Law of Thermodynamics – Basic Concepts

For Engineering course

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.

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

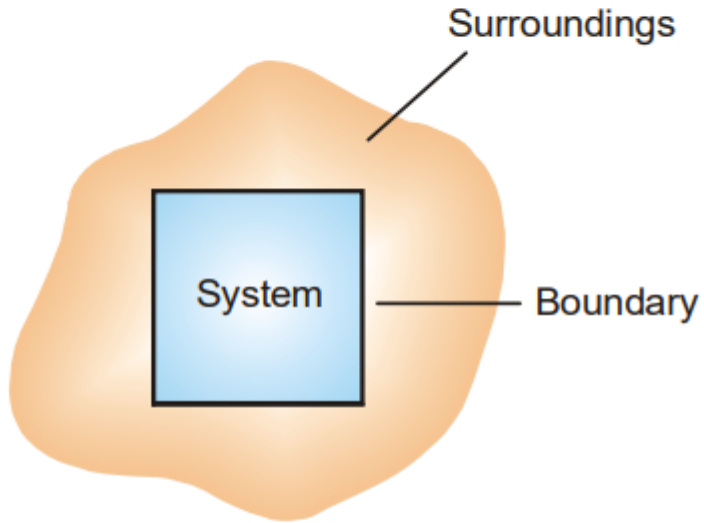
(1) **Thermodynamics is applicable to macroscopic systems** consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. **It ignores the internal structure of atoms and molecules.**

(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.**

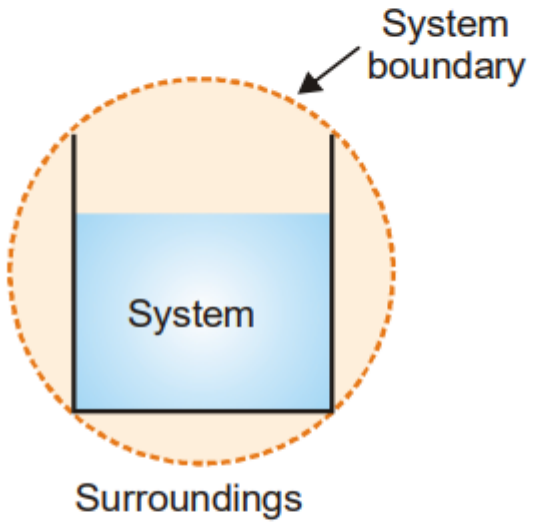
SYSTEM, BOUNDARY, SURROUNDINGS

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.

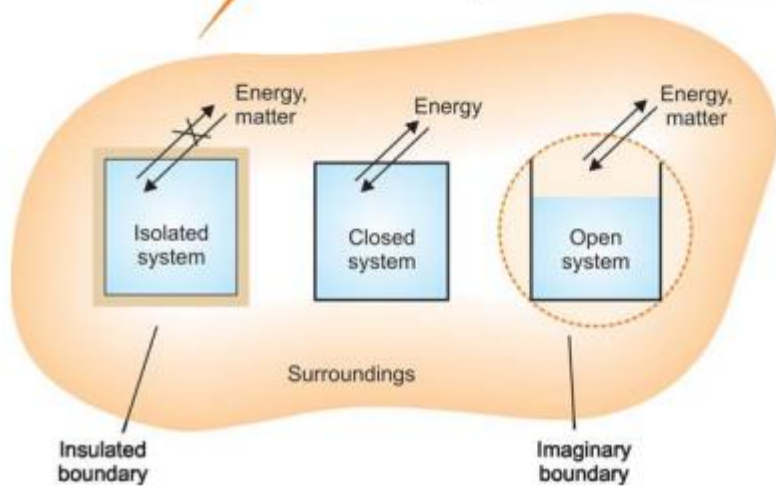
(1) Isolated System

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.





(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.

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 20°C, then any drop of water in that glass has a temperature of 20°C. 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.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25^{\circ}\text{C}$$

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

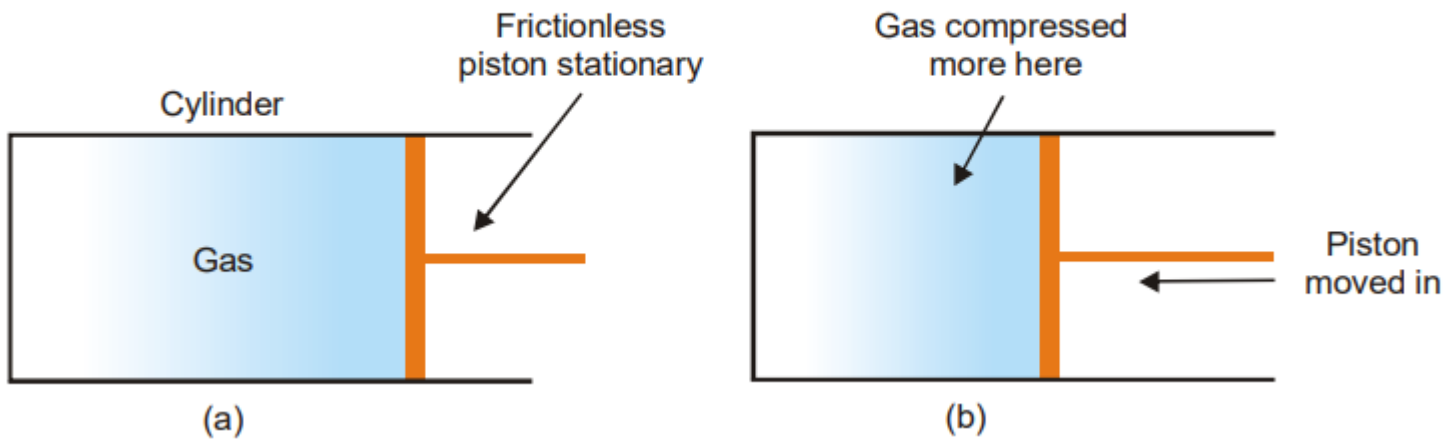
EQUILIBRIUM AND NON–EQUILIBRIUM STATES

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.



