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Core Course PHYSICS

Thermodynamics

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UNIT ONE

ZEROTH LAW AND FIRST LAW OF THERMODYNAMICS

Introduction

Thermodynamics is the branch of physics which deals with processes involving heat, work and internal energy. In other words thermodynamics deals with the transformation of heat into mechanical work. Thermodynamics does not take into account the atómic constitution of matter but only deals with macroscopic properties of the system, such as pressure, volume, temperature, internal energy, etc., that we can observe and measure in experiments. There are mainly four laws in thermodynamics. They are zeroth law, first law, second law and third law of thermodynamics. The zeroth law of thermodynamics introduces the concept of temperature and thermodynamic equilibrium. The first law of thermodynamics gives the relation between heat and mechanical work and the second law which is the backbone of thermodynamics depicts the direction and manner in which heat flow takes place. The third law of thermodynamics explains the nature of bodies in the neighbourhood of absolute zero temperature. Finally, in short, we can say that thermodynamics is an experimental science and based upon the general laws of nature which govern the conversion of heat into mechanical work and vice versa. Before getting into the chapter in detail we give definitions and brief explanations of some of the terms used in thermodynamics such as system, surroundings, closed system, open system and isolated system.

System

In natural science the study of any special branch of it begins with a separation of a restricted region of space or a finite portion of matter from its surroundings by means of a closed surface called the boundary. The region within the arbitrary boundary and on which the attention is focused is called the system. In other words **any portion of matter which is considered as separated from its surroundings is called a system.**

Surrounding

All things which are outside the system and influence its behaviour are known as surroundings. It may be some other system.

Let a gas be filled in a cylinder fitted with a piston heated by a burner. Here the gas is the system while the piston and the burner are the surroundings.

Depending upon the type of interaction between the particles of the system and the surroundings we have the following types of systems.

(i) Open system

A system which can exchange matter and energy with the surroundings is called an open system.

For example in air compressor, air at low pressure enters and air at high pressure leaves the system. i.e., there is an exchange of matter and energy with the surroundings.

(ii) Closed system

A system which can exchange only energy with the surroundings is called a closed system.

For example a gas enclosed in a cylinder expands when heated and pushes the piston upward. Here the matter (gas) in the system remains constant.

(iii) Isolated system

A system which is both thermally and mechanically isolated from the surroundings is called an isolated system.

A thermally isolated system means no heat flows into or out of the system. For example a system (gas) enclosed by perfectly insulating walls.

A mechanically isolated system means a system enclosed by perfectly rigid walls so that its volume remains unchanged. i.e., no communication of energy with the surroundings.

When a system has been chosen our next task is to describe it in terms of quantities related to the behaviour of the system or its interactions with the surroundings or both. In general there are two points of view that may be adopted. One is the macroscopic point of view and the second one is the microscopic point of view.

Macroscopic point of view

Macroscopic point of view considers variables or characteristics of a system at large scale. i.e., we describe a system by specifying the quantities of mass, composition, volume, pressure, and temperature etc. These quantities are called macroscopic coordinates which refer to the large scale characteristics. In general macroscopic coordinates have the following properties.

(i) They involve no special assumptions concerning the structure of a matter, radiation or fields.

(ii) They are few in number needed to describe the system.

(iii) They can be directly experienced by our sense of perception.

(iv) They can be measured directly in the laboratory.

The study of a system under this category leads to thermodynamics. Thus thermodynamics is the branch of natural science that deals with the macroscopic properties of the system such as pressure, volume, temperature etc. Geometrical optics, mechanics, electricity, magnetism etc. are other macroscopic branches of natural science. The presence of temperature in our system of study distinguishes thermodynamics from other macroscopic branches mentioned above.

Microscopic point of view

The microscopic point of view considers variables or characteristics of a system at atomic level. There are large number of variables that describe the internal structure of the system or associated with the constituent of the system. The study of a system under this category leads to statistical mechanics. Thus statistical mechanics is defined as the branch of science that deals with the microscopic characteristic of the system. The microscopic description of a system involves the following properties.

(i) Assumptions are made concerning the structure of matter, fields or radiation.

(ii) Many quantities are needed to describe the system.

(iii) They cannot be experienced by our sense of perceptions.

(iv) They cannot be measured directly in the laboratory.

Macroscopic versus microscopic points of view

If we study a system either by macroscopic point of view or by microscopic point of view both yield same conclusions and results.

In macroscopic study pressure, volume temperature etc are fundamental quantities which can be measured directly in laboratories, where as in microscopic study these are quantities that can be calculated theoretically from the microscopic behaviour of the system. Moreover in macroscopic study of systems we cannot derive the relationship between various macroscopic quantities from fundamental principles. Everything stems from experimental observations. But in microscopic study of systems we can derive every relationship from fundamental principles. For example $PV = nRT$ is an experimentally proved relationship in macroscopic study. However this relationship can be derived in the realm of microscopic study of systems from fundamental principles.

The above discussion shows that the microscopic point of view goes much beyond the macroscopic view point. Microscopic point of view assumes several things about the system, sometimes it may go beyond our sense of perceptions and imaginations. It assumes the structure of microscopic particles, their motion, their energy states, their interactions etc. and we develop a mathematical frame work and predict about our measurable quantities and also derive the relation between various quantities involved in the study. Inspite of all these the final justification should come from the macroscopic point of view, where everything is measurable.

Scope of thermodynamics

We found that in dealing a system by macroscopic point of view, it constitutes a description of the large scale characteristic of a system by means of a few of its measurable quantities suggested by our sensory perceptions i.e., the description of a system by some of the observable quantities associated with the system is the starting point of all investigations in all branches of natural science. For example, we want to deal with the mechanics of a rigid body. Obviously we go for macroscopic point of view. Firstly we find out some observable variables (coordinates) such as position, centre of mass with respect to time: clubbing of position and time we get another observable quantity velocity. The centre of mass, position, time, velocity etc. are some of the measurable quantities called mechanical coordinates. These coordinates enable us determine potential energy and kinetic energy of the rigid body. i.e., it is the purpose of mechanics to find out the relations between different mechanical coordinates which are consistent with Newton's laws of motion.

