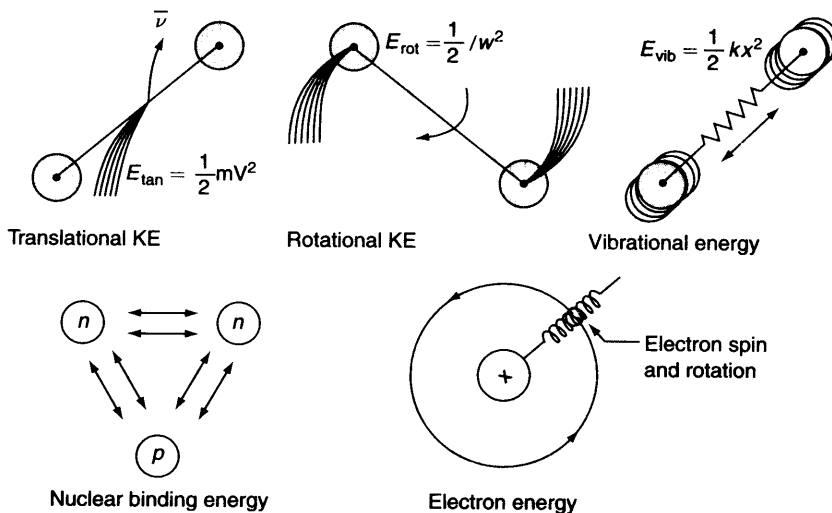


Fig. 4.7 Various components of internal energy stored in a molecule

where  $E_k$ ,  $E_p$ , and  $U$  refer to the kinetic, potential and internal energy, respectively. In the absence of motion and gravity.

$$E_k = 0, \quad E_p = 0$$

$$E = U$$

and Eq. (4.2) becomes

$$Q = \Delta U + W \quad (4.13)$$

$U$  is an extensive property of the system. The specific internal energy  $u$  is equal to  $U/m$  and its unit is J/kg.

In the differential forms, Eqs (4.2) and (4.13) become

$$\delta Q = dE + \delta W \quad (4.14)$$

$$\delta Q = \delta U + \delta W \quad (4.15)$$

where

$$\delta W = \delta W_{pdV} + \delta W_{\text{shaft}} + \delta W_{\text{electrical}} + \dots$$

considering the different forms of work transfer which may be present. When only  $pdV$  work is present, the equations become

$$\delta Q = dE + pdV \quad (4.16)$$

$$\delta Q = dU + pdV \quad (4.17)$$

or, in the integral form

$$Q = \Delta E + \int pdV \quad (4.18)$$

$$Q = \Delta U + \int pdV \quad (4.19)$$

#### 4.5

#### SPECIFIC HEAT AT CONSTANT VOLUME

The specific heat of a substance at constant volume  $c_v$  is defined as the rate of change of specific internal energy with respect to temperature when the volume is held constant, i.e.

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v \quad (4.20)$$

For a constant-volume process

$$(\Delta u)_v = \int_{T_1}^{T_2} c_v \cdot dT \quad (4.21)$$

The first law may be written for a closed stationary system composed of a unit mass of a pure substance

$$Q = \Delta u + W$$

or

$$\delta Q = du + \delta W$$

For a process in the absence of work other than  $pdV$  work

$$\delta W = p \delta V$$

$\therefore$

$$\delta Q = du + p \delta v \quad (4.22)$$

When the volume is held constant

$$(Q)_v = (\Delta u)_v$$

$\therefore$

$$(Q)_v = \int_{T_1}^{T_2} c_v \cdot dT \quad (4.23)$$

Heat transferred at constant volume increases the internal energy of the system.

If the specific heat of a substance is defined in terms of heat transfer, then

$$c_v = \left( \frac{\partial Q}{\partial T} \right)_v$$

Since  $Q$  is not a property, this definition does not imply that  $c_v$  is a property of a substance. Therefore, this is not the appropriate method of defining the specific heat, although  $(dQ)_v = du$ .

Since  $u$ ,  $T$ , and  $v$  are properties,  $c_v$  is a property of the system. The product  $mc_v = C_v$  is called the *heat capacity at constant volume* (J/K).

#### 4.6 ENTHALPY

The enthalpy of a substance,  $h$ , is defined as 
$$h = u + pv \quad (4.24)$$
 It is an intensive property of a system (kJ/kg).

Internal energy change is equal to the heat transferred in a constant volume process involving no work other than  $pdV$  work. From Eq. (4.22), it is possible to derive an expression for the heat transfer in a constant pressure process involving no work other than  $pdV$  work. In such a process in a closed stationary system of unit mass of a pure substance

$$\begin{aligned} \delta Q &= du + pdv \\ \text{At constant pressure} \quad pdv &= d(pv) \\ \therefore \quad (\delta Q)_p &= du + d(pv) \\ \text{or} \quad (\delta Q)_p &= d(u + pv) \\ \text{or} \quad (\delta Q)_p &= dh \end{aligned} \quad (4.25)$$

where  $h = u + pv$  is the *specific enthalpy*, a property of the system.

Heat transferred at constant pressure increases the enthalpy of a system.

