7

First Law of Thermodynamics – Basic Concepts

CHAPTER

CONTENTS

The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation, is called Thermodynamics.

In studying and evaluating the flow of energy into or out of a system, it will be useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of the system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

THE THREE EMPIRICAL LAWS

The study of thermodynamics is based on three broad generalisations derived from well established experimental results. These generalisations are known as **the First, Second and Third law of thermodynamics.** These laws have stood the test of time and are independent of any theory of the atomic or molecular structure. The discussion of these laws will be the subject of our study in the two chapters on thermodynamics.

236

Scope of Thermodynamics

(1) Most of the important laws of Physical Chemistry, including the van't Hoff law of lowering of vapour pressure, Phase Rule and the Distribution Law, can be derived from the laws of thermodynamics.

(2) It tells whether a particular physical or chemical change can occur under a given set of conditions of temperature, pressure and concentration.

(3) It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

Limitations of Thermodynamics

(1) **Thermodynamics is applicable to macroscopic systems** consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. **It ignores the internal structure of atoms and molecules.**

(2) Thermodynamics does not bother about the time factor. That is, it does not tell anything regarding the rate of a physical change or a chemical reaction. **It is concerned only with the initial and the final states of the system.**

THERMODYNAMIC TERMS AND BASIC CONCEPTS

An important part of the study of thermodynamics is a few terms and definitions which must be understood clearly.
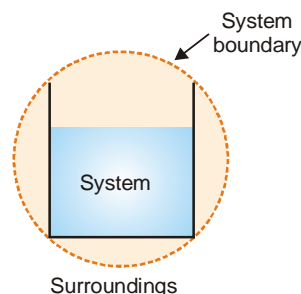
SYSTEM, BOUNDARY, SURROUNDINGS

A system is that part of the universe which is under thermodynamic study and the rest of the universe is surroundings.

The real or imaginary surface separating the system from the surroundings is called the boundary.
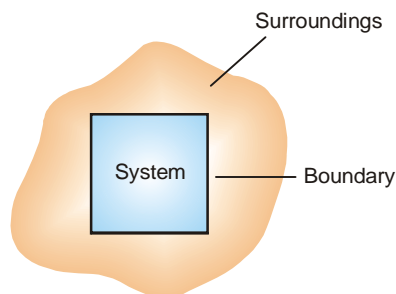
■ **Figure 7.1**
Thermodynamic system.

■ **Figure 7.2**
Water contained in a beaker constitutes a system.

In experimental work, a specific amount of one or more substances constitutes the system. Thus 200 g of water contained in a beaker constitutes a thermodynamic system. The beaker and the air in contact, are the surroundings.

Similarly 1 mole of oxygen confined in a cylinder fitted with a piston, is a thermodynamic system. The cylinder and the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (oxygen) and the surroundings (cylinder and piston) is clearly defined.

HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

When a system is uniform throughout, it is called a Homogeneous System. Examples are : a pure single solid, liquid or gas, mixtures of gases, and true solution of a solid in a liquid. A homogeneous system is made of one phase only. A **phase** is defined as a homogeneous, physically distinct and

mechanically separable portion of a system.

A heterogeneous system is one which consists of two or more phases. In other words it is not uniform throughout. Examples of heterogeneous systems are : ice in contact with water, ice in contact with vapour etc. Here ice, water and vapour constitute separate phases.

TYPES OF THERMODYNAMIC SYSTEMS

There are three types of thermodynamic systems depending on the nature of the boundary. If the boundary is closed or sealed, no *matter* can pass through it. If the boundary is insulated, no *energy* (say heat) can pass through it.

(1) Isolated System

When the boundary is both sealed and insulated, no interaction is possible with the surroundings. Therefore, **an isolated system is one that can transfer neither matter nor energy to and from its surroundings.**

Let us consider a system 100 ml of water in contact with its vapour in a closed vessel which is insulated. Since the vessel is sealed, no water vapour (matter) can escape from it. Also, because the vessel is insulated, no heat (energy) can be exchanged with the surroundings.

A substance, say boiling water, contained in a *thermos flask,* is another example of an isolated system.
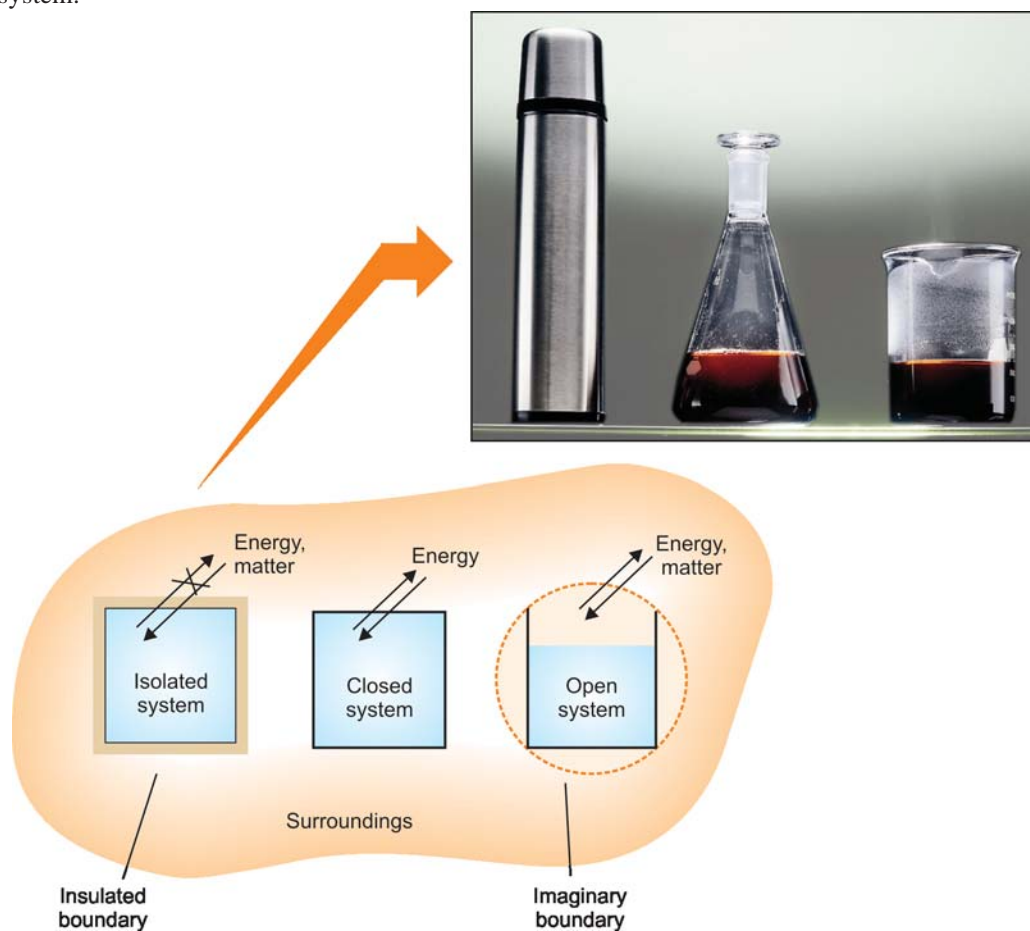
■ **Figure 7.3**
Three types of thermodynamic systems.

(2) Closed System

Here the boundary is sealed but not insulated. Therefore, **a closed system is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings.**

A specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

A gas contained in a cylinder fitted with a piston constitutes a closed system. As the piston is raised, the gas expands and transfers heat (energy) in the form of work to the surroundings.

(3) Open System

In such a system the boundary is open and un-insulated. Therefore, **an open system is one which can transfer both energy and matter to and from its surroundings.**

Hot water contained in a beaker placed on laboratory table is an open system. The water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

Zinc granules reacting with dilute hydrochloric acid to produce hydrogen gas in a beaker, is another example of open system. Hydrogen gas escapes and the heat of the reaction is transferred to the surroundings.

What are Adiabatic Systems ?

Those systems in which no thermal energy passes into or out of the system, are said to be adiabatic systems.

INTENSIVE AND EXTENSIVE PROPERTIES

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes :

(*a*) Intensive properties

(*b*) Extensive properties

Intensive Properties

A property which does not depend on the quantity of matter present in the system, is known as Intensive Property.

Some examples of intensive properties are *pressure, temperature, density*, and *concentration*. If the overall temperature of a glass of water (our system) is 20ºC, then any drop of water in that glass has a temperature of 20ºC. Similarly if the concentration of salt, NaCl, in the glass of water is 0.1 mole/litre, then any drop of water from the glass also has a salt concentration of 0.1 mole/litre.

Extensive Properties

A property that does depend on the quantity of matter present in the system, is called an Extensive Property.

Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy*. Some of these properties are unfamiliar to you but these will be defined and illustrated later.

By definition, **the extensive properties are additive while intensive properties are not.** Let us consider the system 'a glass of water'. If we double the mass of water, the volume is doubled and so is the number of moles and the internal energy of the system.

TABLE 7.1. COMMON PROPERTIES OF A SYSTEM.		
Intensive properties		**Extensive properties**
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed.

The fundamental properties which determine the state of a system are pressure (P), temperature (T), volume (V), mass and composition. Since a change in the magnitude of such properties alters the state of the system, these are referred to as **State variables** or **State functions** or **Thermodynamic parameters.** It also stands to reason that a change of system from the *initial state* to the *final state* (2nd state) will be accompanied by change in the state variables.

It is not necessary to state all the properties (state variables) to define a system completely. For a pure gas, the composition is fixed automatically, as it is cent per cent. The remaining state variables P, V, T are interrelated in the form of an algebraic relationship called the **Equation of State.** Thus for one mole of a pure gas, the equation of state is :

$$PV = RT$$

where R is gas constant. If of the three state variables (P, V, T), P and T are specified, the value of third (V) is fixed automatically and can be calculated from the equation of state. The variables (P and T) which must be necessarily specified to define the state of a system, are designated as **Independent state variables.** The remaining state variable (V) which depends on the value of P and T, is called **Dependent state variable.**

An important characteristic of a state variable (or state function) is that when the state of a system is altered, the change in the variable depends on the initial and final states of the system. For example, if we heat a sample of water from 0° C to 25° C, the change in temperature is equal to difference between the initial and final temperatures.

$$\Delta T = T_{final} - T_{initial} = 25°C$$

The way in which the temperature change is brought about has no effect on the result.