In thermodynamics the situation is slightly different. Here we take observable variables associated with the internal state of the system as pressure, volume, temperature etc. These observable quantities called thermodynamic coordinates. These coordinates enable us to determine the internal energy of the system. i.e., it is the purpose of thermodynamics to find out the relations between different thermodynamic coordinates which are consistent with the fundamental laws of thermodynamics. Some important thermodynamic systems are air, steam, gasoline vapour and air, a vapour in contact with its liquid etc.

Thermal equilibrium and zeroth law

This section deals with the analytic development of the concept of temperature. We found that a thermodynamic system (say gas) is described by specifying its coordinates such as the mass, the pressure, the volume and the temperature. To simplify our discussion we shall deal only with systems of constant mass. For a given mass of gas and constant temperature, the thermodynamic coordinates are the pressure and the volume. May different values of pressure and volume are possible for a gas. It the pressure is kept constant, the volume may vary over a wide range of values. If the volume is kept constant pressure may vary over a wide range of values. This shows that for a given mass of gas and constant temperature two independent coordinates (pressure and volume) are required to specify a thermodynamic system. It may be noted that though pressure and volume are independent but are related through Boyle's law (PV = constant). In general we can say that X and Y are two independent coordinates to specify a thermodynamic system.

Equilibrium state of a system

A state of a system in which the coordinates X and Y have definite values that remain constant so long as the external conditions are unchanged is called an equilibrium state. Or if there is no change in coordinates, by which the system is specified, of the system with respect to time is called an equilibrium state.

Suppose we have two systems A (described by specifying its coordinates as X, Y) and B described by specifying its coordinates as (X', Y') separated by a wall. How is, then, equilibrium of the two be defined. Obviously the equilibrium of the systems depends upon the nature of the wall. If we use an adiabatic wall for separation an equilibrium state for system A may coexist with any equilibrium state of B for all attainable values of the four quantities X, Y and X', Y'. See figure 1.1(a). This is because an adiabatic wall prevents two systems from communicating each other. Examples of adiabatic walls are thick layers of wood, concrete asbestos, felt etc.

On the other hand if the systems are separated by a diathermic wall the values of X, Y and X', Y' will change spontaneously until an equilibrium state of the combined system is attained. Then the systems are said to be in thermal equilibrium with each other (see figure 1.1(b)). This is because a diathermic wall allows heat transfer from one system to another system. The most commonly used dia thermic wall is a thin metallic sheet

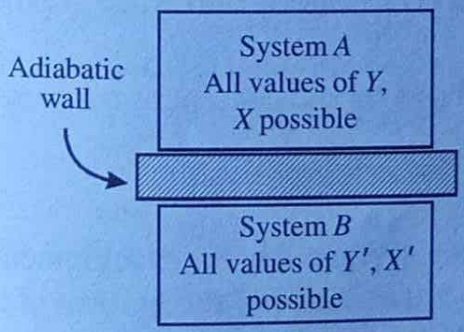


Figure 1.1(a)

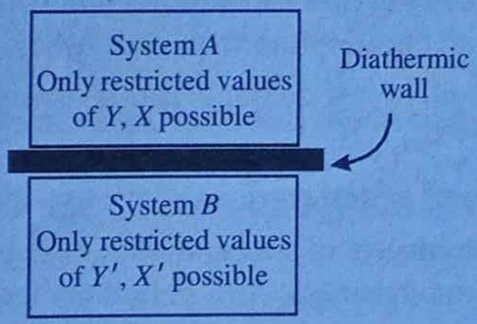
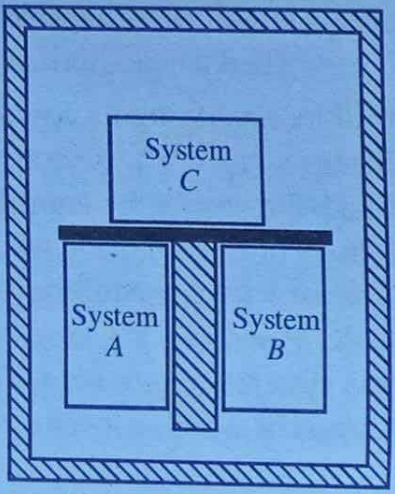


Figure 1.1(b)

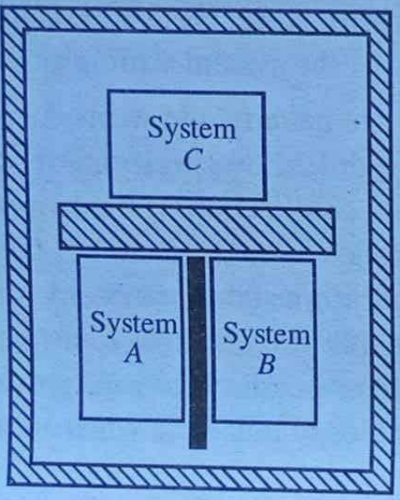
Zeroth law of thermodynamics

Imagine two systems A and B separated from each other by an adiabatic wall obviously A and B are not in equilibrium. Suppose a third system C is in brought in contact with both A and B through a diathermic wall. The entire system (A, B and C) is surrounded by an adiabatic wall (see figure 1.2(a). After sometime A and C will be in thermal equilibrium and B and C will also be in thermal equilibrium. If the adiabatic wall separating A and B is replaced by a diathermic wall and the diathermic wall separating C from both A and B is replaced by an adiabatic wall (see figure 1.2(b), we find that there is no further change. This means that the systems A and B are also in thermal equilibrium with each other. This is known as zeroth law of thermodynamics.



If *A* and *B* are each in thermal equilibrium with *C*

Figure 1.2(a)



A and *B* are in thermal equilibrium with each other

Figure 1.2(b)

Statement

Zeroth law of thermodynamics states that if two bodies A and B are each separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other.

Zeroth law of thermodynamics establishes the basis for the concept of temperature.

Concept of temperature

The concept of temperature is one of the basic tools required in the development of thermodynamics. As a definition, **temperature is a measure of the hotness of a given macroscopic object as felt by the human body.**

Defining temperature in this manner has lost its significance, relevance and the origin of it. But we require a scientific understanding of the concept of temperature. It is built upon thermal equilibrium established in zeroth law of thermodynamics.