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 $dp = 0$

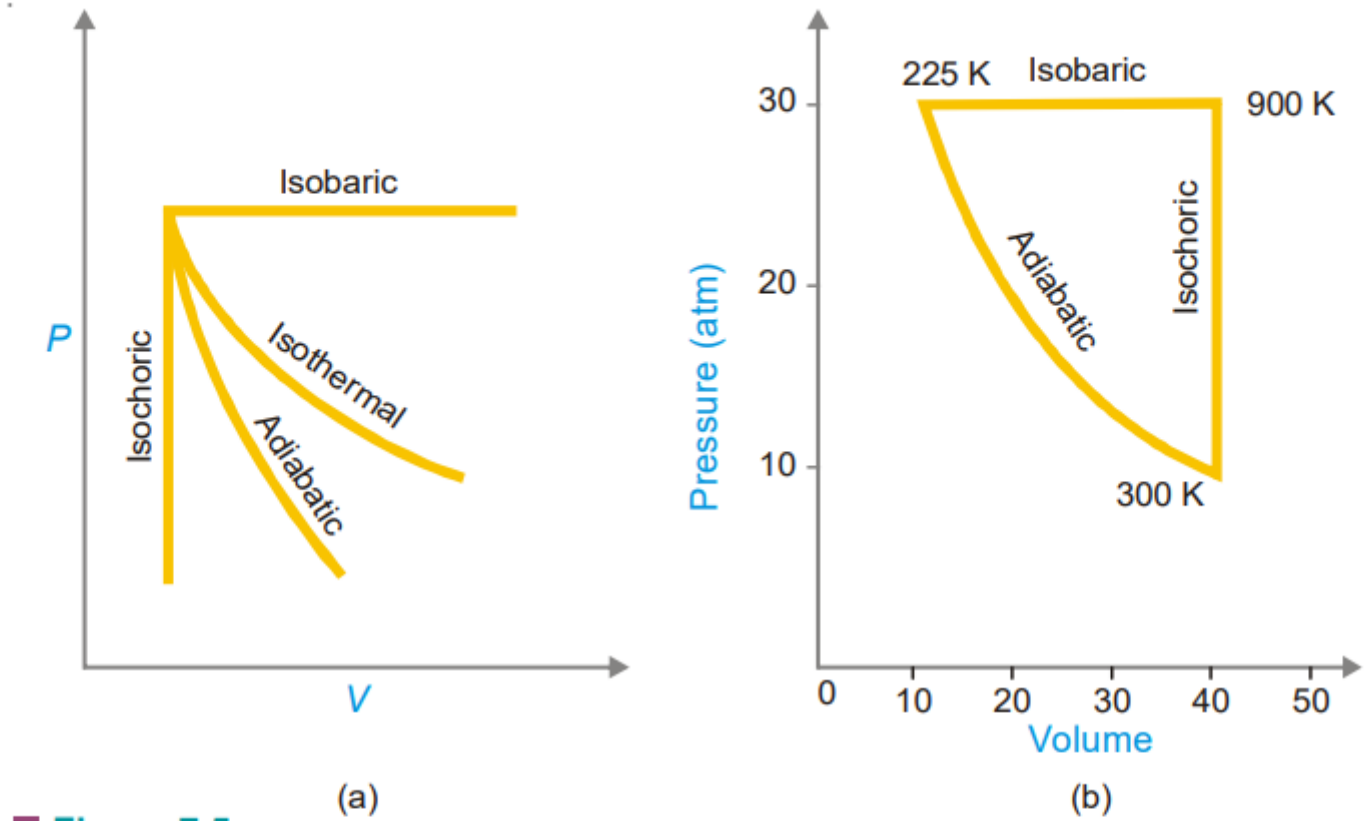


Figure 7.5
(*a*) Four basic thermodynamic processes; (*b*) A cyclic process.

(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 $dV = 0$.

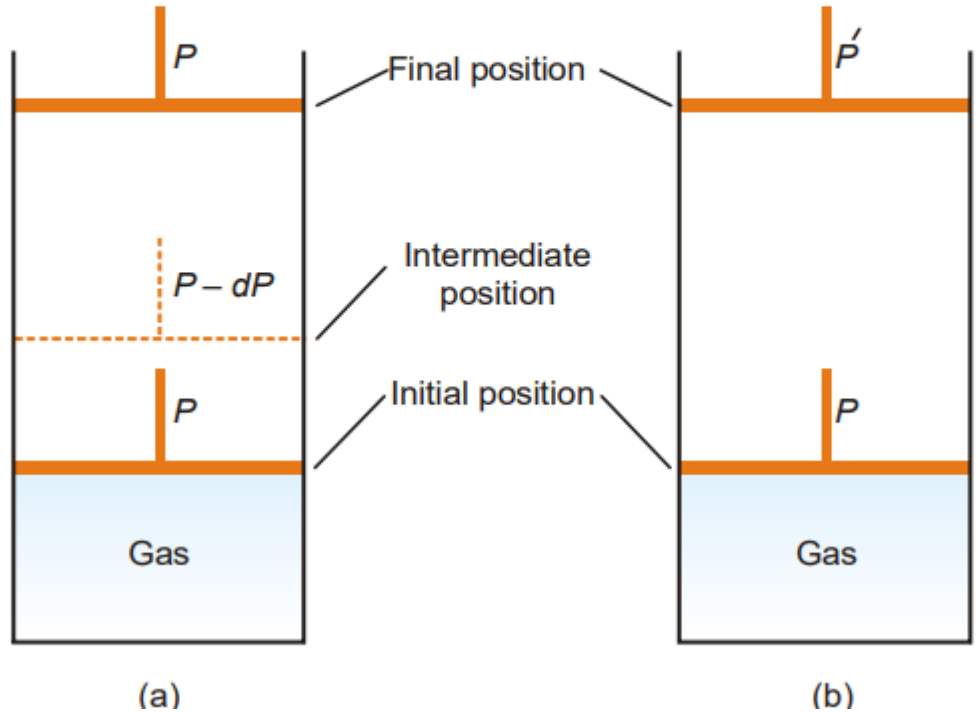
(5) Cyclic Process

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.



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.

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.

Concept of heat and work

- In thermodynamics, heat and work are two fundamental concepts that describe the transfer of energy between a system and its surroundings. Here's a brief overview of each:

- 1. **Heat**: Heat is the transfer of thermal energy between two bodies due to a temperature difference. When two objects at different temperatures are brought into contact, heat flows from the hotter object to the colder one until they reach thermal equilibrium (the same temperature). Heat transfer can occur through conduction, convection, or radiation.

- 2. **Work**: Work, in the context of thermodynamics, is the transfer of energy from one system to another due to the application of a force over a distance. Work can be done by or on a system. When work is done on a system, it generally increases the system's energy, and when work is done by a system, it generally decreases the system's energy. Work can be performed in various forms, such as mechanical work, electrical work, or even by the expansion or compression of gases.

- In thermodynamics, heat and work are crucial in understanding various processes and transformations of energy within systems, as described by the laws of thermodynamics. The first law of thermodynamics, for example, states that energy cannot be created or destroyed in an isolated system, but it can be transformed from one form to another and transferred between the system and its surroundings as heat or work. The second law of thermodynamics deals with the direction of energy transfer and states that the total entropy of an isolated system always increases over time, indicating the tendency towards disorder and the direction of spontaneous processes.

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, $-q$.