EQUILIBRIUM AND NON–EQUILIBRIUM STATES

A system in which the state variables have constant values throughout the system is said to be in a state of thermodynamic equilibrium.

Suppose we have a gas confined in a cylinder that has a frictionless piston. If the piston is stationary, the state of the gas can be specified by giving the values of pressure and volume. The system is then in a *state of equilibrium*.

A system in which the state variables have different values in different parts of the system is said to be in a non-equilibrium state.

If the gas contained in a cylinder, as stated above, is compressed very rapidly by moving down the piston, it passes through states in which pressure and temperature cannot be specified, since these properties vary throughout the gas. The gas near the piston is compressed and heated and that at the far end of the cylinder is not. The gas then would be said to be in non-equilibrium state.
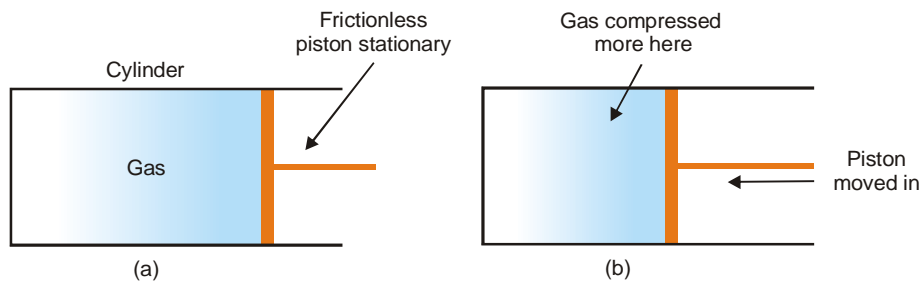
Figure 7.4
(*a*) **Gas in equilibrium state;** (*b*) **Rapidly compressed gas in non-equilibrium state.**

Thermodynamics is concerned only with equilibrium states.

The Criteria for Equilibrium

(1) **The temperature of the system must be uniform and must be the same as the temperature of the surroundings (thermal equilibrium).**

(2) **The mechanical properties must be uniform throughout the system (mechanical equilibrium).** That is, no mechanical work is done by one part of the system on any other part of the system.

(3) **The chemical composition of the system must be uniform with no net chemical change (chemical equilibrium).**

If the system is heterogeneous, the state variables of each phase remain constant in each phase.

THERMODYNAMIC PROCESSES

When a thermodynamic system changes from one state to another, the operation is called a Process. These processes involve the change of conditions (temperature, pressure and volume). The various types of thermodynamic processes are :

(1) Isothermal Processes

Those processes in which the temperature remains fixed, are termed isothermal processes. This is often achieved by placing the system in a thermostat (a constant temperature bath).

For an isothermal process $dT = 0$

(2) Adiabatic Processes

Those processes in which no heat can flow into or out of the system, are called adiabatic processes. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle. High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process $dq = 0$

(3) Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes. For example, heating of water to its boiling point and its vaporisation take place at the same atmospheric pressure. These changes are, therefore, designated as isobaric processes and are said to take place isobarically.

For an isobaric process $dp = 0$
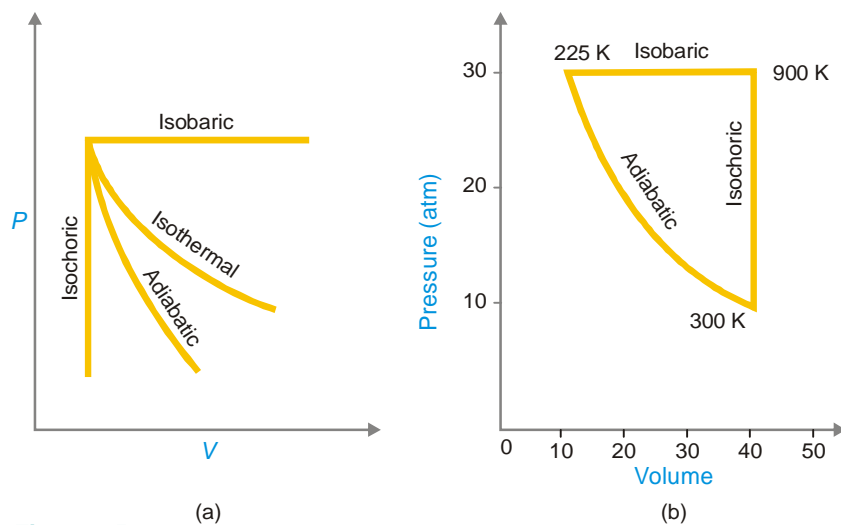
Figure 7.5
(*a*) **Four basic thermodynamic processes; (*b*) A cyclic process.**

(4) Isochoric Processes

Those processes in which the volume remains constant are known as isochoric processes. The heating of a substance in a non-expanding chamber is an example of isochoric process.

For isochoric processes $dV = 0$.

(5) Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

For a cyclic process $dE = 0$, $dH = 0$.

REVERSIBLE AND IRREVERSIBLE PROCESSES

A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.
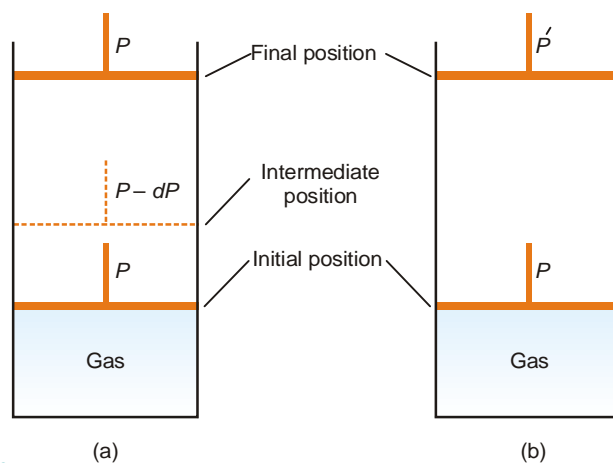
Figure 7.6
(*a*) **Reversible expansion occurs by decreasing the pressure on the piston by infinitesimal amounts. (*b*) Irreversible expansion occurs by sudden decrease of pressure from P to P′, when the gas expands rapidly in a single operation.**

In fact, a reversible process is considered to proceed from the initial state to the final state through an infinite series of infinitesimally small stages. At the initial, final and all intermediate stages, the system is in equilibrium state. This is so because an infinitesimal change in the state of the system at each intermediate step is negligible.

When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an irreversible process. Here the system is in equilibrium state in the beginning and at the end, but not at points in between.

Consider a certain quantity of a gas contained in a cylinder having a weightless and frictionless piston. The expansion of the gas can be carried by two methods illustrated in Fig. 7.6.

Let the pressure applied to the piston be P and this is equal to the internal pressure of the gas. Since the external and internal pressures are exactly counterbalanced, the piston remains stationary and there is no change in volume of the gas. Now suppose the pressure on the piston is decreased by an infinitesimal amount dP. Thus the external pressure on the piston being $P - dP$, the piston moves up and the gas will expand by an infinitesimal small amount. The gas will, therefore, be expanded infinitely slowly *i.e.*, by a thermodynamically *reversible process*. At all stages in the expansion of the gas, dP being negligibly small the gas is maintained in a state of equilibrium throughout. If at any point of the process the pressure is increased by dP, the gas would contract reversibly.

On the other hand, the expansion is irreversible (Fig. 7.6 *b*) if the pressure on the piston is decreased suddenly. It moves upward rapidly in a single operation. The gas is in equilibrium state in the initial and final stages only. The expansion of the gas, in this case, takes place in an irreversible manner.

DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process	Irreversible Process
1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur.	1. It takes place *infinite time*.
2. It is *imaginary* as it assumes the presence of frictionless and weightless piston.	2. It is *real* and can be performed actually.
3. It is in equilibrium state at *all stages* of the operation.	3. It is in equilibrium state only at the *initial and final stages* of the operation.
4. All changes are *reversed* when the process is carried out in reversible direction.	4. After this type of process has occurred all changes *do not return* to the initial state by themselves.
5. It is extremely slow.	5. It proceeds at *measureable speed*.
6. Work done by a reversible process is *greater* than the corresponding irreversible process.	6. Work done by a irreversible process is *smaller* than the corresponding reversible process.

NATURE OF HEAT AND WORK

When a change in the *state* of a system occurs, energy is transferred to or from the surroundings. This energy may be transferred as heat or mechanical work.

We shall refer the term 'work' for mechanical work which is defined as force × distance.

Units of Work

In CGS system the unit of work is erg which is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 centimeter. Since the erg is so small, a bigger unit, the **joule (J)** is now used.

$$1 \text{ joule} = 10^7 \text{ ergs}$$

or $1 \text{ erg} = 10^{-7} \text{ J}$

We often use **kilojoule** (kJ) for large quantities of work

$$1 \text{ kJ} = 1000 \text{ J}$$

Units of Heat

The unit of heat, which was used for many years, is **calorie** (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1° C in the vicinity of 15°C.

Since heat and work are interrelated, **SI unit of heat is the joule (J).**

$$1 \text{ joule} = 0.2390 \text{ calories}$$
$$1 \text{ calorie} = 4.184 \text{ J}$$

or $1 \text{ kcal} = 4.184 \text{ kJ}$

Sign Convention of Heat

The symbol of heat is q. If the heat flows from the surroundings into the system to raise the energy of the system, it is taken to be positive, $+q$. If heat flows from the system into the surroundings, lowering the energy of the system, it is taken to be negative, $-q$.
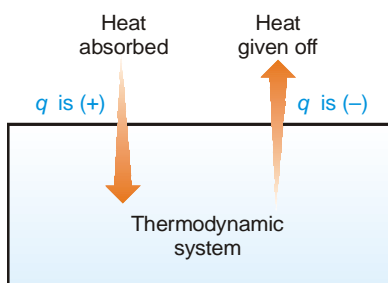
■ Figure 7.7
Sign convention for heat flow in a thermodynamic system.