For an ideal gas, the enthalpy becomes 
$$h = u + RT \quad (4.26)$$

Since the internal energy of an ideal gas depends only on the temperature (Eq. 4.11), the enthalpy of an ideal gas also depends on the temperature only, i.e.

$$h = f(T) \text{ only} \quad (4.27)$$

Total enthalpy  $H = mh$

$$\begin{aligned} \text{Also} \quad H &= U + pV \\ \text{and} \quad h &= H/m \text{ (J/kg)} \end{aligned}$$

#### 4.7 SPECIFIC HEAT AT CONSTANT PRESSURE

The specific heat at constant pressure  $c_p$  is defined as the rate of change of enthalpy with respect to temperature when the pressure is held constant

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p \quad (4.28)$$

Since  $h$ ,  $T$  and  $p$  are properties, so  $c_p$  is a property of the system. Like  $c_v$ ,  $c_p$  should not be defined in terms of heat transfer at constant pressure, although  $(dQ)_p = dh$ .

$$\text{For a constant pressure process} \quad (\Delta h)_p = \int_{T_1}^{T_2} c_p \cdot dT \quad (4.29)$$

The first law for a closed stationary system of unit mass

$$\begin{aligned} \delta Q &= du + pdv \\ \text{Again} \quad h &= u + pv \\ \therefore \quad dh &= du + pdv + vdp \\ &= dQ + vdp \\ \therefore \quad \delta Q &= dh - vdp \end{aligned} \quad (4.30)$$

$$\therefore (\delta Q)_p = dh \quad \text{or} \quad (Q)_p = (\Delta h)_p$$

$$\therefore \text{From Eqs (4.19) and (4.20)} \quad (Q)_p = \int_{T_1}^{T_2} c_p dT$$

$c_p$  is a property of the system, just like  $c_v$ . The *heat capacity at constant pressure*  $C_p$  is equal to  $mc_p$  (J/K).

#### 4.8 ENERGY OF AN ISOLATED SYSTEM

An isolated system is one in which there is no interaction of the system with the surroundings. For an isolated system  $\delta Q = 0$ ,  $\delta W = 0$ .

$$\text{The first law gives} \quad dE = 0 \quad \text{or} \quad E = \text{constant}$$

*The energy of an isolated system is always constant.*

#### 4.9 PERPETUAL MOTION MACHINE OF THE FIRST KIND—PMM1

The first law states the general principle of the conservation of energy. *Energy is neither created nor destroyed, but only gets transformed from one form to another.* There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously (Fig. 4.8). Such a *fictitious machine* is called a *perpetual motion machine of the first kind*, or in brief, PMM1. *A PMM1 is thus impossible.*

The converse of the above statement is also true, i.e., there can be no machine which would continuously consume work without some other form of energy appearing simultaneously (Fig. 4.9).

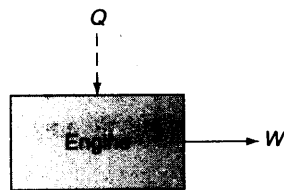


Fig. 4.8 A PMM1

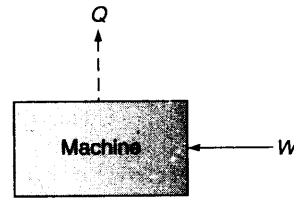


Fig. 4.9 The converse of PMM1

#### 4.10 LIMITATIONS OF THE FIRST LAW

The first law deals with the amount of energy of various forms transferred between the system and its surroundings and with changes in the energy stored in the system. It treats work and heat interactions as equivalent forms of energy in transit and does not indicate the possibility of a spontaneous process proceeding in a certain direction. It is the second law which assigns a quality to different forms of energy, and also indicates the direction of any spontaneous process.

#### Solved Examples

##### Example 4.1

A stationary mass of gas is compressed without friction from an initial state of  $0.3 \text{ m}^3$  and  $0.105 \text{ MPa}$  to a final state of  $0.15 \text{ m}^3$  and  $0.105 \text{ MPa}$ , the pressure remaining constant during the process. There is a transfer of  $37.6 \text{ kJ}$  of heat from the gas during the process. How much does the internal energy of the gas change?

**Solution** First law for a stationary system in a process gives

$$Q = \Delta U + W$$

or

$$Q_{1-2} = U_2 - U_1 + W_{1-2} \quad (1)$$

Here  $W_{1-2} = \int_{V_1}^{V_2} p dV = p(V_2 - V_1) = 0.105(0.15 - 0.30) \text{ MJ} = -15.75 \text{ kJ}$

$$Q_{1-2} = -37.6 \text{ kJ}$$

$\therefore$  Substituting in Eq. (1)

$$-37.6 \text{ kJ} = U_2 - U_1 - 15.75 \text{ kJ}$$

$\therefore$

$$U_2 - U_1 = -21.85 \text{ kJ}$$

Ans.

The internal energy of the gas decreases by 21.85 kJ in the process.

### Example 4.2

When a system is taken from state *a* to state *b*, in Fig. Ex. 4.2, along path *acb*, 84 kJ of heat flow into the system, and the system does 32 kJ of work. (a) How much will the heat that flows into the system along path *adb* be, if the work done is 10.5 kJ? (b) When the system is returned from *b* to *a* along the curved path, the work done on the system is 21 kJ. Does the system absorb or liberate heat, and how much of the heat is absorbed or liberated? (c) If  $U_a = 0$  and  $U_d = 42$  kJ, find the heat absorbed in the processes *ad* and *db*.

**Solution**

$$Q_{acb} = 84 \text{ kJ}$$

$$W_{acb} = 32 \text{ kJ}$$

We have

$$Q_{acb} = U_b - U_a + W_{acb}$$

$$U_b - U_a = 84 - 32 = 52 \text{ kJ} \quad \text{Ans.}$$

(a)

$$Q_{adb} = U_b - U_a + W_{adb}$$

$$= 52 + 10.5 = 62.5 \text{ kJ} \quad \text{Ans.}$$

(b)

$$Q_{b-a} = U_a - U_b + W_{b-a}$$

$$= -52 - 21 = -73 \text{ kJ} \quad \text{Ans.}$$

The system liberates 73 kJ of heat.