Consider a system A in the state X_1, Y_1 in thermal equilibrium with another system B in the state X_1', Y_1'. Suppose we change the state of the system A to X_2, Y_2 that is in thermal equilibrium with X_1', Y_1' of system B. Experiment shows that there exists a set of states (X_1, Y_1), (X_2, Y_2), (X_3, Y_3) .... etc. of system B all are in thermal equilibrium with (X_1', Y_1') of system B. According to zeroth law thermodynamics all states of A are in thermal equilibrium with one another. Now we plot a graph between X and Y of the state. It is seen that the set of states of A lie along a curve I as shown in figure 1.3(a). This curve is called an isotherm. Thus **isotherm is defined as the locus of all points representing states in which a system is in thermal equilibrium with one state of another system.**

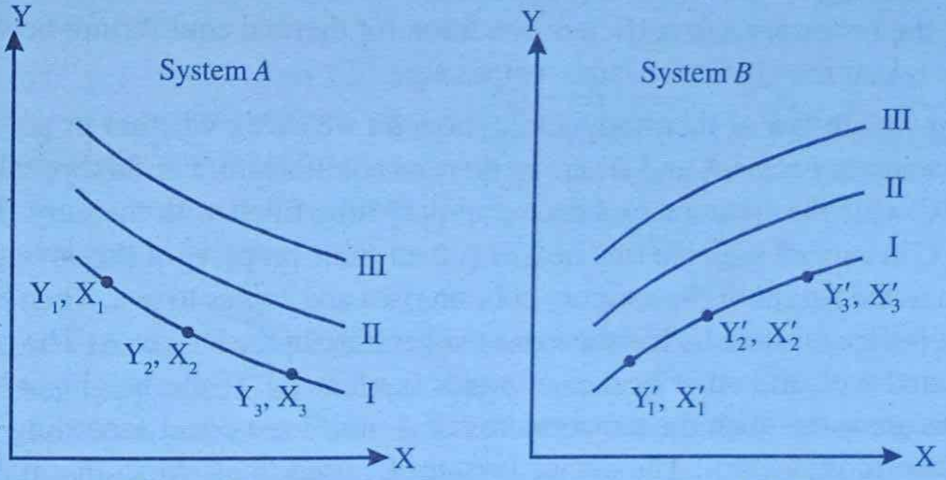


Figure 1.3(a) **Figure 1.3(b)**

Isotherms of two different systems

In a similar way we can find a set of states (X_1', Y_1'), (X_2', Y_2'), (X_3', Y_3').... etc. of the system B all of which are in thermal equilibrium with one state (X_1, Y_1) of A and therefore in thermal equilibrium with another according to zeroth law of thermodynamics. Plotting a graph between X' and Y' of the state, it is seen that the set of states of B lie along a curve called isotherm represented by I' as shown in figure 1.3(b). From zeroth law, it follows that all the states on isotherm I of system A are in thermal equilibrium with all the states on isotherm I' of system B.

The experiment is repeated with different starting conditions (of X, Y), we get a family of isotherms I, II, III ..... of system A and I′, II′, III′..... of system B.

Take the isotherms I and I' each state of set A are in thermal equilibrium with one another and also in thermal equilibrium with each one of set B.

This statement indicates that the two systems have something in common. This common property which makes the systems in equilibrium in themselves also with one another.

We call this property temperature. Now we are in a position to define temperature scientifically. **The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.**

Temperature is a scalar quantity. This may be established on the basis of zeroth law of thermodynamics. For systems A and B to be in thermal equilibrium all the information that is needed is that both A and B are thermal equilibrium with another system C. We know that a scalar quantity is represented by a number. We can assign a number to each corresponding isotherms (say I and I′) with the help of a set of rules. For different corresponding isotherms we assign different number. Once this is done, the necessary and sufficient condition for thermal equilibrium between two systems is that they have the same temperature.

Using zeroth law of thermodynamics how do we check whether or not two beakers of water (systems A and B) are in thermal equilibrium. For this we take a third system C which is an unmarked glass capillary tube filled with mercury. Bring the system C in contact with the first beaker A then some property of the device (system C) such as the height of the mercury column rises and comes to rest. Then by definition the device (system C) has the same temperature in the beaker A. The procedure is repeated with the other beaker of water (system B). If the heights of mercury columns are same then the temperatures of A and B are equal according to zeroth law of thermodynamics. The device (system C) used to establish thermal equilibrium is called a thermoscope. In order to assign a numerical value to the temperature we perform experiments on standard system.

Ideal gas temperature

In this section our aim is to see how to measure temperature. To measure a physical quantity we need some standard reference of the same kind. The standard reference chosen must be highly precise and accurately reproducible and must be invariable with time, place and environmental conditions. In olden days mercury thermometer was used as standard reference subjected to certain rules. However in the ninenteenth century it was realised that gas thermometers are far better than mercury thermometers. In the year 1887 international committee on weights and measures (CIPM) adopted gas thermometer as the standard reference.

The theoretical basis for gas thermometry lies in ideal gas equation

$$PV = nRT \qquad \text{..... (1)}$$

where P is the pressure of the system of gas, V is the volume of the gas, n is the number of moles of gas and R is the molar gas constant. The temperature T is the theoretical thermodynamic temperature. In this section we show the experiment that yields reproducible and accurate empirical temperature θ of a real gas. It may be noted that our governing equation is that of an ideal gas and we are going to measure real gas temperature (θ). How to achieves this, is the problem.

The ideal gas temperature (T) is found using a constant volume gas thermometer (Jolly's bulb) as follows. A schematic diagram of a constant volume gas thermometer is shown in figure 1.4.