Sign Convention of Work

The symbol of work is w. If work is done on a system by the surroundings and the energy of the system is thus increased, it is taken to be positive, $+w$. If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, $-w$.

Summary of Sign Conventions

Heat flows into the system, q is +ve	Heat flows out of the system, q is –ve
Work is done on the system, w is +ve	Work is done by the system, w is –ve

PRESSURE–VOLUME WORK

In physics, mechanical work is defined as force multiplied by the distance through which the force acts. In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as **pressure-volume work** or **PV work** or **expansion work.**

Consider a gas contained in a cylinder fitted with a frictionless piston. The pressure (force per unit area) of the gas, P, exerts a force on the piston. This can be balanced by applying an equal but opposite pressure from outside on the piston. Let it be designated as P_{ext}. **It is important to remember that it is the external pressure, P_{ext}. and not the internal pressure of the gas itself which is used in evaluating work.** This is true whether it be expansion or contraction.

If the gas expands at constant pressure, the piston would move, say through a distance l. We know that

$$work = force \times distance \text{ (by definition)}$$

or $\qquad\qquad\qquad w = f \times l \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad ...(1)$

Since pressure is force per unit area,

$$f = P_{ext} \times A \qquad\qquad\qquad\qquad\qquad\qquad ...(2)$$

where A is the cross-section area of the piston.

From (1) and (2), we have

$$w = P_{ext} \times A \times l$$
$$= P_{ext} \times \Delta V$$

where ΔV is the increase in volume of the gas.

Since the system (gas) is doing work on the surroundings (piston), it bears negative sign. Thus,

$$w = -P_{ext} \times \Delta V$$

Proceeding as above the work done in compression of a gas can also be calculated. In that case the piston will move down and sign of the work will be positive.

$$w = P_{ext} \times \Delta V$$

As already stated, work may be expressed in dynes-centimetres, ergs, or joules. *PV* work can as well be expressed as the product of pressure and volume units *e.g.*, in litre or atmospheres.

It may be noted that **the work done by a system is not a state function.** This is true of the mechanical work of expansion. We shall show presently that the work is related to the process carried out rather than to the internal and final states. This will be evident from a consideration of the *reversible expansion* and an *irreversible process*.
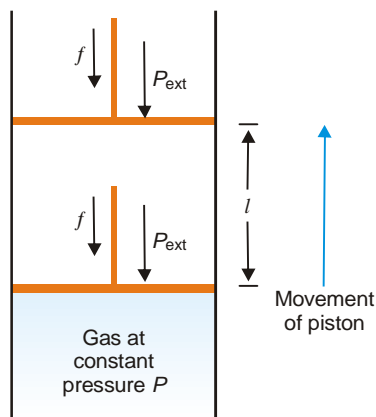
■ **Figure 7.8**
Pressure volume work of a system (gas) confined by a frictionless piston.

SOLVED PROBLEM. Calculate the pressure-volume work done when a system containing a gas expands from 1.0 litre to 2.0 litres against a constant external pressure of 10 atmospheres. Express the answer in calories and joules.

SOLUTION

$$\begin{aligned} w &= -P_{ext}(V_2 - V_1) \\ &= -(10 \text{ atm})(2\,l - 1\,l) \\ &= -10\,l\,\text{atm} \end{aligned}$$

$$= -(10\,l\,\text{atm}) \left(\frac{1.987 \text{ cal}}{0.082\,l\,\text{atm}} \right)$$

$$= -242 \text{ cal}$$

But 1 calorie = 4.184 J

$$w = -\textbf{1012.528 J}$$

ISOTHERMAL REVERSIBLE EXPANSION WORK OF AN IDEAL GAS

Consider an ideal gas confined in a cylinder with a frictionless piston. Suppose it expands in a reversible manner from volume V_1 to V_2 at a constant temperature. The pressure of the gas is successively reduced from P_1 to P_2.

The reversible expansion of the gas takes place in a finite number of infinitesimally small intermediate steps. To start with the external pressure, P_{ext}, is arranged equal to the internal pressure of the gas, P_{gas}, and the piston remains stationary. If P_{ext} is decreased by an infinitesimal amount dP the gas expands reversibly and the piston moves through a distance dl.

Since dP is so small, for all practical purposes,

■ **Figure 7.9**
Isothermal reversible expansion work.

$$P_{ext} = P_{gas} = P$$

The work done by the gas in one infinitesimal step dw, can be expressed as

$$dw = P \times A \times dl \qquad\qquad (A = \text{cross-sectional area of piston})$$

$$= P \times dV$$

where dV is the increase in volume

The total amount of work done by the isothermal reversible expansion of the ideal gas from V_1 to V_2 is, therefore,

$$w = - \int_{v_1}^{v_2} P\,dV \qquad\qquad\qquad ...(1)$$

By the ideal gas equation

$$P = \frac{nRT}{V}$$

∴

$$w = - \int_{v_1}^{v_2} \frac{nRT}{V}\,dV$$

$$= - nRT \int_{v_1}^{v_2} \frac{dV}{V}$$

which integrates to give

$$w = - nRT \ln \frac{V_2}{v_1}$$

Since
$$P_1V_1 = P_2V_2$$
$$V_2/V_1 = P_1/P_2$$

$\therefore$
$$w = -nRT \; \text{In} \; \frac{P_1}{P_2} = -2.303 \; nRT \; \log \frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with the sign changed. Here the pressure on the piston, P_{ext}, is increased by dP which reduces the volume of the gas.

ISOTHERMAL IRREVERSIBLE EXPANSION WORK OF AN IDEAL GAS

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly *i.e.*, by instantaneously dropping the external pressure, P_{ext}, to the final pressure P_2. The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression :

$$w = -P_{ext} \int_{v_1}^{v_2} dV$$

$$= P_2 (V_2 - V_1)$$
$$= P_2 \, dV$$

MAXIMUM WORK DONE IN REVERSIBLE EXPANSION

The isothermal expansion of an ideal gas may be carried either by the *reversible process* or *irreversible process* as stated above.
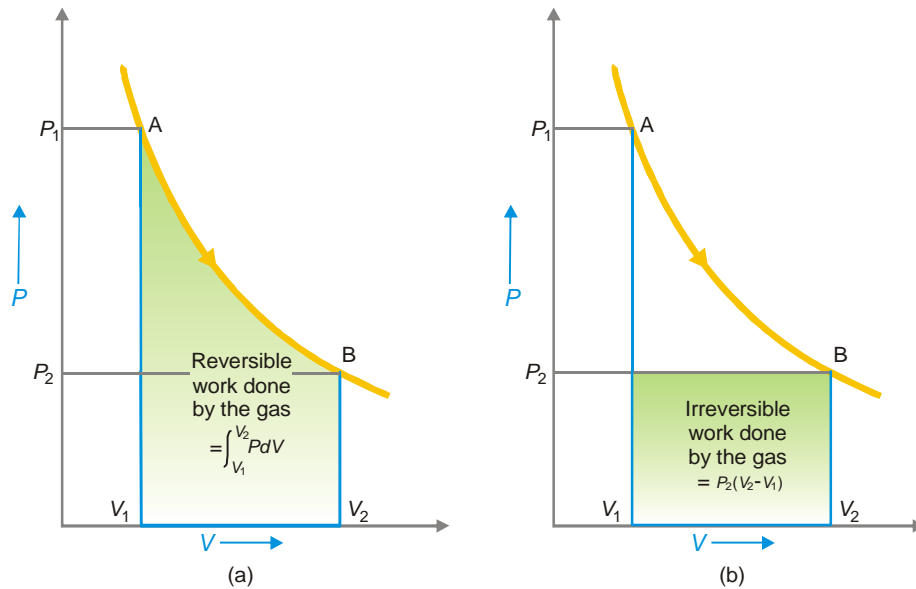
Figure 7.10

(*a*) The reversible work of expansion; (*b*) The irreversible work done by the gas when the external pressure is at once dropped to the final value P_2.

The reversible expansion is shown in Fig. 7.10 in which the pressure is falling as the volume increases. The reversible work done by the gas is given by the expression

$$-w_{irr} = \int_{v_1}^{v_2} PdV$$

which is represented by the shaded area.

If the expansion is performed irreversibly by suddenly reducing the external pressure to the final pressure P_2, the irreversible work is given by

$$- w_{in} = P_2 (V_2 - V_1)$$

which is shown by the shaded area in Fig. 7.10 (b).

In both the processes, the state of the system has changed from A to B but the work done is much less in the irreversible expansion than in the reversible expansion. **Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states. It is a path function.**

It is also important to note that **the work done in the reversible expansion of a gas is the maximum work that can be done by a system (gas) in expansion between the same initial (A) and final state (B).** This is proved as follows :

We know that the work always depends on the external pressure, P_{ext}; the larger the P_{ext} the more work is done by the gas. But the P_{ext} on the gas cannot be more than the pressure of the gas, P_{gas} or a compression will take place. Thus the largest value P_{ext} can have without a compression taking place is equal to P_{gas}. But an expansion that occurs under these conditions is the reversible expansion. Thus, maximum work is done in the reversible expansion of a gas.

SOLVED PROBLEM 1. One mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from a volume of 10 litres to 20 litres. Calculate the work done by the gas in joules and calories.

SOLUTION

$$w = - nRT \ln \frac{V_2}{V_1} = - 2.303 \ nRT \ \log \frac{V_2}{V_1}$$

$$= - 2.303 \times 8.314 \times 298 \log \frac{20}{10} = - 1717.46 \, \text{J}$$

$$= - 1717.46 \, \text{J} \times \frac{1.987 \, \text{cal}}{8.314 \, \text{J}} = -\textbf{410.46 cal}$$

Notes. (1) $\ln x = 2.303 \log x$

(2)   The units of R will determine the units of w in this expression.

(3)   The temperature must be expressed in degrees Kelvin.

SOLVED PROBLEM 2. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C.