(c)

$$W_{adb} = W_{ad} + W_{db} = W_{ad} = 10.5 \text{ kJ}$$

$\therefore$

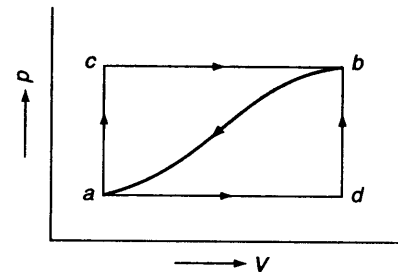
$$Q_{ad} = U_d - U_a + W_{ad} = 42 - 0 + 10.5 = 52.5 \text{ kJ}$$

Now

$$Q_{adb} = 62.5 \text{ kJ} = Q_{ad} + Q_{db}$$

$\therefore$

$$Q_{db} = 62.5 - 52.5 = 10 \text{ kJ} \quad \text{Ans.}$$



### Example 4.3

A piston and cylinder machine contains a fluid system which passes through a complete cycle of four processes. During a cycle, the sum of all heat transfers is  $-170$  kJ. The system completes 100 cycles per min. Complete the following table showing the method for each item, and compute the net rate of work output in kW.

Process	$Q$ (kJ/min)	$W$ (kJ/min)	$\Delta E$ (kJ/min)
a-b	0	2,170	—
b-c	21,000	0	—
c-d	-2,100	—	-36,600
d-a	—	—	—



**Solution** Process a–b:  $Q = \Delta E + W$   
 $0 = \Delta E + 2170$   
 $\therefore \Delta E = -2170 \text{ kJ/min}$   
 Process b–c:  $Q = \Delta E + W$   
 $21,000 = \Delta E + 0$   
 $\therefore \Delta E = 21,000 \text{ kJ/min}$   
 Process c–d:  $Q = \Delta E + W$   
 $-2100 = -36,600 + W$   
 $\therefore W = 34,500 \text{ kJ/min}$   
 Process d–a:  $\sum_{\text{cycle}} Q = -170 \text{ kJ}$

The system completes 100 cycles/min.

$\therefore Q_{ab} + Q_{bc} + Q_{cd} + Q_{da} = -17,000 \text{ kJ/min}$   
 $0 + 21,000 - 2,100 + Q_{da} = -17,000$   
 $\therefore Q_{da} = -35,900 \text{ kJ/min}$

Now  $\oint dE = 0$ , since cyclic integral of any property is zero.

$\therefore \Delta E_{a-b} + \Delta E_{b-c} + \Delta E_{c-d} + \Delta E_{d-a} = 0$   
 $-2,170 + 21,000 - 36,600 + \Delta E_{d-a} = 0$   
 $\therefore \Delta E_{d-a} = 17,770 \text{ kJ/min}$   
 $\therefore W_{d-a} = Q_{d-a} - \Delta E_{d-a}$   
 $= -35,900 - 17,770 = -53,670 \text{ kJ/min}$

The table becomes

Process	$Q$ (kJ/min)	$W$ (kJ/min)	$\Delta E$ (kJ/min)
a–b	0	2,170	-2,170
b–c	21,000	0	21,000
c–d	-2,100	34,500	-36,600
d–a	-35,900	-53,670	17,770

Since

Rate of work output  $\sum_{\text{cycle}} Q = \sum_{\text{cycle}} W$   
 $= -17,000 \text{ kJ/min} = -283.3 \text{ kW}$

Ans.

#### Example 4.4

The internal energy of a certain substance is given by the following equation

$$u = 3.56 pv + 84$$

where  $u$  is given in kJ/kg,  $p$  is in kPa, and  $v$  is in  $\text{m}^3/\text{kg}$ .

A system composed of 3 kg of this substance expands from an initial pressure of 500 kPa and a volume of  $0.22 \text{ m}^3$  to a final pressure 100 kPa in a process in which pressure and volume are related by  $pv^{1.2} = \text{constant}$ .

- If the expansion is quasi-static, find  $Q$ ,  $\Delta U$ , and  $W$  for the process.
- In another process the same system expands according to the same pressure-volume relationship as in part (a), and from the same initial state to the same final state as in part (a), but the heat transfer in this case is 30 kJ. Find the work transfer for this process.
- Explain the difference in work transfer in parts (a) and (b).

## Solution

$$\begin{aligned}
 \text{(a)} \quad u &= 3.56 pv + 84 \\
 \Delta u &= u_2 - u_1 = 3.56 (p_2 v_2 - p_1 v_1) \\
 \therefore \Delta U &= 3.56 (p_2 V_2 - p_1 V_1) \\
 \text{Now } p_1 V_1^{1.2} &= p_2 V_2^{1.2} \\
 \therefore V_2 &= V_1 \left( \frac{p_1}{p_2} \right)^{1/1.2} = 0.2 \left( \frac{5}{1} \right)^{1/1.2} = 0.22 \times 3.83 = 0.845 \text{ m}^3 \\
 \therefore \Delta U &= 356 (1 \times 0.845 - 5 \times 0.22) \text{ kJ} \\
 &= -356 \times 0.255 = -91 \text{ kJ} \qquad \text{Ans. (a)}
 \end{aligned}$$

For a quasi-static process

$$\begin{aligned}
 W &= \int p dV = \frac{p_2 V_2 - p_1 V_1}{1-n} \\
 &= \frac{(1 \times 0.845 - 5 \times 0.22) 100}{1-1.2} = 127.5 \text{ kJ} \\
 \therefore Q &= \Delta U + W \\
 &= -91 + 127.5 = 36.5 \text{ kJ} \qquad \text{Ans. (a)}
 \end{aligned}$$

(b) Here  $Q = 30 \text{ kJ}$

Since the end states are the same,  $\Delta U$  would remain the same as in (a).

$$\begin{aligned}
 \therefore W &= Q - \Delta U \\
 &= 30 - (-91) = 121 \text{ kJ} \qquad \text{Ans. (b)}
 \end{aligned}$$

(c) The work in (b) is not equal to  $\int p dV$  since the process is not quasi-static.