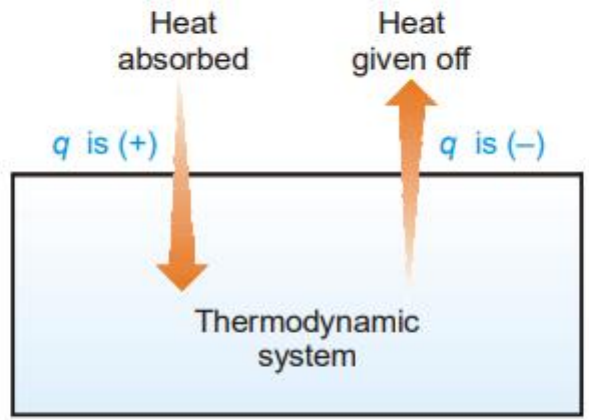


Figure 7.7
Sign convention for heat flow in a thermodynamic system.

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, $-w$.

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

Since pressure is force per unit area,

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

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,

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

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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*.

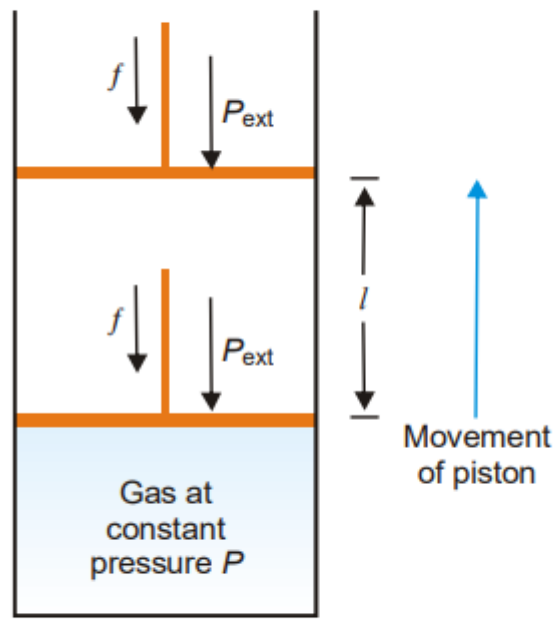


Figure 7.8
Pressure volume work of a system (gas) confined by a frictionless piston.

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

$$
\begin{aligned}
w &= -P_{ext}(V_2 - V_1) \\
&= -(10 \text{ atm})(2\,l - 1\,l) \\
&= -10\,l \text{ atm} \\
&= -(10\,l \text{ atm}) \left(\frac{1.987 \text{ cal}}{0.082\,l \text{ atm}} \right) \\
&= -242 \text{ cal}
\end{aligned}
$$

But 1 calorie = 4.184 J

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

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.

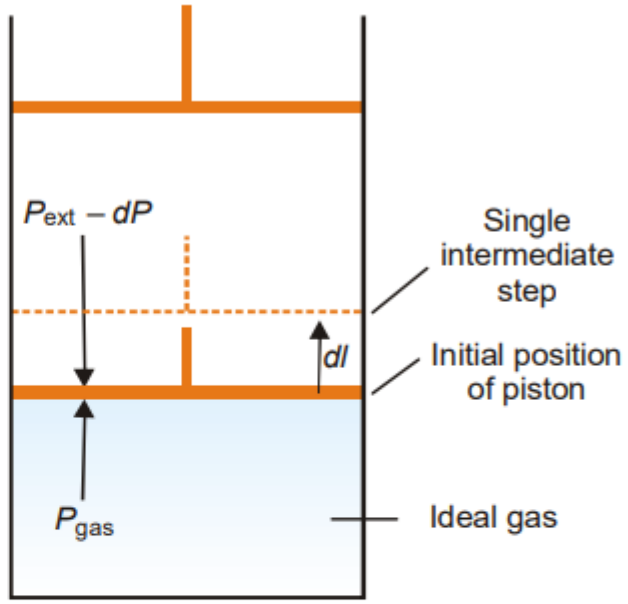


Figure 7.9
Isothermal reversible expansion work.

Since dP is so small, for all practical purposes,

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

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

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

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,

$$w = -\int_{v_1}^{v_2} PdV \qquad \ldots(1)$$

By the ideal gas equation

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

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

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

which integrates to give

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

Since $P_1V_1 = P_2V_2$

$$V_2/V_1 = P_1/P_2$$

$$\therefore \quad w = -\, nRT \ln \frac{P_1}{P_2} = -2.303\, nRT \log \frac{P_1}{P_2}$$

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.

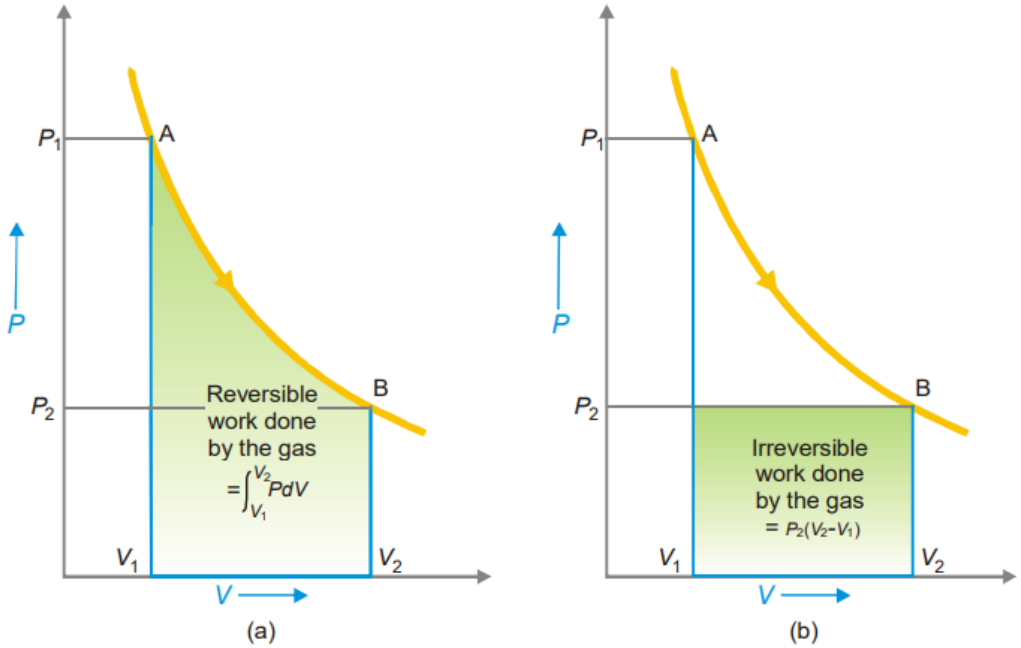


Figure 7.10

(*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

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

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

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

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

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

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

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

$$= \mathbf{-\,3.988\ kJ}$$

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.