SOLUTION

$$w = - nRT \ln \frac{P_1}{P_2}$$

$$= - 1 \times 8.314 \times 298 \times 2.303 \log 5$$

$$= - 3988 \, \text{J}$$

$$= - \textbf{3.988 kJ}$$

INTERNAL ENERGY

A thermodynamic system containing some quantity of matter has within itself a definite quantity of energy. This energy includes not only the translation kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies. The kinetic and potential energy of the nuclei and electrons within the individual molecules also contribute to the energy of the system.

The total of all the possible kinds of energy of a system, is called its Internal Energy.

The word 'internal' is often omitted and the energy of a system always implies internal energy.

The internal energy of a system, like temperature, pressure, volume, etc., is determined by the state of a system and is independent of the path by which it is obtained. **Hence internal energy of a system is a state function.**

For example, we consider the heating of one mole of liquid water from $0°$ to $100°$ C. The change in energy is 1.8 kcal and is the same regardless of the form in which this energy is transferred to the water by heating, by performing work, by electrical means or in any other way.

Since the value of internal energy of a system depends on the mass of the matter contained in a system, it is classed as an **extensive property.**

Symbol Representation of Internal Energy and Sign Conventions

The internal energy of a system is represented by the symbol E (Some books use the symbol U). It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we are concerned only with the energy changes when a system changes from one state to another. If ΔE be the difference of energy of the initial state (E_{in}) and the final state (E_f), we can write

$$\Delta E = E_f - E_{in}$$

ΔE is +ve if E_f is greater than E_{in} and –ve if E_f is less than E_{in}.

A system may transfer energy to or from the surroundings as heat or as work, or both.

UNITS OF INTERNAL ENERGY

The SI unit for internal energy of a system is the joule (J). Another unit of energy which is not an SI unit is the calorie, 1 cal = 4.184 J.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is, in fact, an application of the broad principle known as the Law of Conservation of Energy to the thermodynamic system. It states that :

the total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from state A to state B, it undergoes a change in the internal energy from E_A to E_B. Thus, we can write

$$\Delta E = E_B - E_A$$

This energy change is brought about by the evolution or absorption of heat and/or by work being done by the system. Because the total energy of the system must remain constant, we can write the **mathematical statement of the First Law** as :

■ Figure 7.11

Illustration of First Law. Heat adds to internal energy, while work subtracts.

$$\Delta E = q - w \qquad \qquad ...(1)$$

where
- q = the amount of heat supplied to the system
- w = work done by the system

Thus First Law may also be stated as : **the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.**

To illustrate the mathematical statement of the First Law, let us consider the system 'expanding hot gas' (Fig. 7.11).

The gas expands against an applied constant pressure by volume ΔV. The total mechanical work done is given by the relation

$$w = P \times \Delta V \qquad\qquad ...(2)$$

From (1) and (2), we can restate

$$\Delta E = q - P \times \Delta V$$

Other Definitions of First Law of Thermodynamics

(1) Whenever energy of a particular type disappears equivalent amount of another type must be produced.

(2) Total energy of a system and surroundings remains constant (or conserved)

(3) It is impossible to construct a perpetual motion machine that can produce work without spending energy on it.

Some Special Forms of First Law of Thermodynamics

Mathematical statement of the First law of Thermodynamics is

$$\Delta E = q - w$$

Case 1 : For a cyclic process involving isothermal expansion of an ideal gas

$$\Delta E = o$$
$$\therefore \quad q = w$$

Case 2 : For an isochoric process (no change in volume) there is no work of expansion *i.e.* $w = 0$. Hence

$$\Delta E = q_v$$

Case 3 : For an adiabatic process there is no change in heat gained or lost *i.e.* $q = 0$. Hence

$$\Delta E = -w$$

In other words, the decrease in internal energy is exactly equal to the work done on the system by surroundings.

Case 4 : For an isobaric process there is no change in pressure, *i.e.* P remains constant. Hence

$$\Delta E = q - w$$
or
$$\Delta E = q - P\Delta V$$

SOLVED PROBLEM 1. Find ΔE, q and w if 2 moles of hydrogen at 3 atm pressure expand isothermally at 50°C and reversibly to a pressure of 1 atm.

SOLUTION

Since the operation is isothermal and the gas is ideal

$$\Delta E = 0$$

From the First Law

$$\Delta E = q - w$$
$$\therefore \qquad q - w = 0$$
when
$$\Delta E = 0$$
or
$$q = w$$

For a reversible process

$$w = -nRT \ln (P_1/P_2) \text{ or } -2.303\, nRT \log \frac{P_1}{P_2}$$

$$= -2 \times 1.987 \times 323 \times 2.303 \times \log 3$$
$$= -1410 \text{ cals}$$

Since $\qquad q = w$

$$q = -\textbf{1410 cals}$$

SOLVED PROBLEM 2. 1g of water at 373 K is converted into steam at the same temperature. The volume of water becomes 1671 ml on boiling. Calculate the change in the internal energy of the system if the heat of vaporisation is 540 cal/g.

SOLUTION

As the vaporisation takes place against a constant pressure of 1 atmosphere, work done for an irreversible process, w, is

$$w = P(V_2 - V_1)$$
$$= nRT$$
$$= \frac{1}{18} \times 1.987 \times 373$$
$$= 41 \text{ cal/g}$$

Now $\qquad q = 540 \text{ cal/g}$

Since $\qquad \Delta E = q - w \quad \text{(First Law)}$

$$= 540 - 41$$

$\therefore \qquad \Delta E = \textbf{499 cal/g}$

SOLVED PROBLEM 3. A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J thermal energy from its surroundings. Determine ΔE for the process.

SOLUTION

$$\Delta E = q - w \qquad \qquad \qquad \qquad \text{...(1)}$$

Here $\qquad q = 400 \text{ J}$

$$w = -P(V_2 - V_1) = -(1)(10-5)$$
$$= -5 \ l \text{ atm}$$
$$= -506 \text{ J} \qquad \qquad [\because 1 \ l \text{ atm} = 101.2 \text{ J}]$$

Substituting values in (1)

$$\Delta E = 400 \text{ J} - (-506 \text{ J})$$
$$= 400 \text{ J} + 506 \text{ J}$$
$$= \textbf{906 J}$$

SOLVED PROBLEM 4. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to one atmosphere at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy ? Also calculate 'q'.

SOLUTION. We know

$$w = 2.303 \, nRT \log\left(\frac{P_1}{P_2}\right)$$

Here $\qquad n = \dfrac{10}{2} = 5 \text{ moles}; T = 273 \text{ K}$

$$P_1 = 20 \text{ atm}; P_2 = 1 \text{ atm}.$$

Substituting the values we get

$$w = -2.303 \times 5 \times 1.987 \times 273 \log \frac{20}{1}$$

$$= -\textbf{8126.65 cals.}$$

Since there is no change in temperature

$$\Delta E = 0$$

Hence

$$q = \Delta E + w$$

$$= 0 + (-8126.65)$$

$$= -\textbf{8126.65 cals.}$$

ENTHALPY OF A SYSTEM

In a process carried at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy (E), as no PV work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing PV work. Therefore, **the total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy.** This is called the **Enthalpy** (Greek *en* = in; *thalpos* = heat) of the system and is represented by the symbol H. Thus enthalpy is defined by the equation :

$$H = E + PV \qquad \text{...(1)}$$

Enthalpy – A Function of State

In the equation (1) above, E, P, V are all state functions. Thus H, the value of which depends on the values of E, P, V must also be a function of state. Hence its value is independent of the path by which the state of the system is changed.

Change in Enthalpy

If ΔH be the difference of enthalpy of a system in the final state (H_2) and that in the initial state (H_1),

$$\Delta H = H_2 - H_1 \qquad \text{...(2)}$$

Substituting the values of H_2 and H_1, as from (1) and (2), we have

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

$$= (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

$$= \Delta E + \Delta PV$$

If P is constant while the gas is expanding, we can write

$$\Delta H = \Delta E + P\Delta V$$

or

$$\Delta H = \Delta E + w \; (w = \text{work}) \qquad \text{...(3)}$$

According to the First Law,

$$\Delta E = q - w \qquad \text{...(4)}$$

where

$$q = \text{heat transferred}$$

From equations (3) and (4)

$$\Delta H = q \text{ when change in state occurs at constant pressure}$$

This relationship is usually written as

$$\Delta H = q_p$$

where subscript p means constant pressure.

Thus ΔH can be measured by measuring the heat of a process occurring at constant pressure.

Units and Sign Conventions of Enthalpy

Since

$$\Delta H = H_2 - H_1$$

ΔH is positive if $H_2 > H_1$ and the process or reaction will be endothermic. ΔH is negative if $H_1 > H_2$ and the reaction will be exothermic.

In case of a chemical reaction carried in the laboratory in an open vessel,

$$\Delta H = H \text{ products} - H \text{ reactants} = q_p$$

The heat of reaction at one atmosphere pressure is usually shown along with the equation. Thus,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 68.32 \text{ kcal}$$
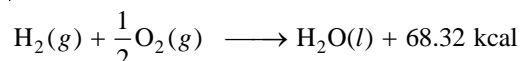
The quantity of heat 68.32 kcal on the right hand represents $-\Delta H$ of the reaction.

The units of ΔH are kilocalories (kcal) or kilojoules (kJ).

Relation Between ΔH and ΔE

Calorific values of many gaseous fuels are determined in constant volume calorimeters. These values are, therefore, given by the expression

$$q_v = \Delta E$$

When any fuel is burnt in the open atmosphere, additional energy of expansion, positive or negative, against the atmosphere is also involved. The value of q thus actually realised, $i.e.$, $q_p = \Delta H$, may be different from the equation

$$\Delta H = \Delta E + P\Delta V \qquad\qquad ...(1)$$

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

Suppose we have n_1 moles of gases before reaction, and n_2 moles of gases after it. Assuming ideal gas behaviour, we have

$$P V_2 = n_2 RT$$
$$P V_1 = n_1 RT$$

$$\therefore \qquad P(V_2 - V_1) = (n_2 - n_1) RT$$

or

$$P\Delta V = \Delta n\, RT$$

Substituting in equation (1) we have,

$$\Delta H = \Delta E + \Delta n\, RT$$

SOLVED PROBLEM. For the reaction

$$H_2F_2(g) \longrightarrow H_2(g) + F_2(g)$$
$$\Delta E = -14.2 \text{ kcal/mole at } 25°\,C$$
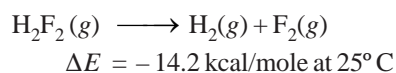
Calculate ΔH for the reaction.