### Example 4.5

A fluid is confined in a cylinder by a spring-loaded, frictionless piston so that the pressure in the fluid is a linear function of the volume ( $p = a + bV$ ). The internal energy of the fluid is given by the following equation

$$U = 34 + 3.15 pV$$

where  $U$  is in kJ,  $p$  in kPa, and  $V$  in cubic metre. If the fluid changes from an initial state of 170 kPa, 0.03 m<sup>3</sup> to a final state of 400 kPa, 0.06 m<sup>3</sup>, with no work other than that done on the piston, find the direction and magnitude of the work and heat transfer.

**Solution** The change in the internal energy of the fluid during the process.

$$\begin{aligned}
 U_2 - U_1 &= 3.15 (p_2 V_2 - p_1 V_1) \\
 &= 315 (4 \times 0.06 - 1.7 \times 0.03) \\
 &= 315 \times 0.189 = 59.5 \text{ kJ}
 \end{aligned}$$

Now

$$\begin{aligned}
 p &= a + bV \\
 170 &= a + b \times 0.03 \\
 400 &= a + b \times 0.06
 \end{aligned}$$

From these two equations

$$\begin{aligned}
 a &= -60 \text{ kN/m}^2 \\
 b &= 7667 \text{ kN/m}^5
 \end{aligned}$$

Work transfer involved during the process

$$W_{1-2} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} (a + bV) dV$$

$$= a(V_2 - V_1) + b \frac{V_2^2 - V_1^2}{2}$$

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$$= (V_2 - V_1) \left[ a + \frac{b}{2}(V_1 + V_2) \right]$$

$$= 0.03 \text{ m}^3 \left[ -60 \text{ kN/m}^2 + \frac{7667 \text{ kN}}{2 \text{ m}^5} \times 0.09 \text{ m}^3 \right] = 8.55 \text{ kJ}$$

Work is done by the system, the magnitude being 8.55 kJ.

∴ Heat transfer involved is given by

$$Q_{1-2} = U_2 - U_1 + W_{1-2} = 59.5 + 8.55 = 68.05 \text{ kJ}$$

68.05 kJ of heat flow into the system during the process.

### Review Questions

- 4.1 State the first law for a closed system undergoing a cycle.
- 4.2 What was the contribution of J.P. Joule in establishing the first law?
- 4.3 What is the caloric theory of heat? Why was it rejected?
- 4.4 Which is the property introduced by the first law?
- 4.5 State the first law for a closed system undergoing a change of state.
- 4.6 Show that energy is a property of a system.
- 4.7 What are the modes in which energy is stored in a system?
- 4.8 Define internal energy. How is energy stored in molecules and atoms?
- 4.9 What is the difference between the standard symbols of  $E$  and  $U$ ?
- 4.10 What is the difference between heat and internal energy?
- 4.11 Define enthalpy. Why does the enthalpy of an ideal gas depend only on temperature?
- 4.12 Define the specific heats at constant volume and at constant pressure.
- 4.13 Why should specific heat not be defined in terms of heat transfer?
- 4.14 Which property of a system increases when heat is transferred: (a) at constant volume, (b) at constant pressure?
- 4.15 What is a PMM1? Why is it impossible?

### Problems

- 4.1 An engine is tested by means of a water brake at 1000 rpm. The measured torque of the engine is 10000 mN and the water consumption of the brake is  $0.5 \text{ m}^3/\text{s}$ , its inlet temperature being  $20^\circ\text{C}$ . Calculate the water temperature at exit, assuming that the whole of the engine power is ultimately transformed into heat which is absorbed by the cooling water. *Ans.*  $20.5^\circ\text{C}$
- 4.2 In a cyclic process, heat transfers are  $+14.7 \text{ kJ}$ ,  $-25.2 \text{ kJ}$ ,  $-3.56 \text{ kJ}$  and  $+31.5 \text{ kJ}$ . What is the net work for this cycle process? *Ans.*  $17.34 \text{ kJ}$
- 4.3 A slow chemical reaction takes place in a fluid at the constant pressure of  $0.1 \text{ MPa}$ . The fluid is surrounded by a perfect heat insulator during the reaction which begins at state 1 and ends at state 2. The insulation is then removed and  $105 \text{ kJ}$

of heat flow to the surroundings as the fluid goes to state 3. The following data are observed for the fluid at states 1, 2 and 3.

State	$V(\text{m}^3)$	$t(^{\circ}\text{C})$
1	0.003	20
2	0.3	370
3	0.06	20

For the fluid system, calculate  $E_2$  and  $E_3$ , if  $E_1 = 0$   
*Ans.*  $E_2 = -29.7 \text{ kJ}$ ,  $E_3 = -110.7 \text{ kJ}$