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 :

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

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.**

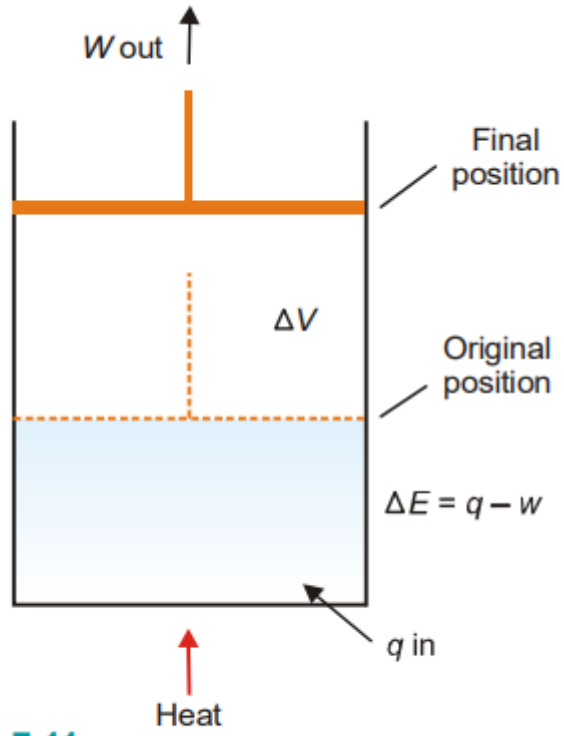


Figure 7.11
Illustration of First Law. Heat adds to internal energy, while work subtracts.

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

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

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

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

NUMERICALS

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

$$\Delta E = q - w$$

$$\therefore \quad q - w = 0$$

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 $q = w$

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

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 $q = 540$ cal/g

Since $\Delta E = q - w$ (First Law)

$= 540 - 41$

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

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

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

Here

$$q = 400\,\text{J}$$

$$w = -P(V_2 - V_1) = -(1)(10-5)$$

$$= -5\,l\,\text{atm}$$

$$= -506\,\text{J} \qquad [\because 1\,l\,\text{atm} = 101.2\,\text{J}]$$

Substituting values in (1)

$$\Delta E = 400\,\text{J} - (-506\,\text{J})$$

$$= 400\,\text{J} + 506\,\text{J}$$

$$= \mathbf{906\ J}$$

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 $$n = \frac{10}{2} = 5 \text{ moles}; \; T = 273 \text{ K}$$

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

Substituting the values we get

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

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

Since there is no change in temperature

$$\Delta E = 0$$

Hence $$q = \Delta E + w$$

$$= 0 + (-8126.65)$$

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

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

$$\begin{aligned} \Delta H &= (E_2 + P_2V_2) - (E_1 + P_1V_1) \\ &= (E_2 - E_1) + (P_2V_2 - P_1V_1) \\ &= \Delta E + \Delta PV \end{aligned}$$

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

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

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

According to the First Law,

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

where q = heat transferred

From equations (3) and (4)

$\Delta H = q$ 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

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

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

$$P V_2 = n_2 RT$$

$$P V_1 = n_1 RT$$

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

$$\text{or} \quad P\Delta V = \Delta n\, RT$$

Substituting in equation (1) we have,

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

SOLVED PROBLEM. For the reaction

$$H_2F_2(g) \longrightarrow H_2(g) + F_2(g)$$
$$\Delta E = -14.2 \text{ kcal/mole at } 25^\circ \text{C}$$

Calculate ΔH for the reaction.

SOLUTION

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

Now

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

$\therefore$

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

■

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

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

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

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

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.

Molar Heat Capacity at Constant Volume

According to the first law of thermodynamics

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

Dividing both sides by dT, we have

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

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

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

We know $H = E + PV$

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

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

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 $$C_p = \frac{dH}{dT} \qquad ...(i)$$

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

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

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

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

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

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

or $$C_p - C_v = R$$

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 $$dE = C_v \times dT$$

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

$$\begin{aligned} \Delta H &= \Delta (E + PV) \\ &= \Delta E + \Delta (PV) \\ &= \Delta E + \Delta RT \qquad [\because \ PV = RT] \\ &= \Delta E + R \Delta T \\ &= C_v (T_2 - T_1) + R (T_2 - T_1) \\ &= (C_v + R)(T_2 - T_1) \\ &= C_p (T_2 - T_1) \qquad [\because \ C_p - C_v = R] \end{aligned}$$

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 $0^{\circ}C$ to $100^{\circ}C$. C_v and C_p on an average are 5.0 and 7.0 cal mol^{-1} $degree^{-1}$.

SOLUTION. We know

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

and

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

Here $n = \dfrac{64}{16} = 4$ moles; $T_2 = 100^{\circ}C = 373$ K

$T_1 = 0^{\circ}C = 273$ 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 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*)
$$\Delta E = n\, C_v dT$$
$$= 3 \times 5 \times (323 - 273)$$
$$= \mathbf{750 \text{ cals}}$$

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

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.

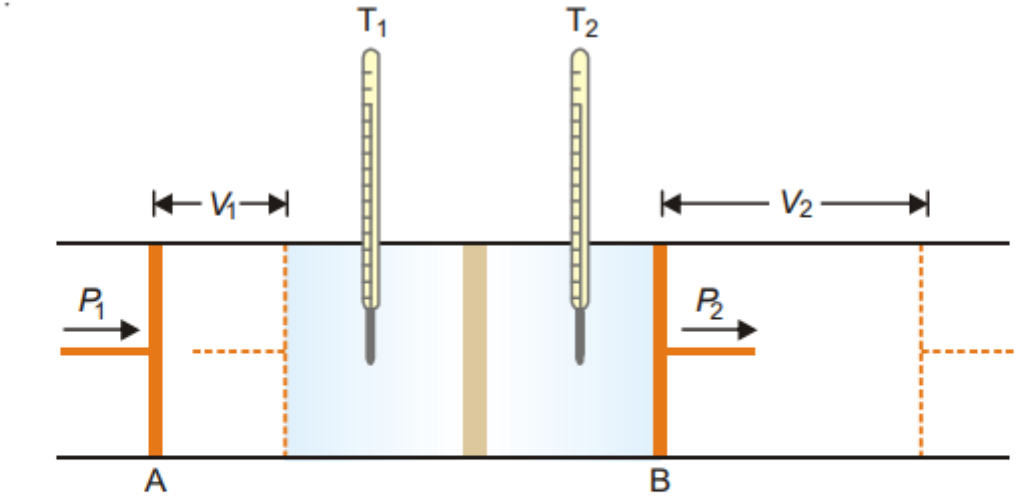


Figure 7.12
Joule-Thomson experiment.

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.