SOLUTION

$$\Delta H = \Delta E + \Delta n\, RT$$
$$\Delta n = n_2 - n_1$$

Now

$$n_2 = 1 + 1 = 2$$
$$n_1 = 1$$
$$n_2 - n_1 = 2 - 1 = 1$$

$$\therefore \qquad \Delta H = \Delta E + 1 \times 1.987 \times 298/1000$$
$$= -14.2 + 0.592$$
$$= \mathbf{-13.6 \ kcal/mole}$$

MOLAR HEAT CAPACITIES

By heat capacity of a system we mean the capacity to absorb heat and store energy. As the system absorbs heat, it goes into the kinetic motion of the atoms and molecules contained in the system. This increased kinetic energy raises the temperature of the system.

If q calories is the heat absorbed by mass m and the temperature rises from T_1 to T_2, the heat capacity (c) is given by the expression

$$c = \frac{q}{m \times (T_2 - T_1)} \qquad \qquad ...(1)$$

Thus heat capacity of a system is the heat absorbed by unit mass in raising the temperature by one degree (K or ° C) at a specified temperature.

When mass considered is 1 mole, the expression (1) can be written as

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \qquad \qquad ...(2)$$

where *C is denoted as Molar heat capacity.*

The molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the substance (system) by 1 K.

Since the heat capacity (C) varies with temperature; its true value will be given as

$$C = \frac{dq}{dT}$$

where dq is a small quantity of heat absorbed by the system, producing a small temperature rise dT.

Thus the molar heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.

Units of Heat Capacity

The usual units of the molar heat capacity are calories per degree per mole (cal K^{-1} mol^{-1}), or joules per degree per mole (J K^{-1} mol^{-1}), the latter being the SI unit.

Heat is not a state function, neither is heat capacity. It is, therefore, necessary to specify the process by which the temperature is raised by one degree. The two important types of molar heat capacities are those : (1) at constant volume; and (2) at constant pressure.

Molar Heat Capacity at Constant Volume

According to the first law of thermodynamics

$$dq = dE + PdV \qquad \qquad ...(i)$$

Dividing both sides by dT, we have

$$\frac{dq}{dT} = \frac{dE + PdV}{dT} \qquad \qquad ...(ii)$$

At constant volume $dV = 0$, the equation reduces to

$$C_V = \left(\frac{dE}{dT} \right)_V$$

Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature at constant volume.

Molar Heat Capacity at Constant Pressure

Equation (*ii*) above may be written as

$$C = \frac{dE}{dT} + \frac{PdV}{dT} \qquad \qquad ...(iii)$$

We know $\qquad \qquad H = E + PV$

Differentiating this equation w.r.t T at constant pressure, we get

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dE}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p \qquad \qquad ...(iv)$$

comparing it with equation (*iii*) we have

$$C_p = \left(\frac{dH}{dT}\right)_p$$

Thus heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature at constant pressure.

Relation Between C_p and C_v

From the definitions, it is clear that two heat capacities are not equal and C_p is greater than C_v by a factor which is related to the work done. At a constant pressure part of heat absorbed by the system is used up in increasing the internal energy of the system and the other for doing work by the system. While at constant volume the whole of heat absorbed is utilised in increasing the temperature of the system as there is no work done by the system. Thus increase in temperature of the system would be lesser at constant pressure than at constant volume. Thus **C_p is greater than C_v.**

We know $\qquad \qquad C_p = \dfrac{dH}{dT} \qquad \qquad ...(i)$

and $\qquad \qquad C_v = \dfrac{dE}{dT} \qquad \qquad ...(ii)$

By definition $H = E + PV$ for 1 mole of an ideal gas

or $\qquad \qquad H = E + RT \qquad \qquad (\because PV = RT)$

Differentiating w.r.t. temperature, T, we get

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

or $\qquad \qquad C_p = C_v + R \qquad \qquad$ [By using equations (*i*) and (*ii*)]

or $\qquad \qquad C_p - C_v = R$

Thus C_p is greater than C_v by a gas constant whose value is 1.987 cal K^{-1} mol^{-1} or 8.314 J K^{-1} mol^{-1} in S.I. units.

Calculation of ΔE and ΔH

(A) ΔE : For one mole of an ideal gas, we have

$$C_v = \frac{dE}{dT}$$

or $\qquad \qquad dE = C_v \times dT$

For a finite change, we have

$$\Delta E = E_2 - E_1 = C_v (T_2 - T_1)$$

and for n moles of an ideal gas we get

$$\Delta E = E_2 - E_1 = n \times C_v \times (T_2 - T_1)$$

(B) ΔH : We know

$$\Delta H = \Delta (E + PV)$$
$$= \Delta E + \Delta (PV)$$
$$= \Delta E + \Delta RT \qquad\qquad [\because\ PV = RT]$$
$$= \Delta E + R \Delta T$$
$$= C_v (T_2 - T_1) + R (T_2 - T_1)$$
$$= (C_v + R)(T_2 - T_1)$$
$$= C_p (T_2 - T_1) \qquad\qquad [\because\ C_p - C_v = R]$$

and for n moles of an ideal gas we get

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

SOLVED PROBLEM 1. Calculate the value of ΔE and ΔH on heating 64.0 g of oxygen from 0°C to 100°C. C_v and C_p on an average are 5.0 and 7.0 cal mol^{-1} degree^{-1}.

SOLUTION. We know

$$\Delta E = n \times C_v \times (T_2 - T_1) \qquad\qquad ...(i)$$

and

$$\Delta H = n \times C_p \times (T_2 - T_1) \qquad\qquad ...(ii)$$

Here

$$n = \frac{64}{16} = 4 \text{ moles}; T_2 = 100°C = 373 \text{ K}$$
$$T_1 = 0° C = 273 \text{ K}$$

On substitution we get

$$\Delta E = 4 \times 5.0 \times (373 - 273)$$
$$= 4 \times 5.0 \times 100 = \mathbf{2000\ cals}$$

and

$$\Delta H = 4 \times 7.0 \times (373 - 273)$$
$$= 4 \times 7 \times 100$$
$$= \mathbf{2800\ cals}$$

SOLVED PROBLEM 2. Calculate the amount of heat necessary to raise 213.5 g of water from 25° to 100°C. Molar heat capacity of water is 18 cal mol^{-1} K^{-1}.

SOLUTION

By definition

$$C = \frac{q}{T_2 - T_1}$$

or

$$q = C (T_2 - T_1) \qquad\quad \text{– for 1 mole}$$
$$q = n C (T_2 - T_1) \qquad\quad \text{– for } n \text{ moles} \qquad\qquad ...(1)$$

In the present case

$$n = 213.5/18$$
$$C = 18 \text{ cal mol}^{-1} \text{K}^{-1}$$
$$T_2 - T_1 = (373 - 298)\text{K}$$

Substituting the value in (1)

$$q = \frac{213.5}{18} \times 18 \times (373 - 298)$$
$$= \mathbf{16,012\ cals = 16.012\ kcals}$$

SOLVED PROBLEM 3. Three moles of an ideal gas ($C_v = 5$ cal deg^{-1} mol^{-1}) at 10.0 atm and 0° are converted to 2.0 atm at 50°. Find ΔE and ΔH for the change.

$$R = 2 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

SOLUTION.

(a)
$$\Delta E = n\, C_v\, dT$$
$$= 3 \times 5 \times (323 - 273)$$
$$= \textbf{750 cals}$$

(b)
$$\Delta H = n\, C_p\, dT = n\,(C_v + R)\, dT$$
$$= 3 \times (5 + 2) \times (323 - 273)$$
$$= \textbf{1050 cals}$$

JOULE-THOMSON EFFECT

Joule and Thomson (later Lord Kelvin) showed that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson Effect or Joule-Kelvin Effect.

Joule-Thomson Experiment

The apparatus used by Joule and Thomson to measure the temperature change on expansion of a given volume of gas is illustrated in Fig. 7.12. An insulated tube is fitted with a porous plug in the middle and two frictionless pistons A and B on the sides. Let a volume V_1 of a gas at pressure P_1 be forced through the porous plug by a slow movement of piston A. The gas in the right-hand chamber is allowed to expand to volume V_2 and pressure P_2 by moving the piston B outward. The change in temperature is found by taking readings on the two thermometers.
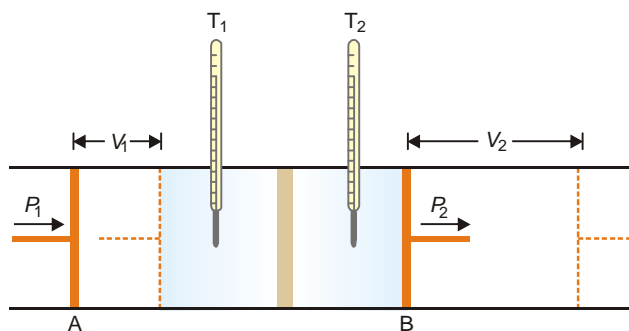
■ **Figure 7.12**
Joule-Thomson experiment.

Most gases were found to undergo cooling on expansion through the porous plug. Hydrogen and helium were exceptions as these gases showed a warming up instead of cooling.

Explanation. The work done on the gas at the piston A is P_1V_1 and the work done by the gas at the piston B is P_2V_2. Hence the net work (w) done by the gas is

$$w = P_2V_2 - P_1V_1$$
$$\Delta E = q - w \quad \text{(First Law)}$$

But the process is adiabatic and, therefore, $q = 0$

$\therefore$ $\qquad\qquad\qquad \Delta E = E_2 - E_1 = -w = -(P_2V_2 - P_1V_1)$

or $\qquad\qquad\qquad\quad E_2 - E_1 = -(P_2V_2 - P_1V_1)$

Rearranging,

$$E_2 + P_2V_2 = E_1 + P_1V_1$$
$$H_2 = H_1 \text{ or } \Delta H = 0$$

Thus the process in Joule-Thomson experiment takes place at constant enthalpy.