- 4.4 During one cycle the working fluid in an engine engages in two work interactions: 15 kJ to the fluid and 44 kJ from the fluid, and three heat interactions, two of which are known: 75 kJ to the fluid and 40 kJ from the fluid. Evaluate the magnitude and direction of the third heat transfer. *Ans.*  $-6 \text{ kJ}$
- 4.5 A domestic refrigerator is loaded with food and the door closed. During a certain period the machine consumes 1 kW h of energy and the internal energy of the system drops by 5000 kJ. Find the net heat transfer for the system. *Ans.*  $-8.6 \text{ MJ}$
- 4.6 1.5 kg of liquid having a constant specific heat of 2.5 kJ/kg K is stirred in a well-insulated chamber causing the temperature to rise by 15°C. Find  $\Delta E$  and  $W$  for the process.  
*Ans.*  $\Delta E = 56.25 \text{ kJ}$ ,  $W = -56.25 \text{ kJ}$
- 4.7 The same liquid as in Problem 4.6 is stirred in a conducting chamber. During the process 1.7 kJ of heat are transferred from the liquid to the surroundings, while the temperature of the liquid is rising to 15°C. Find  $\Delta E$  and  $W$  for the process.  
*Ans.*  $\Delta E = 56.25 \text{ kJ}$ ,  $W = 57.95 \text{ kJ}$
- 4.8 The properties of a certain fluid are related as follows
- $$u = 196 + 0.718 t$$
- $$pv = 0.287 (t + 273)$$
- where  $u$  is the specific internal energy (kJ/kg),  $t$  is in °C,  $p$  is pressure (kN/m<sup>2</sup>), and  $v$  is specific volume (m<sup>3</sup>/kg). For this fluid, find  $c_v$  and  $c_p$ . *Ans.* 0.718, 1.005 kJ/kg K
- 4.9 A system composed of 2 kg of the above fluid expands in a frictionless piston and cylinder machine from an initial state of 1 MPa, 100°C to a final temperature of 30°C. If there is no heat transfer, find the net work for the process. *Ans.* 100.52 kJ
- 4.10 If all the work in the expansion of Problem 4.9 is done on the moving piston, show that the equation representing the path of the expansion in the  $pv$ -plane is given by  $pv^{1.4} = \text{constant}$ .
- 4.11 A stationary system consisting of 2 kg of the fluid of Problem 4.8 expands in an adiabatic process according to  $pv^{1.2} = \text{constant}$ . The initial conditions are 1 MPa and 200°C, and the final pressure is 0.1 MPa. Find  $W$  and  $\Delta U$  for the process. Why is the work transfer not equal to  $\int pdV$ ?  
*Ans.*  $W = 216.83$ ,  $\Delta U = -216.83 \text{ kJ}$ ,  
 $\int pdV = 434.4 \text{ kJ}$
- 4.12 A mixture of gases expands at constant pressure from 1 MPa, 0.03 m<sup>3</sup> to 0.06 m<sup>3</sup> with 84 kJ positive heat transfer. There is no work other than that done on a piston. Find  $\Delta E$  for the gaseous mixture. *Ans.* 54 kJ  
 The same mixture expands through the same state path while a stirring device does 21 kJ of work on the system. Find  $\Delta E$ ,  $W$ , and  $Q$  for the process.  
*Ans.* 54 kJ,  $-21 \text{ kJ}$ , 33 kJ
- 4.13 A mass of 8 kg gas expands within a flexible container so that the  $p$ - $v$  relationship is of the form  $pv^{1.2} = \text{const}$ . The initial pressure is 1000 kPa and the initial volume is 1 m<sup>3</sup>. The final pressure is 5 kPa. If specific internal energy of the gas decreases by 40 kJ/kg, find the heat transfer in magnitude and direction. *Ans.*  $+2615 \text{ kJ}$
- 4.14 A gas of mass 1.5 kg undergoes a quasi-static expansion which follows a relationship  $p = a + bV$ , where  $a$  and  $b$  are constants. The initial and final pressures are 1000 kPa and 200 kPa respectively and the corresponding volumes are 0.20 m<sup>3</sup> and 1.20 m<sup>3</sup>. The specific internal energy of the gas is given by the relation  
 $u = 1.5 pv - 85 \text{ kJ/kg}$   
 where  $p$  is the kPa and  $v$  is in m<sup>3</sup>/kg. Calculate the net heat transfer and the maximum internal energy of the gas attained during expansion.  
*Ans.* 660 kJ, 503.3 kJ
- 4.15 The heat capacity at constant pressure of a certain system is a function of temperature only and may be expressed as
- $$C_p = 2.093 \frac{41.87}{t + 100} \text{ J/K}$$
- where  $t$  is the temperature of the system in °C. The system is heated while it is maintained at a pressure of 1 atmosphere until its volume increases from 2000 cm<sup>3</sup> to 2400 cm<sup>3</sup> and its temperature increases from 0°C to 100°C. (a) Find the magnitude of the heat interaction. (b) How much does the internal energy of the system increase?  
*Ans.* (a) 238.32 J (b) 197.79 J

- 4.16 An imaginary engine receives heat and does work on a slowly moving piston at such rates that the cycle of operation of 1 kg of working fluid can be represented as a circle 10 cm in diameter on a  $p$ - $v$  diagram on which 1 cm = 300 kPa and 1 cm = 0.1 m<sup>3</sup>/kg. (a) How much work is done by each kg of working fluid for each cycle of operation? (b) The thermal efficiency of an engine is defined as the ratio of work done and heat input in a cycle. If the heat rejected by the engine in a cycle is 1000 kJ per kg of working fluid, what would be its thermal efficiency?  
*Ans.* (a) 2356.19 kJ/kg, (b) 0.702
- 4.17 A gas undergoes a thermodynamic cycle consisting of three processes beginning at an initial state where  $p_1 = 1$  bar,  $V_1 = 1.5$  m<sup>3</sup> and  $U_1 = 512$  kJ. The processes are as follows:
- Process 1–2: Compression with  $pV = \text{constant}$  to  $p_2 = 2$  bar,  $U_2 = 690$  kJ
  - Process 2–3:  $W_{23} = 0$ ,  $Q_{23} = -150$  kJ, and
  - Process 3–1:  $W_{31} = +50$  kJ. Neglecting KE and PE changes, determine the heat interactions  $Q_{12}$  and  $Q_{31}$ . *Ans.* 74 kJ, 22 kJ
- 4.18 A gas undergoes a thermodynamic cycle consisting of the following processes: (i) Process 1–2: Constant pressure  $p = 1.4$  bar,  $V_1 = 0.028$  m<sup>3</sup>,  $W_{12} = 10.5$  kJ, (ii) Process 2–3: Compression with  $pV = \text{constant}$ ,  $U_3 = U_2$ , (iii) Process 3–1: Constant volume,  $U_1 - U_3 = -26.4$  kJ. There are no significant changes in KE and PE. (a) Sketch the cycle on a  $p$ - $V$  diagram. (b) Calculate the net work for the cycle in kJ. (c) Calculate the heat transfer for process 1–2 (d) Show that  $\sum_{\text{cycle}} Q = \sum_{\text{cycle}} W$ .  
*Ans.* (b) - 8.28 kJ, (c) 36.9 kJ
- 4.19 A certain gas of mass 4 kg is contained within a piston cylinder assembly. The gas undergoes a process for which  $pV^{1.5} = \text{constant}$ . The initial state is given by 3 bar, 0.1 m<sup>3</sup>. The change in internal energy of the gas in the process is  $u_2 - u_1 = -4.6$  kJ/kg. Find the net heat transfer for the process when the final volume is 0.2 m<sup>3</sup>. Neglect the changes in KE and PE. *Ans.* - 0.8 kJ
- 4.20 An electric generator coupled to a windmill produces an average electrical power output of 5 kW. The power is used to charge a storage battery. Heat transfer from the battery to the surroundings occurs at a constant rate of 0.6 kW. Determine the total amount of energy stored in the battery in 8h of operation. *Ans.*  $1.27 \times 10^5$  kJ
- 4.21 A gas in a piston-cylinder assembly undergoes two processes in series. From state 1 to state 2 there is energy transfer by heat to the gas of 500 kJ, and the gas does work on the piston amounting 800 kJ. The second process, from state 2 to state 3, is a constant pressure compression at 400 kPa, during which there is a heat transfer from the gas amounting 450 kJ. The following data are also known:  $U_1 = 2000$  kJ and  $U_3 = 3500$  kJ. Neglecting changes in KE and PE, calculate the change in volume of the gas during process 2–3. *Ans.* -5.625 m<sup>3</sup>
- 4.22 Air is contained in a rigid well-insulated tank with a volume of 0.2 m<sup>3</sup>. The tank is fitted with a paddle wheel which transfers energy to the air at a constant rate of 4 W for 20 min. The initial density of the air is 1.2 kg/m<sup>3</sup>. If no changes in KE or PE occur, determine (a) the specific volume at the final state, (b) the change in specific internal energy of the air. *Ans.* (a) 0.833 m<sup>3</sup>/kg, (b) 20 kJ/kg