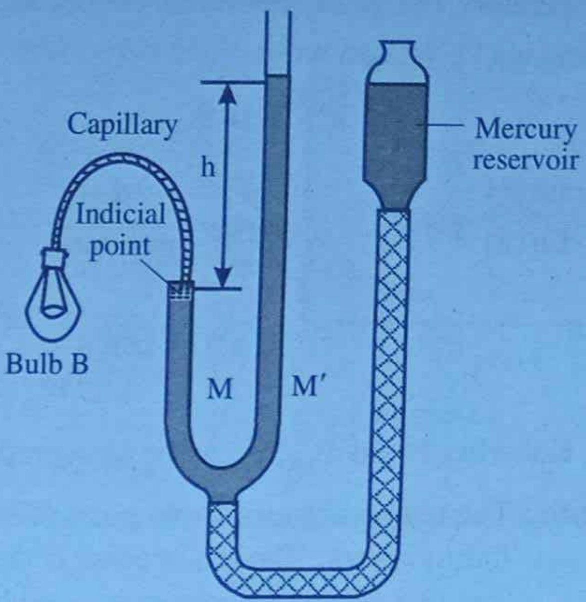


Figure 1.4 : Constant volume gas thermometer. Mercury reservoir is raised or lowered so that the meniscus at the left always touches the indicial point. Bulb pressure equals *h* plus atmospheric pressure

The gas is contained in the bulb B. The bulb B is connected to a mercury column through a capillary tube. There is a marking at the top of the mercury column called indicial point. By adjusting the height of the reservoir (raising or lowering) until the mercury column in M just touches the indicial point we can make the volume of the gas always constant. The pressure in the bulb is equal to atmospheric pressure plus the difference in height h between the two mercury columns M and M′.

i.e., $P = P_{atm} + \rho g h$

To begin the experiment the bulb is inserted in a triple point cell whose temperature is assigned as 273-16 K. Adjust the height of the reservoir until the mercury in the column M just touches the indicial point. Noting h, pressure of the gas P_{TP} is calculated.

Using equation (1), we can write

$$P_{TP} \propto 273.16\,\mathrm{K} \qquad ..... (2)$$

(since volume of the gas is constant)

Remove the triple point cell and surround bulb with unknown real gas whose temperature (θ) to be measured. As before measure the pressure inside bulb as P. Using eq(1), we can write

$$P \alpha \theta \qquad \text{..... (3)}$$

$$\frac{\text{Eq(3)}}{\text{Eq(2)}} \text{ gives} \qquad \frac{P}{P_{TP}} = \frac{\theta}{273.16K}$$

or

$$\theta = 273.16K \frac{P}{P_{TP}} \qquad \text{..... (4)}$$

Knowing P and P_{TP}, θ can be measured.

Note : The temperature of triple point (TP) of water is the standard fixed point of thermometry. The triple point is the temperature at which the solid, liquid and vapour phases coexist in equilibrium. A device that gives this temperature is called triple point cell.

Now we consider measuring ideal gas temperature (T) at the normal boiling point (NBP) of water (The steam point). For this an amount of gas is introduced into bulb B and measure P_{TP} when the bulb is inserted in the triple point cell. Suppose that P_{TP} is equal to 120kPa. Keeping volume constant carry out the following procedure.

(i) Surround the bulb B with steam at standard atmospheric pressure, measure the gas pressure P_{NBT} as described earlier, then calculate the real gas temperature θ using equation 4.

i.e.,

$$\theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{120}$$

(ii) Remove some of the gas from the bulb B so that P_{TP} has a smaller value (say 60 kPa). Measure the new value of P_{NBP} and calculate new value of θ.

$$\theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{60}$$

(iii) Repeat the experiment by reducing the amount of gas step by step. Each time measure corresponding θ value.

(iv) Plot a graph between $\theta(P_{NBP})$ against P_{TP}. Extra polate the resulting curve to the axis where $P_{TP} = 0$

From the graph we can measure

$$\underset{P_{PT}\to 0}{LT}\ \theta(P_{NBP})$$

The whole experiment was repeated for three different gases, each time measured $\theta(P)$ for the normal point of water. (see figure)

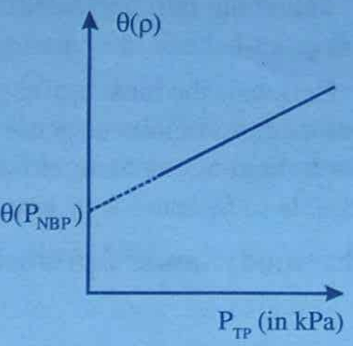


Figure 1.5

It is seen that although the readings of a constant volume gas thermometer depend upon the nature of the gas at ordinary values of P_{NBP}, all gases indicate the same pressure as $P_{T_p} \to 0$. Therefore we define the ideal gas temperature T by the equation

$$T = 273.16K \lim_{P_{TP}\to 0} \frac{P}{P_{TP}} \qquad \text{constant V.} \qquad .....(5)$$

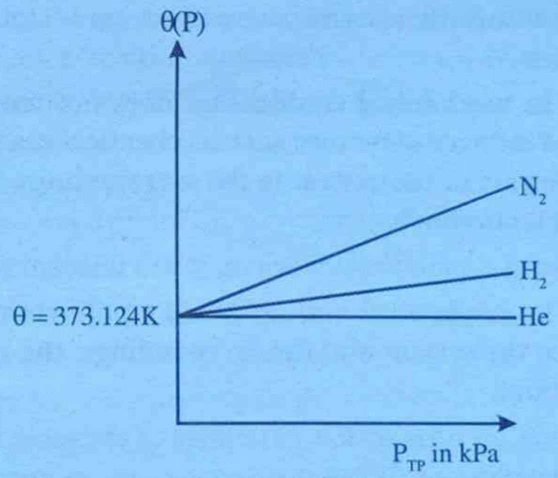


Figure 1.6

The above experiment shows that the behaviour of the real gases approaches the behaviour of ideal gas in limiting condition

i.e., $\theta = T$ when $P_{T_p} \to 0$.

This is our familiar statement that at low pressure and high temperature (NBP) all real gases behave like ideal gases.

Helium is the most useful gas for thermometric purposes for two reasons. At high temperatures helium does not diffuse, where as hydrogen does. The second reason is that helium becomes liquid at a temperature lower than any other gas so that it is feasible to measure very low temperature than any other gas thermometers.