Joule-Thomson Coefficient

The number of degrees temperature change produced per atmosphere drop in pressure under constant enthalpy conditions on passing a gas through the porous plug, is called Joule-Thomson coefficient. It is represented by the symbol μ. Thus,

$$\mu = \frac{dT}{dP}$$

If μ is positive, the gas cools on expansion; if μ is negative, the gas warms on expansion. The temperature at which the sign changes is called the **Inversion temperature.** Most gases have positive Joule-Thomson coefficients and hence they cool on expansion at room temperature. Thus liquefaction of gases is accomplished by a succession of Joule-Thomson expansion.

The inversion temperature for H_2 is –80°C. Above the inversion temperature, μ is negative. Thus at room temperature hydrogen warms on expansion. Hydrogen must first be cooled below –80°C (with liquid nitrogen) so that it can be liquefied by further Joule-Thomson expansion. So is the case with helium.

Explanation of Joule-Thomson Effect

We have shown above that Joule-Thomson expansion of a gas is carried at constant enthalpy. But

$$H = E + PV$$

Since H remains constant, any increase in PV during the process must be compensated by decrease of E, the internal energy. This leads to a fall in temperature *i.e.*, $T_2 < T_1$. For hydrogen and helium PV decreases with lowering of pressure, resulting in increase of E and $T_2 > T_1$. Below the inversion temperature, PV increases with lowering of pressure and cooling is produced.

ADIABATIC EXPANSION OF AN IDEAL GAS

A process carried in a vessel whose walls are perfectly insulated so that no heat can pass through them, is said to be **adiabatic.** In such a process there is no heat exchange between a system and surroundings, and $q = 0$.

According to the First law

$$\Delta E = q - w = 0 - w$$

or $\qquad\qquad\qquad\quad \Delta E = -w$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ ...(1)

Since the work is done at the expense of internal energy, the internal energy decreases and the temperature falls.

Consider 1 mole of an ideal gas at pressure P and a volume V. For an infinitesimal increase in volume dV at pressure P, the work done by the gas is $-PdV$. The internal energy decreases by dE.

According to equation (1)

$$dE = -PdV \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{...(2)}$$

By definition of molar heat capacity at constant volume

$$dE = C_v dT \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{...(3)}$$

From (2) and (3)

$$C_v dT = - P dV$$

For an ideal gas

$$P = RT/V$$

and hence

$$C_v dT = - RT \frac{dV}{V}$$

or

$$C_v \frac{dT}{T} = - R \frac{dV}{V}$$

Integrating between T_1, T_2 and V_1, V_2 and considering C_v to be constant,

$$C_v \int_{T_2}^{T_1} \frac{dT}{T} = - R \int_{V_2}^{V_1} \frac{dV}{V}$$

Thus

$$C_v \ln \frac{T_2}{T_1} = - R \ln \frac{V_2}{V_1}$$

Since $R = C_p - C_v$, this equation may be written as

$$\ln \frac{T_2}{T_1} = - \frac{(C_p - C_v)}{C_v} \ln \frac{V_2}{V_1} \qquad \text{...(4)}$$

The ratio of C_p to C_v is often written as γ,

$$\gamma = \frac{C_p}{C_v}$$

and equation (4) thus becomes

$$\ln \frac{T_2}{T_1} = - (\gamma - 1) \ln \frac{V_2}{V_1}$$

Replacing – ve sign by inverting V_2/V_1 to V_1/V_2 and taking antilogarithms

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \qquad \text{...(5)}$$

$$T_2 V_2^{\gamma - 1} = T_1 V_1^{\gamma - 1}$$

or

$$TV^{\gamma - 1} = \text{a constant}$$

We can also eliminate the temperature by making use of the ideal gas relationship

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left[\frac{V_1}{V_2} \right]^{\gamma - 1} \qquad \text{...(6)}$$

Equating the right-hand sides of equations (5) and (6)

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \qquad \text{or} \qquad PV^{\gamma} = k$$

Comparison between Isothermal and Adiabatic Expansions

Boyle's law describes pressure-volume relations of an ideal gas under isothermal conditions (T, constant). This is similar to the relation derived for adiabatic expansion.

$$PV = constant \qquad (Boyle's\ law)$$
$$PV^{\gamma} = constant \qquad (Adiabatic\ expansion)$$

γ for an ideal monoatomic gas = 1.67. The difference between the two processes is : **in an isothermal process, temperature of a system remains constant while in an adiabatic process, temperature must change.**

Explanation. In an isothermal process heat is absorbed to make up for the work done by the gas in expansion and the temperature remains unchanged. On the other hand, adiabatic expansion takes place at the expense of internal energy which decreases and the temperature falls. For the same reason, the curve for the adiabatic process (Fig. 7.13) is steeper than that for the isothermal process.
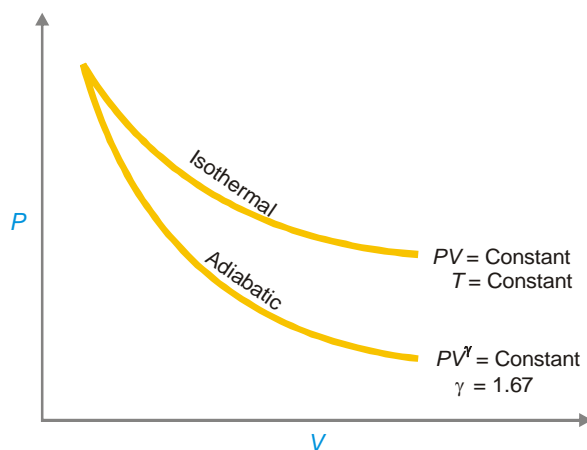
■ **Figure 7.13**
Curves for isothermal and adiabatic expansions for a monoatomic ideal gas.

WORK DONE IN ADIABATIC REVERSIBLE EXPANSION

Step 1. Value of VdP from adiabatic equation

For an adiabatic process
$$PV^{\gamma} = constant$$

Differentiating it, we have
$$\gamma\, PV^{\gamma-1}\, dV + V^{\gamma}\, dp = 0$$

Dividing by $V^{\gamma-1}$, we get
$$\gamma\, PdV + VdP = 0$$

or
$$VdP = -\gamma\, PdV \qquad\qquad ...(1)$$

Step 2. Value of *VdP* from ideal gas equation

For 1 mole of an ideal gas
$$PV = RT$$

Complete differentiation gives
$$PdV + VdP = RdT$$
$$VdP = RdT - PdV \qquad\qquad ...(2)$$

Step 3. Substitution

Substituting the value of VdP from (1) in (2) we get

$$RdT - PdV = -\gamma \, PdV$$

or

$$RdT = P \, (1 - \gamma) \, dV$$

or

$$PdV = \frac{RdT}{1 - \gamma}$$

If there are n moles of a gas

$$PdV = \frac{n \, R \, d \, T}{1 - \gamma}$$

Step 4. Integration

Integrating from T_1, V_1 to T_2, V_2 with γ constant

$$w_{max} = P \, (V_2 - V_1)$$

$$= \int_{T_1}^{T_2} \frac{n \, RdT}{1 - \gamma}$$

$$= \frac{n \, R \, (T_2 - T_1)}{1 - \gamma}$$

When $T_2 > T_1$, w_{max} *is negative* because $1 - \gamma$ is negative. This means that work is done on the gas. On the other hand, when $T_2 < T_1$, w_{max} is positive which means that work is done by the gas.

SOLVED PROBLEM. Calculate w for the adiabatic reversible expansion of 2 moles of an ideal gas at 273.2 K and 20 atm to a final pressure of 2 atm.

SOLUTION

Given

$$C_p = 5R/2, \text{mole}^{-1}\text{deg}^{-1}$$
$$C_v = 3R/2, \text{mole}^{-1}\text{deg}^{-1}$$
$$R = 8.314\text{J mole}^{-1}\text{deg}^{-1}$$

Step 1. To calculate the value of T_2, the final temperature, using the equation

$$(T_2 / T_1)^\gamma = (P_2 / P_1)^{\gamma - 1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

Substituting the value of γ in (1)

$$(T_2 / 273.2)^{5/3} = (2 / 20)$$

Solving it, we get

$$T_2 = \textbf{108.8 K}$$

Step 2. To calculate maximum work under adiabatic conditions

$$w_{max} = \frac{nR \, (T_2 - T_1)}{1 - \gamma}$$

$$= \frac{2 \times 8.314 \, (108.8 - 273.2)}{1 - 5/3}$$

$$= 4100 \, \text{J} = \textbf{4.1 kJ}$$

ALTERNATIVE SOLUTION

The work done under adiabatic conditions may be obtained by calculating decrease in internal energy.

$$w = -\Delta E = -nC_v (T_2 - T_1)$$
$$= -2 \times 3/2 \times 8.314 \,(108.8 - 273.2)$$
$$= 4100 \, J = 4.1 \, kJ$$

SOLVED PROBLEM. At 25°C for the combustion of 1 mole of liquid benzene the heat of reaction at constant pressure is given by

$$C_6H_6 \,(l) + 7\tfrac{1}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(1) \, \Delta H = -780980 \, cal$$
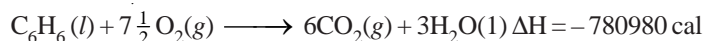
What would be the heat of reaction at constant volume ?

SOLUTION. We have

$$\Delta H = \Delta E + \Delta n \, R \, T$$

Here

$$\Delta n = n_p - n_R = 6 - 7.5 = -1.5$$

Thus

$$\Delta E = \Delta H - \Delta n \,(RT)$$
$$= -780980 - (-1.5) \times (2 \times 298)$$
$$= -780980 + 894$$
$$= -780086 \, cals$$
$$= -\mathbf{780.086 \ kcals}$$

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (a) First law of thermodynamics
   - (b) An isothermal reversible expansion
   - (c) Irreversible expansion
   - (d) Internal energy
   - (e) Enthalpy
   - (f) Molar heat capacities
   - (g) Molar heat capacity
   - (h) Adiabatic expansion
   - (i) Ideal gas

2. Explain the following terms :
   - (a) State of a System
   - (b) Extensive Properties
   - (c) Closed System
   - (d) Isothermal Process

3. What do you understand by C_P and C_V of gases? Why is the value of C_P always greater than that of C_V? How are they related?