# First Law Applied to Flow Processes

## 5.1 CONTROL VOLUME

For any system and in any process, the first law can be written as

$$Q = \Delta E + W$$

where  $E$  represents all forms of energy stored in the system.

For a pure substance

$$E = E_k + E_p + U$$

where  $E_k$  is the K.E.,  $E_p$  the P.E., and  $U$  the residual energy stored in the molecular structure of the substance.

$$Q = \Delta E_k + \Delta E_p + \Delta U + W \quad (5.1)$$

When there is mass transfer across the system boundary, the system is called an open system. Most of the engineering devices are open systems involving the flow of fluids through them.

Equation (5.1) refers to a system having a particular mass of substance, and is free to move from place to place.

Consider a steam turbine (Fig. 5.1) in which steam enters at a high pressure, does work upon the turbine rotor, and then leaves the turbine at low pressure through the exhaust pipe.

If a certain mass of steam is considered as the thermodynamic system, then the energy equation becomes

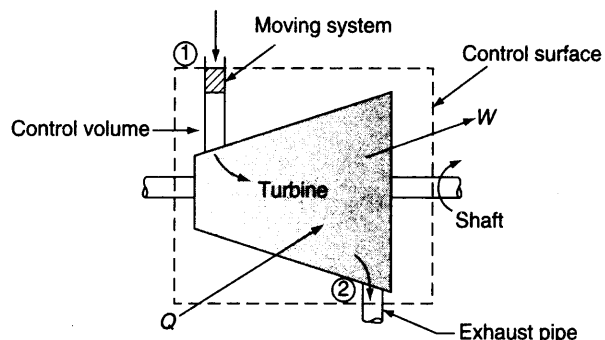
$$Q = \Delta E_k + \Delta E_p + \Delta U + W$$

and in order to analyze the expansion process in turbine the moving system is to be followed as it travels through the turbine, taking into account the work and heat interactions all the way through. This method of analysis is similar to that of Lagrange in fluid mechanics.

Although the system approach is quite valid, there is another approach which is found to be highly convenient. Instead of concentrating attention upon a certain quantity of fluid, which constitutes a moving system in flow process, attention is focussed upon a certain fixed region in space called a *control volume* through which the moving substance flows. This is similar to the analysis of Euler in fluid mechanics.

To distinguish the two concepts, it may be noted that while the system (closed) boundary usually changes shape, position and orientation relative to the observer, the control volume boundary remains fixed and unaltered. Again, while matter usually crosses the control volume boundary, no such flow occurs across the system boundary.

The broken line in Fig. 5.1 represents the surface of the control volume which is known as the *control surface*. This is the same as the system boundary of the open system. The method of analysis is to inspect the control



surface and account for all energy quantities transferred through this surface. Since there is mass transfer across the control surface, a mass balance also has to be made. Sections 1 and 2 allow mass transfer to take place, and  $Q$  and  $W$  are the heat and work interactions respectively.

## 5.2 STEADY FLOW PROCESS

As a fluid flows through a certain control volume, its thermodynamic properties may vary along the space coordinates as well as with time. If the rates of flow of mass and energy through the control surface change with time, the mass and energy within the control volume also would change with time.

'Steady flow' means that the rates of flow of mass and energy across the control surface are constant.

In most engineering devices, there is a constant rate of flow of mass and energy through the control surface, and the control volume in course of time attains a steady state. *At the steady state of a system, any thermodynamic property will have a fixed value at a particular location, and will not alter with time.* Thermodynamic properties may vary along space coordinates, but do not vary with time. 'Steady state' means that the state is steady or invariant with time.

## 5.3 MASS BALANCE AND ENERGY BALANCE IN A SIMPLE STEADY FLOW PROCESS

In Fig. 5.2, a steady flow system has been shown in which one stream of fluid enters and one another stream leaves the control volume. There is no accumulation of mass or energy within the control volume, and the properties at any location within the control volume are steady with time. Sections 1-1 and 2-2 indicate, respectively, the entrance and exit of the fluid across the control surface. The following quantities are defined with reference to Fig. 5.2.