JOULE-THOMSON EFFECT

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

$$w = P_2V_2 - P_1V_1$$

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

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

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

or $$E_2 - E_1 = -(P_2V_2 - P_1V_1)$$

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

$$\Delta E = -w \qquad \ldots(1)$$

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)

$$dE = -PdV \qquad \ldots(2)$$

By definition of molar heat capacity at constant volume

$$dE = C_v dT \qquad \ldots(3)$$

From (2) and (3)

$$C_v dT = -PdV$$

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

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

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

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

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

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

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.

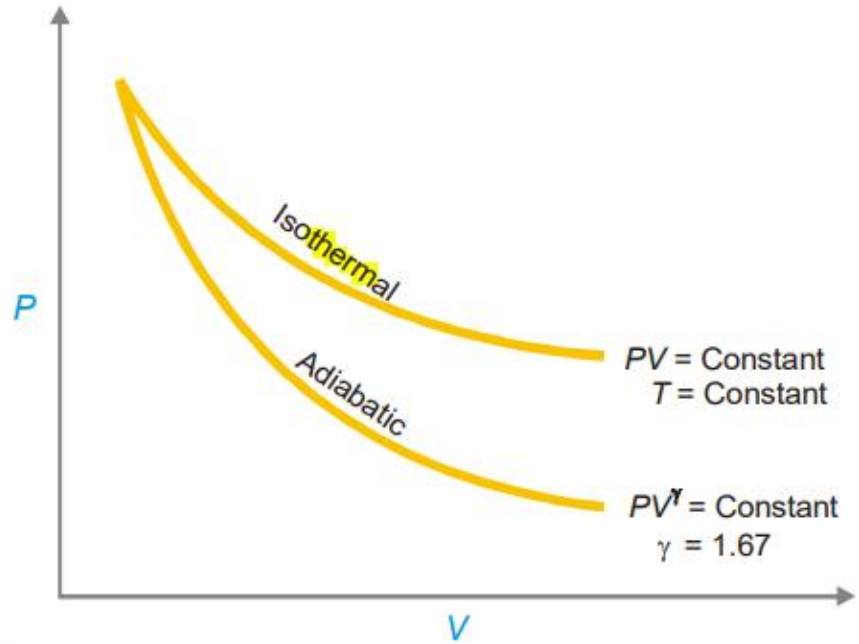


Figure 7.13
Curves for isothermal and adiabatic expansions for a monoatomic ideal gas.

WORK DONE IN ADIABATIC REVERSIBLE EXPANSION

Step 1. Value of V*d*P from adiabatic equation

For an adiabatic process

$$PV^{\gamma} = \text{constant}$$

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
$$VdP = -\gamma PdV \qquad \text{...(1)}$$

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

For 1 mole of an ideal gas

$$PV = RT$$

Complete differentiation gives

$$PdV + VdP = RdT$$

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

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

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

Step 2. To calculate maximum work under adiabatic conditions

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

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

$$= 4100\text{ J} = \mathbf{4.1\ kJ}$$

Second Law of Thermodynamics

The first law of thermodynamics states that one form of energy can change into another form but the total amount of energy remains the same. Once we specify a particular process or change, this law helps us to balance the internal energy, heat released and work done in the process. But the first law says nothing about whether the process of change we specify can, in fact, occur and if so in which direction. This question concerns the second law of thermodynamics. Before we can state the second law in a usable form, we must define some terms.

SPONTANEOUS PROCESSES

A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process.

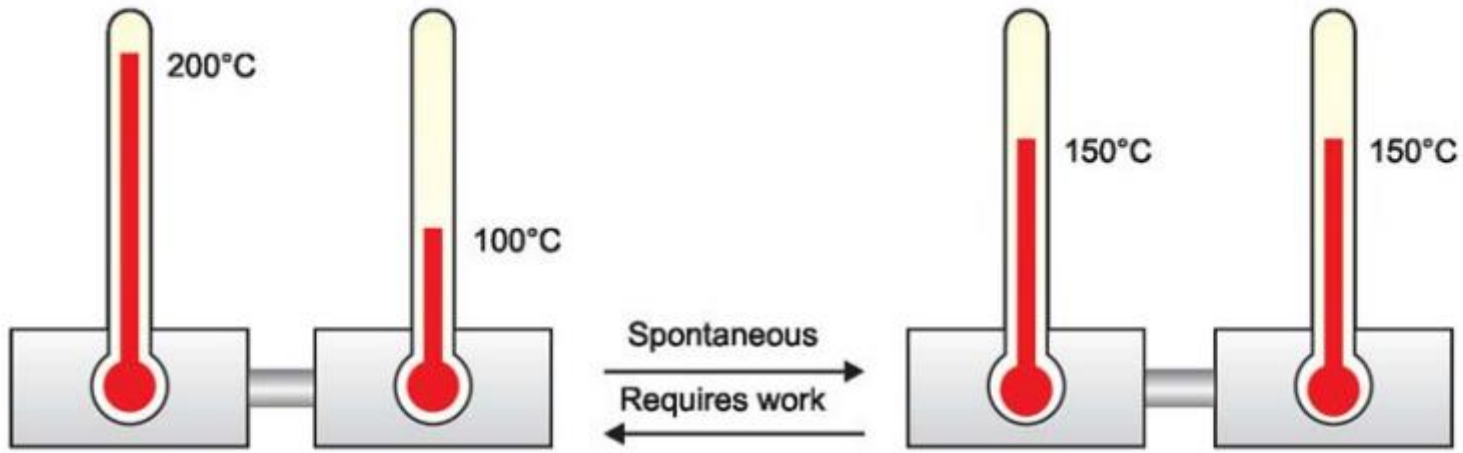
The reverse process which does not proceed on its own, is referred to as a nonspontaneous or unnatural process.

In general, the tendency of a process to occur naturally is called the spontaneity.

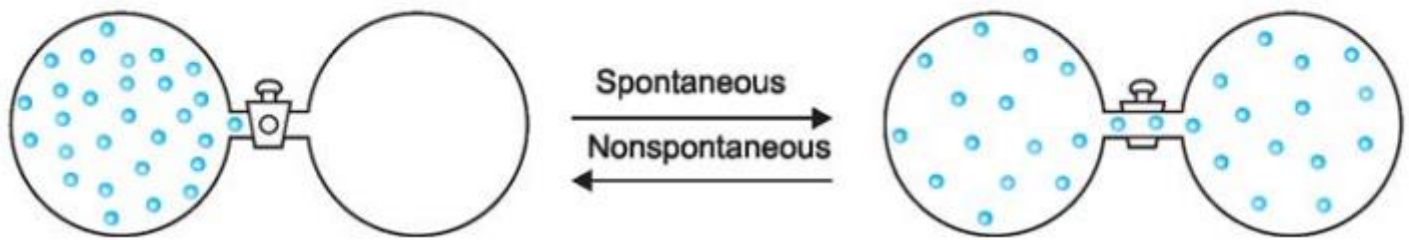
Examples of Spontaneous Processes

(1) **Cliff Jumping and Mountain Climbing.** Cliff jumping is a spontaneous process, whereas mountain climbing requires work.