4. State the first law of thermodynamics in as many ways as possible. Obtain the mathematical expression for the law with sign conventions.

5. Give a concise statement of the first law of thermodynamics. Deduce its mathematical form and explain the terms involved.

6. (a) What do you understand by thermodynamic system and surroundings?
   - (b) Which of the following are intensive properties :
     - (i) Density
     - (ii) Surface Tension
     - (iii) Volume
     - (iv) Entropy

7. (a) Show thermodynamically that for an ideal gas $C_P - C_V = R$

(b) A dry gas at NTP is expanded adiabatically from 1 litre to 5 litre. Calculate the final temperature and pressure assuming ideal behaviour ($C_P/C_V = 1.4$)

Answer. (b) $T_2 = 143.31$ K; $P_2 = 0.105$ atm

8. (a) State and explain First law of Thermodynamics

(b) Prove that $Q_V = \Delta E$ and $Q_P = \Delta H$ and discuss the relation amongst heat, internal energy and work.

9. Derive the relationship $\Delta H = \Delta E + \Delta n\, RT$

10. Explain heat capacity at constant volume thermodynamically.

11. Distinguish between isothermal and adiabatic process.

12. How would the energy of an ideal gas change if it is made to expand into vacuum at constant temperature.

13. (a) Derive the expression for maximum work done when n moles of an ideal gas are expanded isothermally and reversibly from V_1 to V_2 volume.

(b) Describe different types of thermodynamic processes.

14. (a) Explain the term enthalpy.

(b) State the first law of thermodynamics.

(c) Define C_P and C_V. State their relation.

15. (a) What are state functions? How do these differ from path functions.

(b) State the first law of thermodynamics. Give its mathematical statement and explain each term involved.

16. (a) Describe open, closed and isolated systems.

(b) What do you understand by the terms : Extensive properties and Intensive properties. Give two examples of each category.

(c) Calculate the work of expansion of one mole of an ideal gas at 25°C under isothermal conditions, the pressure being changed from 1 to 5 atmosphere.

Answer. (c) –3988.2 J

17. (a) Give two definitions of First law of thermodynamics.

(b) State "Kirchoff's Law". Derive it with the help of first law of thermodynamics.

(c) Calculate the value of ΔE and ΔH on heating 64.0 grams of oxygen from 0°C to 1000°C. C_V and C_P on an average are 5.0 and 7.0 cal. mol^{-1} deg^{-1} respectively.

Answer. (c) 1000 cals; 1400 cals

18. (a) Under what conditions $\Delta E = \Delta H$ for a chemical reaction?

(b) One mole of an ideal gas expands isothermally and reversibly from 1 litre to 100 litres at 27°C. Calculate w, q, ΔE, ΔH and ΔS for the process.

Answer. (b) 2745.63 cal; 2745.63 cal; zero; 596.1 cal, 9.152 cal K^{-1}

19. State the first law of thermodynamics. With the help of this law show that:

(i) Heat absorbed by a system at constant volume is equal to increase in internal energy of the system.

(ii) Heat absorbed by a system at constant pressure is equal to the increase in the enthalpy.

20. Explain the difference between isothermal and adiabatic processes.

21. (a) Distinguish between open, closed and isolated system. Give examples.

(b) Differentiate between reversible and irreversible processes.

22. (a) Prove that the value of Joule Thomson coefficient is zero for an ideal gas.

(b) Explain First law of Thermodynamics. Calculate the work done in an isothermal and reversible expansion process of an ideal gas.

23. (a) Derive an expression for the work done by a gas in isothermal reversible expansion of an ideal gas.

(b) One mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from volume 10 litres to 20 litres. Calculate the work done by the gas in Joules and calories.

Answer. (b) –1717.46 J or –410.46 cal   (*Guru Nanak Dev BSc, 2002*)

24. Calculate the work done in expanding 2 moles of an ideal gas from 2L to 5L at 273°C.

Answer. –5683.5 J   (*Andhra BSc, 2002*)

25. Distinguish between

(*a*) Isothermal and adiabatic process   (*b*) State function and path function

(*c*) Reversible and irreversible process   (*d*) Gibbs and Helmholtz free energy

(*Andhra BSc, 2002*)

26. (*a*) Write short notes on following :

(*i*)   Enthalpy   (*ii*)   Internal Energy

(*iii*) Free Energy

(*b*) Heat supplied to a Carnot engine is 453.6 kcal. How much useful work can be done by the engine between 0°C and 100°C?

Answer. (*b*) 1.216×10^5 cal   (*HS Gaur BSc, 2002*)

27. What is the efficiency of Carnot engine working between 500 K and 850 K? If the engine absorbs 1200 cal of work, how much heat is given to sink?

Answer. 0.4117; 705.96 cal   (*Andhra BSc, 2002*)

28. Calculate q, w, ΔH, ΔS_{system}, ΔS_{surr} and $\Delta S_{universe}$ for one mole of an ideal gas which expands from V_1 to $10V_1$ at 300 K isothermally under reversible conditions (Use $R = 8.314$ J K^{-1} mol^{-1})

Answer. 5744.14 J, 5744.14 J, 0, 0, 19.147 J K^{-1}, –19.147 J K^{-1}, 0   (*Delhi BSc, 2003*)

29. Two moles of an ideal gas expanded isothermally and reversibly at 300 K to twice the original volume. Calculate q, w, ΔE and ΔH (Given log 2 = 0.3010, $R = 8.314$ J K^{-1} mol^{-1})

Answer. 3457.97 J, 3457.97 J, 0, 0   (*Sambalpur BSc, 2003*)

30. Calculate maximum amount of heat withdrawn from a hot reservoir at 410 K to obtain work equivalent to 15 kJ per cycle. The temperature of the sink is 290 K.

Answer. 512.50 kJ   (*Sambalpur BSc, 2003*)

31. A gas at 10 atm pressure occupies a volume of 10 litres at 300 K. It is allowed to expand at the constant temperature of 300 K under a constant external pressure till the volume equilibrates at 100 litres. Calculate the work done.

Answer. 900 atm litre   (*Kolkata BSc, 2003*)

32. What is the basic principle of Joule-Thomson effect?   (*Nagpur BSc, 2003*)

33. Which of the following parameters are state functions : q, H, E and w. The terms have their usual meanings. Show that the work done in an isothermal expansion of an ideal gas is greater than that of a van der Waal's gas.   (*Kalyani BSc, 2003*)

34. Distinguish between :

(*a*) Isothermal and adiabatic process

(*b*) Reversible and Irreversible process   (*Panjab BSc, 2003*)

35. Define heat capacity at constant pressure and heat capacity at constant volume.

(*Arunachal BSc, 2003*)

36. How many calories of heat are required to heat 18 grams of Argon from 40°C to 100°C at

(*i*)   constant volume and   (*ii*)   constant pressure

Molar heat capacity of Argon at constant volume is 3 cal/degree and molar heat capacity of Argon at constant pressure is 5 cal/degree.

Answer. 180 cals; 300 cals   (*Meerut BSc, 2004*)

37. (*a*) Calculate the maximum work done when 44 g of Neon gas expands reversibly and isothermally from 10 atm. to 2 atm. pressure at constant temperature 27°C. (Neon at wt. = 20; $R = 2$ cal deg^{-1} mol^{-1})

(*b*) Derive Kirchoff's equation.

Answer. (*a*) 2124.84 cals   (*Dibrugarh BSc, 2004*)

38. (*a*) Explain the following :

Heat capacity, Thermodynamic state, Isolated state, Intensive properties.

(*b*) Calculate the maximum work obtained when 2 moles of nitrogen were expanded isothermally and reversibly from 10 litres to 20 litres at 25°C.

Answer. (*b*) 3434.9 J   (*Sri Venkateswara BSc, 2004*)

39. (*a*) Write notes on objectives and limitations of Thermodynamics.

(*b*) Calculate ΔE and ΔH when the temperature of one mole of water is increased from 10°C to 70°C. The density of water is 0.9778 g cm^{-3} and 0.9997 g cm^{-3} at 70°C and 10°C respectively.

Answer. (*b*) 1080 cal mol^{-1}; 1079.99 cal mol^{-1} (*Gulbarga BSc, 2004*)

40. Calculate *w* and ΔE for the conversion of 1 mole of water into l mole of steam at a temperature of 373 K and 1 atm pressure. Latent heat of vaporisation of water 540 cal g^{-1}.

Answer. 8.979 kcal   (*Delhi BSc, 2005*)

41. Calculate the work done when 5 moles of hydrogen gas expand isothermally and reversibly at 298 K from 10 to 50 litres.

Answer. 4.766 kcal   (*Bangalore BSc, 2005*)

42. When one mole of liquid Br_2 is converted to Br_2 vapour at 25 °C and 1 atm pressure, 7.3 kcal of heat is absorbed and 0.59 k cal of expansion work is done by the system. Calculate ΔE for this process.

Answer. + 6.7 kcal   (*Nagpur BSc, 2005*)

43. Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.

Answer. 1085 cal   (*Madras BSc, 2006*)

44. What is the maximum work which can be obtained by the isothermal reversible expansion of two moles to three moles of an ideal gas at 273 K from 1.12 litre to 11.2 litres ?

Answer. 1627.35 cal   (*Utkal BSc, 2006*)

45. Calculate ΔE for the combustion of one mole of Magnesium in an open container at 298 K and 1 atm pressure, if $\Delta H_{combustion} = -143.9$ k cal ?