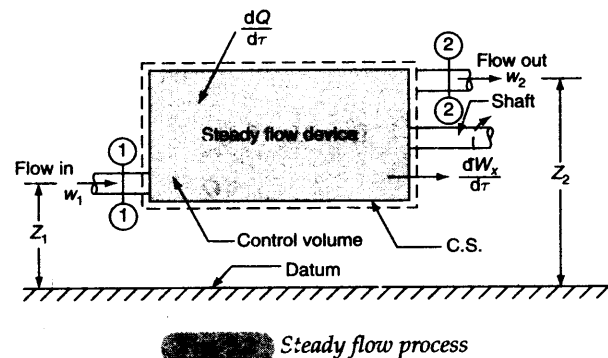
- $A_1, A_2$ —cross-section of stream,  $m^2$
- $w_1, w_2$ —mass flow rate,  $kg/s$
- $p_1, p_2$ —pressure, absolute,  $N/m^2$
- $v_1, v_2$ —specific volume,  $m^3/kg$
- $u_1, u_2$ —specific internal energy,  $J/kg$
- $V_1, V_2$ —velocity,  $m/s$
- $Z_1, Z_2$ —elevation above an arbitrary datum,  $m$

$\frac{dQ}{d\tau}$ —net rate of heat transfer through the control surface,  $J/s$

$\frac{dW_x}{d\tau}$ —net rate of work transfer through the control surface,  $J/s$  exclusive of work done at Sections 1 and 2 in transferring the fluid through the control surface.

$\tau$ —time,  $s$ .

Subscripts 1 and 2 refer to the inlet and exit sections.



### 5.3.1 Mass Balance

By the conservation of mass, if there is no accumulation of mass within the control volume, the mass flow rate entering must equal the mass flow rate leaving, or

$$w_1 = w_2$$

or

$$\frac{A_1 V_1}{v_1} = \frac{A_2 V_2}{v_2} \quad (5.2)$$

This equation is known as the *equation of continuity*.

### 5.3.2 Energy Balance

In a flow process, the work transfer may be of two types: the *external work* and the *flow work*. The external work refers to all the work transfer across the control surface other than that due to normal fluid forces. In engineering thermodynamics the only kinds of external work of importance are *shear* (shaft or stirring) *work* and *electrical work*. In Fig. 5.2 the only external work occurs in the form of shaft work,  $W_x$ . The flow work, as discussed in Sec. 3.4, is the displacement work done by the fluid of mass  $dm_1$  at the inlet Section 1 and that of mass  $dm_2$  at the exit Section 2, which are  $(-p_1 v_1 dm_1)$  and  $(+p_2 v_2 dm_2)$  respectively. Therefore, the total work transfer is given by

$$W = W_x - p_1 v_1 dm_1 + p_2 v_2 dm_2 \quad (5.3)$$

In the rate form,

$$\frac{dW}{d\tau} = \frac{dW_x}{d\tau} - p_1 v_1 \frac{dm_1}{d\tau} + p_2 v_2 \frac{dm_2}{d\tau}$$

or

$$\frac{dW}{d\tau} = \frac{dW_x}{d\tau} - w_1 p_1 v_1 + w_2 p_2 v_2 \quad (5.4)$$

Since there is no accumulation of energy, by the conservation of energy, the total rate of flow of all energy streams entering the control volume must equal the total rate of flow of all energy streams leaving the control volume. This may be expressed in the following equation.

$$w_1 e_1 + \frac{dQ}{d\tau} = w_2 e_2 + \frac{dW}{d\tau}$$

Substituting for  $\frac{dW}{d\tau}$  from Eq. (5.4)

$$w_1 e_1 + \frac{dQ}{d\tau} = w_2 e_2 + \frac{dW_x}{d\tau} - w_1 p_1 v_1 + w_2 p_2 v_2$$

$$w_1 e_1 + w_1 p_1 v_1 + \frac{dQ}{d\tau} = w_2 e_2 + w_2 p_2 v_2 + \frac{dW_x}{d\tau} \quad (5.5)$$

where  $e_1$  and  $e_2$  refer to the energy carried into or out of the control volume with unit mass of fluid.

The specific energy  $e$  is given by

$$e = e_k + e_p + u = \frac{V^2}{2} + Zg + u \quad (5.6)$$

Substituting the expression for  $e$  in Eq. (5.5)

$$w_1 \left( \frac{V_1^2}{2} + Z_1 g + u_1 \right) + w_1 p_1 v_1 + \frac{dQ}{d\tau} = w_2 \left( \frac{V_2^2}{2} + Z_2 g + u_2 \right) + w_2 p_2 v_2 + \frac{dW_x}{d\tau}$$

or

$$w_1 \left( h_1 + \frac{V_1^2}{2} + Z_1 g \right) + \frac{dQ}{d\tau} = w_2 \left( h_2 + \frac{V_2^2}{2} + Z_2 g \right) + \frac{dW_x}{d\tau} \quad (5.7)$$



where

$$h = u + pv.$$

And, since

$$w_1 = w_2, \quad \text{let } w = w_1 = w_2 = \frac{dm}{d\tau}$$

Dividing Eq. (5.7) by  $\frac{dm}{d\tau}$

$$h_1 + \frac{V_1^2}{2} + Z_1g + \frac{dQ}{dm} = h_2 + \frac{V_2^2}{2} + Z_2g + \frac{dW_x}{dm} \quad (5.8)$$

Equations (5.7) and (5.8) are known as *steady flow energy equations* (S.F.E.E.), for a single stream of fluid entering and a single stream of fluid leaving the control volume. All the terms in Eq. (5.8) represent energy flow per unit mass of fluid (J/kg), whereas the terms in Eq. (5.7) represent energy flow per unit time (J/kg). The basis of energy flow per unit mass is usually more convenient when only a single stream of fluid enters and leaves a control volume. When more than one fluid stream is involved the basis of energy flow per unit time is more convenient.