Thermodynamic equilibrium

Suppose we want to conduct experiments on a thermodynamic system. Firstly identify two thermodynamic variables for the complete description of the macroscopic system. When these variables change either spontaneously or by outside influence the system is said to undergo change of state. When the system is not influenced in any way by its surroundings it is said to be an isolated system. This systems are of little use and importance. Usually we deal with systems influenced by its surroundings. The surroundings may exert forces on the system or provide exchange of energy. It is due to this interaction between the system and the surroundings the state of the system changes.

When there is no resultant force or torque in the interior of the system and also none between the system and its surroundings, the system is said to be in a state of mechanical equilibrium when these conditions are not satisfied the system undergoes change of state.

When a system is in mechanical equilibrium does not tend to undergo a spontaneous change of internal structure such as chemical reaction or a transfer of matter from one part of the system to the surroundings, then the system is said to be in chemical equilibrium.

When a system is not in chemical equilibrium, it will undergo change of state.

When a system is in mechanical and chemical equilibrium, if it does not exchange heat between the system and the surroundings, the system is said to be in thermal equilibrium.

In thermal equilibrium all parts of the system are at the same temperature and also the surroundings temperature. When these conditions are not satisfied the system will undergo change of state.

When a system is mechanical, chemical and thermal equilibriums, the system is said to be in thermodynamic equilibrium.

When a system is in thermodynamic equilibrium the variables (coordinates) representing the state of the system will not undergo change with respect to time.

It may be noted that thermodynamics does not deal with any problem involving time. However time factor plays a crucial role when we deal with kinetic theory of gases, hydrodynamics, chemical kinetics etc.

When any one of the three conditions required for a system to be in thermodynamic equilibrium is not satisfied, the system is said to be in non equilibrium state.

In non-equilibrium states as the thermodynamic variables change, the state of the system cannot be described by thermodynamic variables. Thus we are helpless in dealing with such systems partially. However approximation methods are available to deal with non-equilibrium states.

Equation of state

For simplicity consider a closed system. A system (gas) enclosed in a cylinder provided with a piston. This being a closed system the matter (gas) remains constant and can exchange energy with the surroundings, we can very well measure the pressure P, the volume V and the temperature T of the system. If we fix P and V, automatically T will be fixed by nature. If V and T are fixed, the pressure P assumes a constant value. It shows among the three variables only two are independent variables. This implies that there exists an equation of equilibrium which connects the thermodynamic variables (coordinates). This is called an equation of state. Thus, **equation of state is a relation connecting between thermodynamical coordinates of the system in thermodynamic equilibrium.**

Equation of state in thermodynamics cannot be deducted theoretically but must come from experimental results. Thus the equation of state is valid only within the range of values measured experimentally. Beyond this range some other equation of state may come into play.

For example, the equation of state for an ideal gas is

$$PV = nRT$$

This is valid only at very low pressure.

At high pressures, the equation of state is Vander Waals equation given by

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \qquad \text{..... (6)}$$

Where a and b are constants for a given gas but differ from gas to gas. The constant a takes into account particles interaction and b takes into account the finite side of the particles.

In both these equations of state three dynamical variables are used. This does not mean that these three variables (P, V, T) are the only variables used to write equation of state. For example the relationship between the entropy (S), the internal energy (U) and pressure (P) is as good as an equation of state as the above two equations. Therefore any two out of three can be chosen as independent variables, the third being a dependent variable. In general the three coordinates chosen is designated as X, Y and Z. Such ZYZ systems will be called simple systems. PVT system is an important type of simple system.

Hydrostatic systems

Any isotropic system of constant mass and constant composition that exerts on the surroundings a uniform hydrostatic pressure in the absence of gravitation a electric and magnetic effects is called a hydrostatic system.

Hydrostatic system is divided into three categories.

(i) **A pure substance** : which is a single chemical compound in the form of a solid, a liquid, a gas, a mixture of any two or a mixture of all three

(ii) **A homogeneous mixture of different compounds** such as a mixture of inert gases, a mixture of chemically active gases or mixture of liquids.

(iii) **A hetrogeneous mixture** such as mixture of gases in contact with a mixture of different liquids.

Note : An isotropic system means showing same property in all directions. A homogeneous system is a system which is completely uniform. When a system consists of two or more phases which are separated from one another by definite boundary surfaces is said to be a hetrogenous system.

It has been experimentally shown that the states of thermodynamic equilibrium of a hydrostatic system can be described in terms of three thermodynamic coordinates P, V and T. i.e., every hydrostatic system is a PVT system, thus having an equation of state.

If the system undergoes a small change of state from its initial equilibrium state to very close equilibrium state, then all the coordinates (P, V, T) undergo slight change. If the change in P is very small in comparison with P and very large in comparison with local fluctuations of pressure due to few number of molecule, then the change of P may be written as a differential dP. Similarly change in V is differential dV and that in T is dT. i.e., every infinitesimal change in thermodynamic coordinates (differential change) requires two conditions to be satisfied, that is the change is very small with respect to the quantity itself and large is in comparison with the effect produced by the behaviour of a few molecules. The reason for this is that P, V and T refer to macroscopic behaviour. In other words thermodynamic system is a collection of an extra large number of particles.

The equation of state of a system is represented by expressed by a coordinate in terms of other two.

Thus, V = V (T, P)

Using the rule of partial differentiation, we can find the differential on both sides.

$$\text{i.e., } dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial T}\right)_P dP$$

Where the partial derivative $\left(\frac{\partial V}{\partial T}\right)_P$ means the infinitesimal change in V with respect to infintesimal change in T, keeping P constant. Similarly $\left(\frac{\partial V}{\partial P}\right)_T$. Both partial derivatives have an important physical meaning.

From the definition of average coefficient of volume expansion (β) we have:

$$\text{Average coefficient of expansion} = \frac{\text{change in volume per unit volume}}{\text{change in temperature}}$$

where the changes occur at constant pressure.

$$\text{i.e.,} \qquad \beta = \left(\frac{\Delta V}{V\Delta T}\right)_P = \frac{1}{V}\left(\frac{\Delta V}{\Delta T}\right)_P$$

When the change is made smaller and smaller it becomes infinitesimal.

i.e., $\Delta V \rightarrow dV$ and $\Delta T \rightarrow dT$.

$$\text{Thus} \qquad \beta = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad \text{..... (7)}$$

Remember that β is a positive quantity since when T increases, V also increases except for water between 0°C and 4°C. This is because when temperature of water increases from 0°C to 4°C, volume decreases there by β becomes negative. This is also true for rubber.