Answer. – 143.6 k cal   (*Baroda BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The study of the flow of heat or any other form of energy into or out of a system undergoing physical or chemical change is called

(*a*) thermochemistry   (*b*) thermokinetics

(*c*) thermodynamics   (*d*) thermochemical studies

Answer. (*c*)

2. Thermodynamics is applicable to

(*a*) microscopic systems only   (*b*) macroscopic systems only

(*c*) homogeneous systems only   (*d*) heterogeneous systems only

Answer. (*b*)

3. Which is not true about thermodynamics?

(*a*) it ignores the internal structure of atoms and molecules

(*b*) it involves the matter in bulk

(*c*) it is concerned only with the initial and final states of the system

(*d*) it is not applicable to macroscopic systems

Answer. (*d*)

4. A system that can transfer neither matter nor energy to and from its surroundings is called
   (a) a closed system
   (b) an isolated system
   (c) an open system
   (d) a homogeneous system
   Answer. (b)

5. A thermos flask is an example of
   (a) isolated system
   (b) closed system
   (c) open system
   (d) heterogeneous system
   Answer. (a)

6. A closed system is one which cannot transfer matter but transfer _____ to and from its surrounding
   (a) heat
   (b) work
   (c) radiations
   (d) all of these
   Answer. (d)

7. A gas contained in a cylinder filled with a piston constitutes
   (a) an open system
   (b) a heterogeneous system
   (c) a closed system
   (d) an isolated system
   Answer. (c)

8. A system that can transfer both energy and matter to and from its surroundings is called
   (a) an isolated system
   (b) a closed system
   (c) an open system
   (d) a heterogeneous system
   Answer. (c)

9. Zinc granules reacting with dilute hydrochloric acid in an open beaker constitutes
   (a) an isolated system
   (b) an open system
   (c) a closed system
   (d) a heterogeneous system
   Answer. (b)

10. A system in which no thermal energy passes into or out of the system is called
    (a) adiabatic system
    (b) an open system
    (c) a reversible system
    (d) a closed system
    Answer. (a)

11. An intensive property does not depend upon
    (a) nature of the substance
    (b) quantity of matter
    (c) external temperature
    (d) atmospheric pressure
    Answer. (b)

12. Which out of the following is not an intensive property?
    (a) pressure
    (b) concentration
    (c) density
    (d) volume
    Answer. (d)

13. A property that depends upon the quantity of matter is called an extensive property. Which of the following is not an extensive property?
    (a) mass
    (b) volume
    (c) density
    (d) internal energy
    Answer. (c)

14. Which of the following sets of properties constitute intensive properties?
    (a) temperature, pressure and volume
    (b) mass, density and volume
    (c) density, pressure and temperature
    (d) internal energy, density and pressure
    Answer. (c)

15. A system in which state variables have constant values throughout the system is called in a state of
   (*a*) equilibrium
   (*b*) non-equilibrium
   (*c*) isothermal equilibrium
   (*d*) none of these
   Answer. (*a*)

16. In an adiabatic process _____ can flow into or out of the system.
   (*a*) no heat
   (*b*) heat
   (*c*) matter
   (*d*) no matter
   Answer. (*a*)

17. Which of the following conditions holds good for an adiabatic process?
   (*a*) $dq < 0$
   (*b*) $dq > 0$
   (*c*) $dq = 0$
   (*d*) $dq = \alpha$
   Answer. (*c*)

18. An isobaric process takes place at constant _____.
   (*a*) temperature
   (*b*) pressure
   (*c*) volume
   (*d*) concentration
   Answer. (*b*)

19. Which is true for an isobaric process?
   (*a*) $dp > 0$
   (*b*) $dp < 0$
   (*c*) $dp = \alpha$
   (*d*) $dp = 0$
   Answer. (*d*)

20. An isochoric process takes place at constant_____.
   (*a*) volume
   (*b*) temperature
   (*c*) pressure
   (*d*) concentration
   Answer. (*a*)

21. For a cyclic process, the change in internal energy of the system is
   (*a*) always positive
   (*b*) always negative
   (*c*) equal to zero
   (*d*) equal to infinity
   Answer. (*c*)

22. Which out of the following is incorrect?
   (*a*) heat flow into the system is +ve
   (*b*) heat flow out of the system is –ve
   (*c*) work done on the system is –ve
   (*d*) none of these
   Answer. (*c*)

23. The units erg, joule and calorie are interconvertible, which of the following is incorrect?
   (*a*) 10^7 ergs = 1 Joule
   (*b*) 4.184 J = 1 cal
   (*c*) 1 Joule = 0.2390 cal
   (*d*) 1 erg = 4.184 cal
   Answer. (*d*)

24. A gas expands from 10 litres to 20 litres against a constant external pressure of 10 atm. The pressure-volume work done by the system is
   (*a*) 100 lit atm
   (*b*) –100 lit atm
   (*c*) 10 lit atm
   (*d*) –10 lit atm
   Answer. (*b*)

25. Which out of the following is incorrect, for an ideal gas?
   (*a*) $P V = n R T$
   (*b*) $V = \dfrac{n R T}{P}$

(c) $P = \dfrac{n\,R\,T}{V}$ (d)   all are correct

Answer. (d)

26.   The work done in the reversible expansion of a gas from the initial state A to final state B is

(a)   maximum   (b)   minimum

(c)   equal to zero   (d)   equal to infinity

Answer. (a)

27.   The first law of thermodynamics is

(a)   the total energy of an isolated system remains constant though it may change from one form to another

(b)   total energy of a system and surroundings remains constant

(c)   whenever energy of one type disappears, equivalent amount of another type is produced

(d)   all of the above

Answer. (d)

28.   The mathematical relation for the first law of thermodynamics is

(a) $\Delta E = q - w$ (b) $\Delta E = 0$ for a cyclic process

(c) $\Delta E = q$ for an isochoric process   (d)   all of these

Answer. (d)

29.   For an adiabatic process, according to first law of thermodynamics,

(a) $\Delta E = -w$ (b) $\Delta E = w$

(c) $\Delta E = q - w$ (d)   none of these

Answer. (a)

30.   The change in internal energy for an isobaric process is given by

(a) $\Delta E = q + p\,\Delta v$ (b) $\Delta E = q - p\,\Delta v$

(c) $\Delta E = q$ (d) $\Delta E = p\,\Delta v$

Answer. (b)

31.   Which of the following properties is not a function of state?

(a)   concentration   (b)   internal energy

(c)   enthalpy   (d)   entropy

Answer. (a)

32.   The change in enthalpy of a system is measured by measuring

(a)   heat of the process at constant volume   (b)   heat of the process at constant temperature

(c)   heat of the process at constant pressure   (d)   none of these

Answer. (c)

33.   The enthalpy change, ΔH of a process is given by the relation

(a) $\Delta H = \Delta E + p\,\Delta v$ (b) $\Delta H = \Delta E + \Delta n\,R\,T$

(c) $\Delta H = \Delta E + w$ (d)   all of these

Answer. (b)

34.   The amount of heat required to raise the temperature of one mole of the substance by 1 K is called

(a)   heat capacity   (b)   molar heat capacity

(c)   molar heat   (d)   molar capacity

Answer. (b)

35.   Which of the following statements is not correct?

(a)   heat is not a state function   (b)   heat capacity is not a state function

(c) neither of these   (d) both

Answer. (c)

36. Heat capacity at constant pressure is the change in
    (a) internal energy with temperature at constant volume
    (b) internal energy with temperature at constant pressure
    (c) enthalpy with temperature at constant volume
    (d) enthalpy with temperature at constant pressure

    Answer. (d)

37. Heat capacity at constant volume is the change in
    (a) internal energy with temperature at constant volume
    (b) internal energy with temperature at constant pressure
    (c) enthalpy with temperature at constant volume
    (d) enthalpy with temperature at constant pressure

    Answer. (a)

38. Which of the following relations is true ?
    (a) $C_p > C_v$ (b) $C_v > C_p$
    (c) $C_p = C_v$ (d) $C_p = C_v = 0$

    Answer. (a)

39. The heat capacity at constant pressure is related to heat capacity at constant volume by the relation
    (a) $C_p - R = C_v$ (b) $C_v - R = C_p$
    (c) $C_p - C_v = R$ (d) $R - C_p = C_v$

    Answer. (c)

40. The phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as
    (a) First law of thermodynamics   (b) Second law of thermodynamics
    (c) Le Chatlier's principle   (d) Joule Thomson effect

    Answer. (d)

41. Which of the following relations is applicable to adiabatic expansion of an ideal gas?
    (a) $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ (b) $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$
    (c) both   (d) none of these

    Answer. (c)

42. In an adiabatic process _____ must change
    (a) pressure   (b) volume
    (c) concentration   (d) temperature

    Answer. (d)

43. The enthalpy change of a reaction is independent of
    (a) state of the reactants and products
    (b) nature of the reactants and products
    (c) initial and final enthalpy change of the reaction
    (d) different intermediate reaction

    Answer. (d)

44. Which of the following is not correct?
    (a) $H = E + P V$ (b) $H - E = P V$
    (c) $H - E - P V = 0$ (d) $H = E - P V$

    Answer. (d)

45. When the total energy change in an isothermal cycle is zero, it represents
(a) a reversible cycle
(b) an adiabatic change
(c) a thermodynamic equilibrium
(d) an irreversible cycle
Answer. (a)

46. One mole of an ideal gas at 300 K is expanded isothermally from 1 litre volume to 10 litre volume. ΔE for this process is ($R = 2$ cal K^{-1} mol^{-1})
(a) 300 cal
(b) 600 cal
(c) 1200 cal
(d) 0 cal
Answer. (d)

47. A system absorbs 100 kJ heat and performs 50 kJ work on the surroundings. The increase in internal energy of the system is
(a) 50 kJ
(b) 100 kJ
(c) 150 kJ
(d) 5000 kJ
Answer. (a)

48. For the reaction $H_2 + I_2 \rightleftharpoons 2HI$, ΔH is equal to
(a) $\Delta E + 2RT$
(b) $\Delta E - 2RT$
(c) ΔE
(d) $\Delta E + RT$
Answer. (c)

49. The work done when 1 mole of a gas expands reversibly and isothermally from 5 atm to 1 atm at 300 K is
(a) -4015 J
(b) $+4015$ J
(c) zero
(d) 150 J
Answer. (a)

50. Three moles of an ideal gas ($C_v = 5$ cal K^{-1} mol^{-1}) at 10.0 atm and 0° are converted to 2.0 atm at 50°. The ΔE for the process is
(a) 150 cal
(b) 300 cal
(c) 750 cal
(d) 1500 cal
Answer. (c)

Top