Equation (5.8) can be written in the following form,

$$Q - W_x = (h_2 - h_1) + \frac{\bar{V}_2^2 - \bar{V}_1^2}{2} + g(Z_2 - Z_1) \quad (5.9)$$

where  $Q$  and  $W_x$  refer to energy transfer per unit mass. In the differential form, the SFEE becomes

$$dQ - dW_x = dh + \bar{V}d\bar{V} + gdZ \quad (5.10)$$

When more than one stream of fluid enters or leaves the control volume (Fig. 5.3), the mass balance and energy balance for steady flow are given below.

*Mass balance*

$$w_1 + w_2 = w_3 + w_4 \quad (5.11)$$

$$\frac{A_1V_1}{v_1} + \frac{A_2V_2}{v_2} = \frac{A_3V_3}{v_3} + \frac{A_4V_4}{v_4} \quad (5.12)$$

*Energy balance*

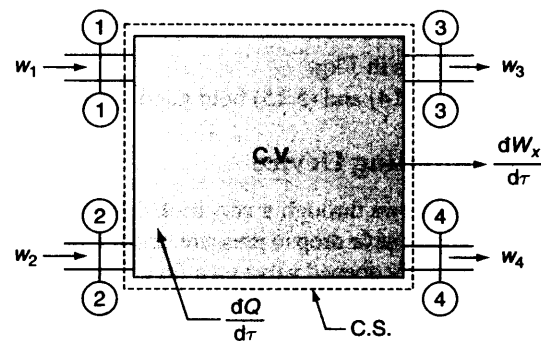
$$\begin{aligned} w_1 \left( h_1 + \frac{V_1^2}{2} + Z_1g \right) + w_2 \left( h_2 + \frac{V_2^2}{2} + Z_2g \right) + \frac{dQ}{d\tau} \\ = w_3 \left( h_3 + \frac{V_3^2}{2} + Z_3g \right) + w_4 \left( h_4 + \frac{V_4^2}{2} + Z_4g \right) + \frac{dW_x}{d\tau} \end{aligned} \quad (5.13)$$

The steady flow energy equation applies to a wide variety of processes like pipe line flows, heat transfer processes, mechanical power generation in engines and turbines, combustion processes, and flows through nozzles and diffusors. In certain problems, some of the terms in steady flow energy equation may be negligible or zero. But it is best to write the full equation first, and then eliminate the terms which are unnecessary.

### 5.4

### SOME EXAMPLES OF STEADY FLOW PROCESSES

The following examples illustrate the applications of the steady flow energy equation in some of the engineering systems.



Steady flow process involving two fluid streams at the inlet and exit of the control volume

### 5.4.1 Nozzle and Diffusor

A nozzle is a device which increases the velocity or K.E. of a fluid at the expense of its pressure drop, whereas a diffusor increases the pressure of a fluid at the expense of its K.E. Figure 5.4 shows a nozzle which is insulated. The steady flow energy equation of the control surface gives

$$h_1 + \frac{V_1^2}{2} + Z_1g + \frac{dQ}{dm} = h_2 + \frac{V_2^2}{2} + Z_2g + \frac{dW_x}{dm}$$

Here  $\frac{dQ}{dm} = 0$ ,  $\frac{dW_x}{dm} = 0$ , and the change in potential energy is zero. The equation reduces to

$$h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2} \quad (5.14)$$

The continuity equation gives

$$w = \frac{A_1 V_1}{v_1} = \frac{A_2 V_2}{v_2} \quad (5.15)$$

When the inlet velocity or the 'velocity of approach'  $V_1$  is small compared to the exit velocity  $V_2$ , Eq. (5.14) becomes

$$h_1 = h_2 + \frac{V_2^2}{2} \quad \text{or} \quad V_2 = \sqrt{2(h_1 - h_2)} \quad \text{m/s}$$

where  $(h_1 - h_2)$  is in J/kg.

Equations (5.14) and (5.15) hold good for a diffusor as well.

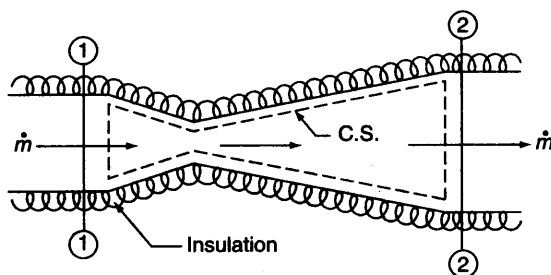
### 5.4.2 Throttling Device

When a fluid flows through a constricted passage, like a partially opened valve, an orifice, or a porous plug, there is an appreciable drop in pressure, and the flow is said to be throttled. Figure 5.5 shows the process of throttling by a partially opened valve on a fluid flowing in an insulated pipe. In the steady-flow energy Eq. (5.8),

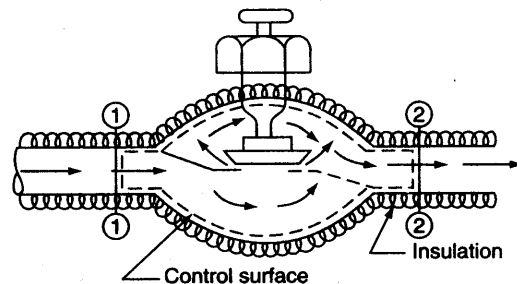
$$\frac{dQ}{dm} = 0, \quad \frac{dW_x}{dm} = 0$$

and the changes in P.E. are very small and ignored. Thus, the S.F.E.E. reduces to

$$h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2}$$



Steady flow process involving one fluid stream at the inlet and at exit of the control volume



Flow through a valve