(b) Heat Flow



(c) Gas Flow



CRITERIA OF SPONTANEITY

Some important criteria of spontaneous physical and chemical changes are listed below.

(1) **A spontaneous change is one-way or unidirectional.** For reverse change to occur, work has to be done.

(2) **For a spontaneous change to occur, time is no factor.** A spontaneous reaction may take place rapidly or very slowly.

(3) **If the system is not in equilibrium state (unstable), a spontaneous change is inevitable.** The change will continue till the system attains the state of equilibrium.

(4) **Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed.** To take the system away from equilibrium, some external work must be done on the system.

(5) **A spontaneous change is accompanied by decrease of internal energy or enthalpy (ΔH).**

It implies that only such reactions will occur which are exothermic. But the melting of ice and evaporation of rain water are endothermic processes which proceed spontaneously. Clearly, there is some other factor in addition to ΔH which governs spontaneity. It is the second law of thermodynamics which introduces this new factor that is called *entropy*.

ENTROPY

For many years scientists believed that only exothermic changes resulting in a lowering of internal energy or enthalpy could occur spontaneously. But melting of ice is an endothermic process and yet occurs spontaneously. On a warm day, ice melts by itself. The evaporation of water is another example of a spontaneous endothermic process. Thus arose the need of inventing another driving force that affects the spontaneity. This was known as the entropy change, ΔS.



Melting of Ice is a classic example of 'Increasing Entropy'.

Spontaneity and Randomness

Careful examination shows that in each of the processes *viz*., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer still when the water evaporates into space as now they can roam about throughout the entire atmosphere. In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

Increase in Randomness Favours a Spontaneous Change

A change that brings about randomness is more likely to occur than one that brings about order. Let us suppose we have a suit of playing cards arranged numerically (Fig. 9.2 *a*). We can see that the sequence of cards is certainly highly organised. Now, if we throw the cards into the air, collect them and re-stack them, we will almost surely find that they have been placed at random. This is expected because when the cards are tossed, there are many ways for them to be disordered, while there is only one way for them to come together again in their original sequence. Thus on the basis of pure chance a disordered sequence is far more probable than the ordered one with which we started. The same law of chance applies to any physical or chemical process.

DEFINITION OF ENTROPY

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

The symbol of entropy is S, while the change in disorder accompanying a process from start to completion is represented by ΔS. The entropy of a system is a state function and depends only on the initial and final states of the system. The change in entropy, ΔS, for any process is given by the equation,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When $S_{\text{final}} > S_{\text{initial}}$, ΔS is positive.

A process accompanied by an increase in entropy tends to be spontaneous. Let us consider a molecular system in states A and B (Fig. 9.3). In state A all the molecules are arranged and highly ordered, while in state B the molecules are present at random and it is highly disordered.

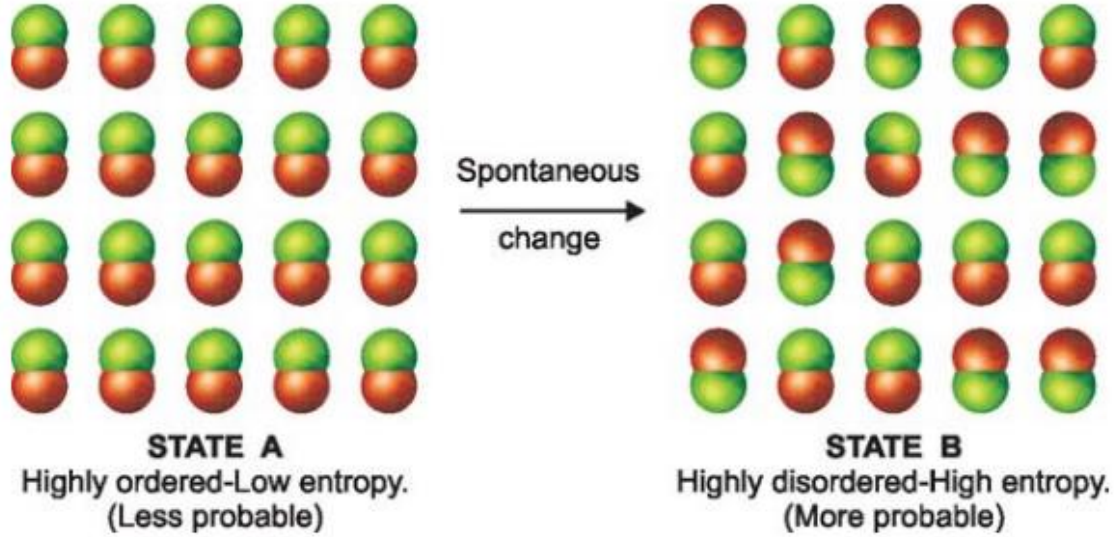


Figure 9.3
(a) State A is highly ordered, low entropy and less probable;
(b) State B is highly disordered high entropy and more probable.

(1) By definition, the entropy of A is low and that of B high. Thus an increase of entropy occurs in the change from A to B.

(2) According to the law of chance (probability), A is less probable and B is more probable. Therefore, the change from A to B is spontaneous.

(3) From (1) and (2), it follows that the change from A to B which is accompanied by increase of entropy will tend to be spontaneous.

Hence we can say, in general, that a change in a system which is accompanied by an increase in entropy, tends to be spontaneous.