The unit of β is K^{-1}.

Similarly we recall the definition of average bulk modulus (B).

$$\text{Bulk modulus} = \frac{\text{change in pressure}}{\text{change in volume per unit volume}}$$

As before, for infinitesimal changes we can write

$$B = \frac{dP}{dV / V} = V\left(\frac{\partial P}{\partial V}\right)$$

But we know that a positive change in pressure produces a negative change in volume, we introduce a negative sign to make B a positive quantity.

$$\therefore \qquad B = -V\left(\frac{\partial P}{\partial V}\right)$$

Further we assume that changes occur at constant temperature. Then B is called isothermal bulk modulus

i.e.,
$$B = -V\left(\frac{\partial P}{\partial T}\right) \qquad \text{..... (8)}$$

In thermodynamics we always go for measuring reciprocal of isothermal bulk modulus called isothermal compressibility denoted by k_T

$$k_T = \frac{1}{(B)_T}$$

i.e.,
$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{..... (9)}$$

The unit of k_T is $(Pa)^{-1}$. Equations 7 and 9 are very important in thermodynamics because on the L.H.S of equations we have experimentally measured quantities. From this we can calculate the change in thermodynamic coordinates on the R.H.S.

If the equation of state is

$$P = P(T, V)$$

we get
$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV.$$

If
$$T = T(P, V)$$

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$$

To see the physical meaning of $\left(\frac{\partial T}{\partial P}\right)_V$, see example 1. The above discussion shows that for any closed system the expressions for dV, dP and dT enable us to use an equation of thermodynamic equilibrium to solve it for any coordinate in terms (see example 2) of the other two. Since dP, dV and dT are differentials of actual functions, they are called exact differentials.

Finally it may also be worth recalling two theorems on partial differentiation

(i) $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z}$

(ii) $\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$

The negative sign on the R.H.S of theorem (ii) comes simply because of the three coordinates only two are independent.

Intensive and extensive coordinates

We found that quantities such as pressure (P), volume (V), temperature (T) etc. of the system which determine the state of a system are known as thermodynamical variables. Thermodynamical variables fall into two broad categories. They are (i) intensive variables and (ii) extensive variables.

Imagine a **system in thermodynamic equilibrium to be divided into two equal parts each with equal mass. Those properties of each half of the system that remain the same are said to be intensive, those that are halved are called extensive.**

Pressure, temperature, surface tension, viscosity, emf, electric field, magnetic etc. are intensive variables. Intensive variables are independent of mass of the system. It is a characteristic property of the system.

Volume, length, area, charge, internal energy, number of moles etc. are extensive variables. Extensive variables depend on the mass or size of the substance present in the system.

Example 1

Show that $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$

Solution

We have $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{..... (1)}$$

and $$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{..... (2)}$$

$\frac{\text{Eq (1)}}{\text{Eq (2)}}$ gives $$\frac{\beta}{k} = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

i.e., $$\frac{\beta}{k} = -\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T$$

or $$\frac{\beta}{k} = \left(\frac{\partial P}{\partial T}\right)_V$$

Used theorem (i) and (ii) of partial differentiation.

Example 2

A mass of mercury at standard atmospheric pressure and a temperature of about 15°C is kept at constant volume. If the temperatured is raised to 25°C what will be final pressure. $\beta = 1.81 \times 10^{-4} K^{-1}$ and $k = 4.01 \times 10^{-11} (Pa)^{-1}$

Solution

$T_i = 15 + 273 = 288 K$, $T_f = 25 + 273 = 298K$.

From example 1, we have

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$$

or $$dP = \frac{\beta}{k} dT \text{ Integrating}$$

we get $$\int_{P_i}^{P_f} dP = \frac{\beta}{k} \int_{T_i}^{T_f} dT$$

$$P_f - P_i = \frac{\beta}{k}(T_f - T_i)$$

$$P_f - P_i = \frac{1.81 \times 10^{-4} \times 10}{4.01 \times 10^{-11}} = 4.51 \times 10^7 \text{ Pa}$$

Example 3

The equation of state of an ideal gas is $PV = nRT$. Show that the volume expansivity β is equal to $\frac{1}{T}$ also show that the isothermal compressibility is equal to $\frac{1}{P}$.

Solution

We have
$$PV = nRT \qquad \text{..... (1)}$$

Take the derivative on both sides with respect to T, keeping pressure constant, we get

$$P\left(\frac{\partial V}{\partial T}\right)_P = nR \qquad \text{..... (2)}$$

equation 2 by 1 gives

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}$$

By definition L.H.S is β

$$\therefore \qquad \beta = \frac{1}{T}$$

Now take the derivative equation (1) with respect, to P, keeping temperature constant, we get

$$P\left(\frac{\partial V}{\partial P}\right)_T + V = 0$$

or
$$P\left(\frac{\partial V}{\partial P}\right)_T = -V \qquad \text{..... (3)}$$

$\frac{\text{Eq (3)}}{\text{Eq (1)}}$ gives
$$\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{nRT}$$

or
$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{V}{nRT} = \frac{V}{PV} = \frac{1}{P}$$

By definition L.H.S is k_T

i.e.,
$$k_T = \frac{1}{P}$$

Example 4

A block of copper at a pressure of 1 atm, a volume of 100cm^3 and a temperature of 10°C experiences a rise in temperature of 5°C and an increase in volume of 0.005cm^3. Calculate the final pressure. $\beta = 4.95\times10^{-5}\text{K}^{-1}$, $k = 6.17\times10^{-12}(\text{Pa})^{-1}$

Solution

$$P_i = 10^5\,\text{Pa},\ \ V_i = 100\times10^{-6}\,\text{m}^3$$

$$T_i = 10 + 273 = 373\text{K}$$

$$T_f = 15 + 273 = 378\text{K}$$

$$V_f = (100.005)\times10^{-6}\,\text{m}^3$$

Our aim is to find the pressure coordinate. P is a function of V and T

$$P = P(T, V)$$

$\therefore$
$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

Substituting for
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$$

and
$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{kV}$$

We get $dP = \frac{\beta}{k}dT - \frac{1}{kV}dV$ Integrating, we get

$$P_f - P_i = \frac{\beta}{k}(T_f - T_i) - \frac{1}{k}\ln\frac{V_f}{V_i}$$

Substituting the values, we get

$$P_f - P_i = \frac{4.95\times10^{-5}}{6.17\times10^{-12}}\times5 - \frac{1}{6.17\times10^{-12}}\ln\frac{100.005}{100}$$

$$P_f - P_i = 4.01\times10^{7} - 16.21\times10^{10}\times\ln 1.00005$$

$$P_f - P_i = 4.01\times10^{7} - 16.21\times10^{10}\times4.99\times10^{-5}$$

$$P_f - P_i = 4.01\times10^{7} - 80.89\times10^{5}$$

$$P_f - 1\text{ atm} = 401\text{ atm} - 80.89\text{ atm}$$

$$P_f - 1\text{ atm} = 320.11\text{ atm}$$

$$P_f = 321.11\text{ atm}$$

Work

Whenever a system undergoes a displacement under the action of a constant force, work is said to be done. Work is measured as the product of force and the component of displacement parallel to the force

i.e., $W = \vec{F}\cdot\vec{S} = Fs\cos\theta$

If the force is variable work done is given by $W = \int \vec{F}\cdot d\vec{r}$

If a system as a whole exterts a force $(\vec{F})$ on the surroundings and a displacement $(\vec{S})$ takes place, depending upon the direction of $\vec{F}$ and $\vec{S}$, the work done is either by the system or on the system is called external work done. i.e., external work done is due to interaction between the system and the surroundings. For example a gas is enclosed in a cylinder provided with a piston. When the gas expands, it is imparting motion to the piston thereby doing work on its surroundings (piston). The work done by any part of the system on any other part is called internal work. It is due to interaction between the constituents (atom or molecules) of the system. Internal work done cannot be discussed in macroscopic thermodynomics. Thus in this chapter whenever we say work it implies external work.

When a system does external work parameters required to find the work done can be expressed in terms of thermodynamical variables specifying the system.

Sign convention of work

In mechanics when a force exerts on a mechanical system in the same direction of displacement, work is positive and work is said to be done on the system. In this case energy of the system increases. For thermodynamics to be consistent with mechanics, we adopt the same convention. Thus work is done on the system, work is considered as positive. When work is done by the system, work is considered as negative.

Quasi static process

When a system is in thermodynamic equilibrium and the surroundings are kept unchanged, no motion will take place and no work will be done. If some how there is an unbalanced force acting on the system, the mechanical equilibrium, thermal equilibrium and chemical equilibrium may upset, then the system will be no longer in thermodynamic equilibrium. This system will pass through non-equilibrium states, then the system will not be described by thermodynamic variables. To overcome this we imagine an ideal situation in which the unbalanced force is infinitesimal and the process proceeds infinitesimally slowly. A process performed in this ideal way said to be quasi-static. During a quasi-static process, the system is at all times infinitesimally close to a state of thermodynamic equilibrium.

Thus a quasi-static process is a process in which a system successively changes from one equilibrium state to the next equilibrium state differing only infinitesimally from the first one.

A quasi-static process is an ideal concept which can never be realised in the laboratory. However in the laboratory many processes approach quasi-static process with no significant error.

The introduction of the concept of quasi-static processes enable us to calculate the work done. In thermodynamics we deal with only reversible quasistatic processes only in which dissipative forces are ignored. It may be noted that all processes that we deal in thermodynamics are quasi-static.

Depending upon the conditions imposed on a given hydrostatic system it can undergo several types of processes such as quasi-static isothermal expansion or compression of an ideal gas, quastic-static increase of pressure on a solid, quasi-static expansion or compression of a gas in an adiabatic container, quasi-static isobaric process, quasi-static isochoric process, quasi-static cyclic process and quasi-static non cyclic process.

(i) Quasi-static isothermal process

A process in which pressure and volume change at constant temperature is known as an isothermal process. In such a process there is always heat transaction between the system and surroundings so that the system must be in very good thermal contact with surroundings. This means that the wall of the container is a perfect heat conductor (diathermic).

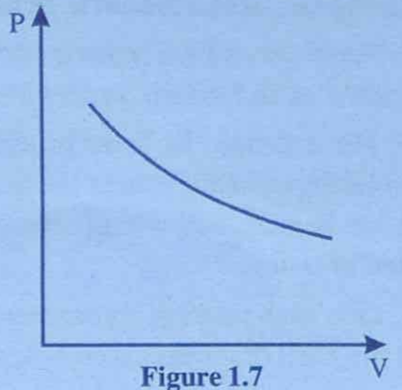


Figure 1.7

As an example let us consider a perfect gas enclosed in a cylinder of diathermic wall and equipped with a smooth piston. When the gas is compressed by pushing the piston inward, the work is done on the gas and its temperature increases. In order to keep the temperature constant, heat, equivalent to the work done, must flow out the system. Similarly during an expansion process heat flows from surroundings to the system

The equation of state for isothermal processes of a perfect gas is,

$$PV = \text{constant}$$

A graph between volume and pressure in an isothermal process is known as an *isothermal.*

Since the internal energy of a perfect gas depends only on temperature, the internal energy of a perfect gas remains constant in an isothermal process.

(ii) Quasi-static adiabatic process

In adiabatic process, the system is isolated from the surroundings so that heat neither enters nor leaves the system. In this process pressure, volume and temperature may change. Obviously the system must be enclosed in a perfect insulator of heat.

Now let us consider a perfect gas enclosed in cylinder fitted with a piston. Both the cylinder and piston are made of perfect insulators of heat. Any change in the pressure and volume is always accompanied by a *temperature change,* since the work done in this case is converted as internal energy of the system.