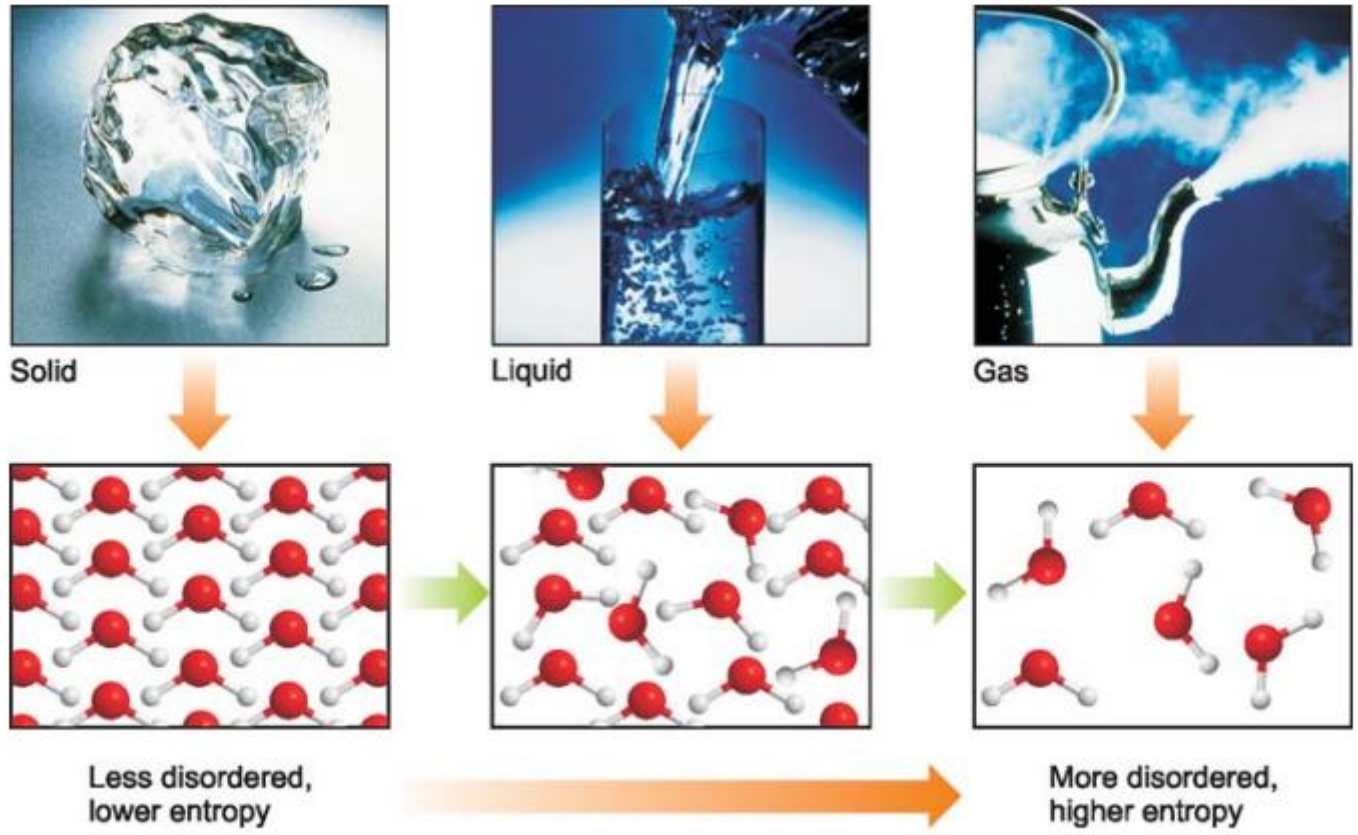
STATEMENT OF THE SECOND LAW

The second law of thermodynamics states that : **whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.**

More specifically, we take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$$

The second law, as stated above, tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases. In other words $\Delta S_{univ} > 0$. When a reversible process occurs, the entropy of the system remains constant. $\Delta S_{univ} = 0$. Since the entire universe is undergoing spontaneous change, the second law can be most generally and concisely stated as : **the entropy of the system is constantly increasing.**



NUMERICAL DEFINITION OF ENTROPY

We have discussed the physical definition of entropy. But classical thermodynamics does not require a physical explanation of the concept of entropy. All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.

In 1850 Clausius introduced a numerical definition of entropy. According to him entropy of a system (not undergoing chemical or physical changes), is a constant quantity when there is no communication of heat. When heat (q) flows into a system, the entropy increases by q/T . Heat flowing out of a system produces a corresponding decrease. Thus entropy could be precisely defined as : **for a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature (T).** That is,

$$\Delta S = \frac{q}{T}$$

If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved, ΔS is negative and there is a decrease in entropy.

UNITS OF ENTROPY

As stated above, entropy is equal to heat energy divided by absolute temperature. Therefore, it is measured in entropy units (*'eu'*) which are calories per degree per mole *i.e.*, cal mol^{-1} K^{-1}.

In the SI system, the units are joules per mole per degree *i.e.*, J mol^{-1} K^{-1}. These are represented by *eu*.

$$1\,eu = 4.184$$

(2) Heat Engines

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of a suitable device.

A machine which can do work by using heat that flows out spontaneously from a high-temperature source to a low-temperature sink, is called a heat engine.

A heat engine takes heat energy from a high-temperature reservoir and converts some of it into work, returning the unconverted heat to a low-temperature sink. A basic heat engine is illustrated in Fig. 9.6. A steam engine is a typical heat engine. It takes heat from the boiler (high-temperature source), converts some heat to work and returns the unused heat to the surroundings (low-temperature sink).

A heat engine running on a periodic cyclic process can yield work continuously.

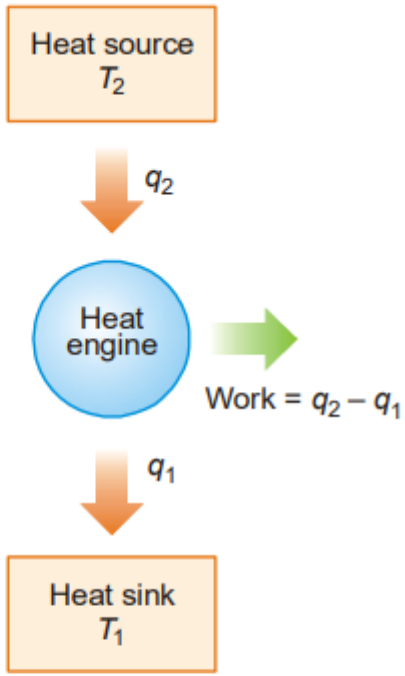


Figure 9.6
Principle of heat engine (illustration).

(3) Efficiency of a Heat Engine

The ratio of the work obtained in a cyclic process (w) to the heat taken from the high-temperature reservoir (q) is referred to as the efficiency of a heat engine.

No heat engine, no matter how well constructed, can convert all the heat from the high-temperature reservoir into work. Such an engine would be 100% efficient. Sadi Carnot was the first scientist to realise this and deduce an expression showing the limitations of heat engines.

THE CARNOT CYCLE

In 1824 Sadi Carnot proposed a theoretical heat engine to show that the efficiency was based upon the temperatures between which it operated. Carnot's imaginary engine could perform a series of operations between temperatures T_1 and T_2, so that at the end of these operations the system was restored to the original state. **This cycle of processes which occurred under reversible conditions is referred to as the Carnot cycle.** The medium employed in operating Carnot's engine was one mole of an ideal gas which could be imagined to be contained in a cylinder fitted with a frictionless piston.

The Carnot cycle comprises four operations or processes.

(1) Isothermal reversible expansion
(2) Adiabatic reversible expansion
(3) Isothermal reversible compression
(4) Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle (Fig. 9.7).

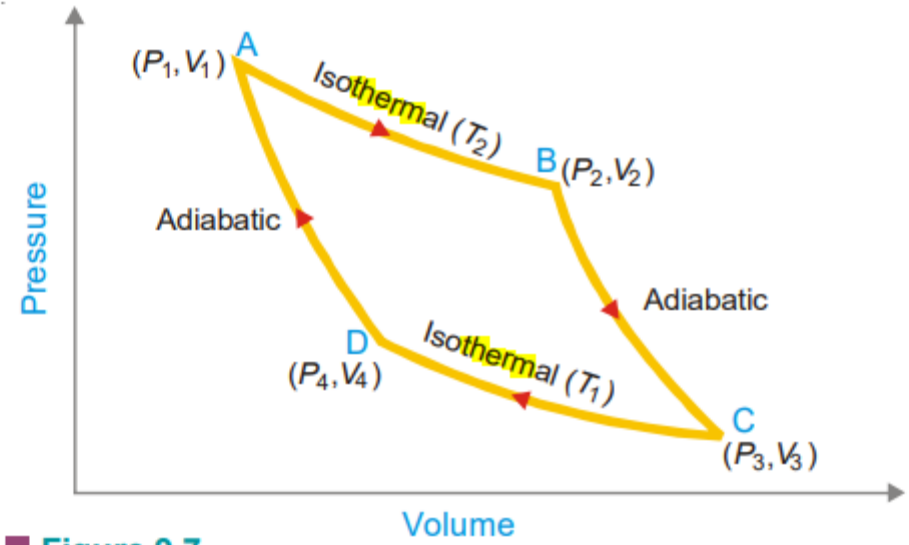


Figure 9.7
Indicator diagram of the Carnot cycle.

First Operation – Isothermal Reversible Expansion

Let T_2, P_1 and V_1 be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature (T_2). Now the gas is allowed to expand isothermally and reversibly so that the volume increases from V_1 to V_2. AB represents the path of the process in the diagram.

Work done. Since the process in operation 1 is isothermal, $\Delta E = 0$. If q_2 be the heat absorbed by the system and w_1 the work done by it, according to the first law equation ($\Delta E = q - w$),

$$q_2 = w_1$$

But $$w_1 = RT_2 \ln \frac{V_2}{V_1}$$

Therefore, $$q_2 = RT_2 \ln \frac{V_2}{V_1} \quad \text{...(1)}$$

Second Operation – Adiabatic Reversible Expansion

The gas at B is at a temperature T_2 and has volume V_2 under the new pressure P_2. The gas is now allowed to expand reversibly from volume V_2 to V_3 when the temperature drops from T_2 to T_3 (along BC).

Work done. Since this step is adiabatic, $q = 0$. If w_2 be the work done, according to the first law equation ($\Delta E = q - w$),

$$\Delta E = -w_2$$

or $$w_2 = -\Delta E$$

But $$\Delta E = C_v (T_1 - T_2)$$

Therefore, $$w_2 = C_v (T_2 - T_1) \quad \text{...(2)}$$

Third Operation – Isothermal Reversible Compression

Now the cylinder is placed in contact with a heat reservoir at a lower temperature, T_1. The volume of the gas is then compressed isothermally and reversibly from V_3 to V_4 (represented by CD in diagram).

Work done. During compression, the gas produces heat which is transferred to the low temperature reservoir. Since the process takes place isothermally, $\Delta E = 0$. If q_1 is the heat given to the reservoir and w_3 the work done on the gas, using proper signs for q and w, we have

$$-q_1 = -w_3 = RT_1 \ln \frac{V_4}{V_3} \qquad ...(3)$$

Fourth Operation – Adiabatic Reversible Compression

The gas with volume V_4 and temperature T_1 at D is compressed adiabatically (along DA) until it regains the original state. That is, the volume of the system becomes V_1 and its temperature T_2.

Work done. In this step work is done on the system and, therefore, bears the negative (–) sign. If it is denoted by w_4, we can write

$$-w_4 = -C_v (T_2 - T_1) \qquad ...(4)$$

Net Work Done in One Cycle

Adding up the work done (w) in all the four operations of the cycle as shown in equations (1), (2), (3) and (4), we have

$$\begin{aligned} w &= w_1 + w_2 + (-w_3) + (-w_4) \\ &= RT_2 \ln \frac{V_2}{V_1} + C_v (T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - C_v (T_2 - T_1) \end{aligned}$$

$w_4 = C_v (T_2 - T_1)$ ...(4)

Net Work Done in One Cycle

Adding up the work done (w) in all the four operations of the cycle as shown in equations (1), (2), (3) and (4), we have

$$w = w_1 + w_2 + (-w_3) + (-w_4)$$

$$= RT_2 \ln \frac{V_2}{V_1} + C_v (T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - C_v (T_2 - T_1)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

Net Heat Absorbed in One Cycle

If q is the net heat absorbed in the whole cycle.

$$q = q_2 - q_1$$

where q_2 is heat absorbed by the system in operation 1 and q_1 is the heat transferred to the sink reservoir.

From (1) and (3)

$$q = q_2 - q_1 = RT_2 \ln\frac{V_2}{V_1} + RT_1 \ln\frac{V_4}{V_3}$$

or
$$q = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_3}{V_4} \quad ...(5)$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma - 1} \quad \textit{...for adiabatic expansion}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \quad \textit{...for adiabatic compression}$$

or
$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or
$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore, substituting the value of V_3/V_4 in equation (5), the value of net heat may be given as

$$q = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \ln\frac{V_2}{V_1} \quad ...(6)$$

Calculation of Thermodynamic Efficiency

Since the total work done in a cycle is equal to net heat absorbed, from (6) we can write

$$w = R\,(T_2 - T_1)\,\ln\frac{V_2}{V_1} \qquad ...(7)$$

The heat absorbed, q_2, at higher temperature T_2 is given by equation (1),

$$q_2 = RT_2\,\ln\frac{V_2}{V_1} \qquad ...(8)$$

Dividing (7) by (8)

$$\frac{w}{q_2} = \frac{R\,(T_2 - T_1)\,\ln V_2/V_1}{RT_2\,\ln V_2/V_1} = \frac{T_2 - T_1}{T_2}$$

or

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} \qquad ...(9)$$

The factor w/q_2 is called **thermodynamical efficiency.** It is denoted by η and gives the fraction of the heat taken from the high-temperature reservoir which it is possible to convert into work by a heat

engine. Therefore, the efficiency of a Carnot engine, the most ideal of all engines, is limited by the operating temperatures of the engine. The larger the temperature difference $(T_2 - T_1)$ between the high and the low temperature reservoirs, the more the heat converted to work by the heat engine. For a given temperature of the high-temperature reservoir, the lower the temperature of the sink, the greater will be the efficiency of the machine. Similarly, for a given temperature of the sink, the efficiency will be increased by using a high temperature of the source reservoir.

Carnot Theorem

We have shown above that

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

This result deduced for a perfect gas depends upon the temperature limits between which the cycle operates. It is independent of all other factors. Thus Carnot stated an important relation known as the **Carnot theorem.** It states that : **every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance.**