Since perfect thermal isolation is not possible the quick and sudden processes are considered as adiabatic processes. The bursting of an inflated motor car tyre, the compression and expansion of the working substance during the compression stroke and power stroke respectively of a petrol engine or a diesel engine etc. are examples of adiabatic process. Since pressure, volume and temperature change in an adiabatic process we cannot draw a graph in a single plane. But we can show that at any point the adiabatic curve has a steeper negative slope than does an isothermal curve at the same point.

The equation of state for adiabatic processes of a perfect gas is

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

where γ is the ratio of specific heats i.e. $\gamma = \frac{C_P}{C_V}$

(iii) Quasi-static isobaric process

A process taking place at constant pressure is known as an isobaric process.

For example isobaric process occurs in the boiler super heater where the heat of the existing steam is increased without increasing its associated pressure.

One such process is represented by a line AB in the P–V diagram given below.

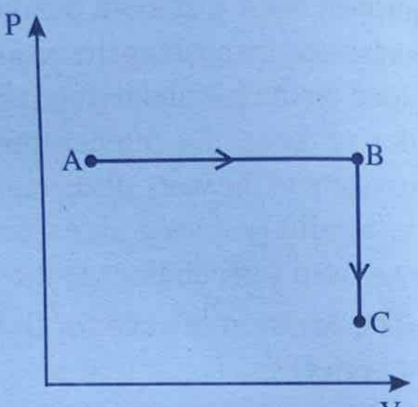


Figure 1.8

(iv) Quasi-static isochoric process

A process taking place at constant volume is called an isochoric process. It is also called as isometric process. For example addition or removal of heat from a system (gas) enclosed in a sealed non-deformation container. The ideal ottocycle is another example of isochoric process. When it is assumed that the burning of the gasoline-air mixture in an internal combustion engine car is instantaneous, there is an increase in temperature and pressure of the gas inside the cylinder while the volume remains constant. One such process is represented by the line BC in the P–V diagram given above.

(v) Quasi-static cyclic process

Cyclic process is a process in which a system is taken from an initial state A (P_i, V_i, T_i) to a succession of states but is always brought back to the initial state. Such a process is represented by a closed path in a P–V diagram (see figure 1.9).

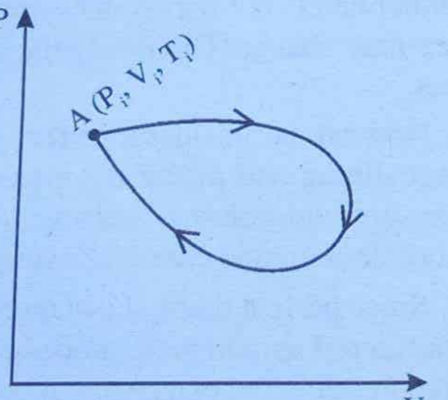


Figure 1.9

It is obvious that there is no change in the state of the system at the end of a cycle in such a process. i.e. P, V, T, U, S, etc. remain unchanged at the end of a cycle. The internal energy U of the system depends only on the state of the system; so in a cyclic process the net change of internal energy dU will be equal to zero. i.e., $dU = 0$.

The carnot cycle is the best example for a cyclic process. A devise that converts heat into mechanical work continuously by performing cyclic processes is known as a heat engine.

(vi) Quasi-static non-cyclic process

A thermodynamic system which undergoes series of changes and does not come back to the original state is called as non-cyclic process.

A gas enclosed in a cylinder is compressed by a piston, if the piston doesnot come back to the original position, we can say gas undergoes a non-cyclic process.

Work in changing the volume of hydrostatic system

Consider a system (gas) enclosed in a cylinder provided with a frictionless piston. Let A be the area of cross section of the cylinder. Let P be the pressure exerted by the system on the piston, therefore the corresponding force is PA. The surroundings also extert an opposing force on the piston. Let F be the force act on the system from the surroundings. The force F is slightly different from the force PA of the system. Under this condition the piston moves through an infinitesimal distance dx during compression. See figure below. The surroundings perform an infinitesimal work on the system (positive) denoted by $đW$ (d-bar W)

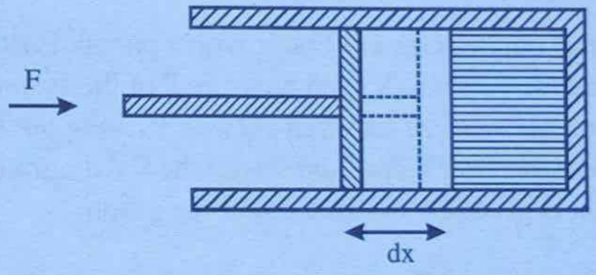


Figure 1.10

Thus $đW = Fdx = PAdx$

$Adx = dV$ infinitesimal change in volume. During compression the volume of the system decreases, so we put a negative sign before dV, this makes dW positive. Hence $đW = -PdV$

Note that here P and V denote some intermediate stage of the quasistatic process. Integrating this we get the total work done during a finite quasistatic process in which volume changes from V_i to V_f.

$$W = -\int_{V_i}^{V_f} PdV \qquad \text{..... (10)}$$

Since we perform a quasistatic process P is the thermodynamic coordinate. But we know that P is a function of V and T. Thus the above integration can be done provided T is specified. When T is specified P is only function of V. When this is achieved, the path of integration through successive equilibrium states is defined.

Suppose T of a quasistatic process is specified (path specified) and going from an initial volume V_i to final volume V_f then work done is

$$W_{if} = -\int_{V_i}^{V_f} PdV$$

Along the same path we come back from volume V_f to V_i, then work done is

$$W_{fi} = -\int_{V_f}^{V_i} PdV$$

Comparing the two we get

$$W_{if} = -W_{fi}$$

PV diagram

Consider a system (gas) enclosed in a cylinder with a piston. Piston is allowed to move. Each time measure the volume (V) and pressure P of the system. Plot *a graph between pressure P along the vertical axis and volume V along the horizontal axis. The graph so obtained is called a PV diagram.* From the PV diagram we can calculate the work done which is given by the area under the graph.

i.e., $W_{if} = -\int_{V_i}^{V_f} PdV$ = Area under the graph

Various PV diagrams are show in figure below.

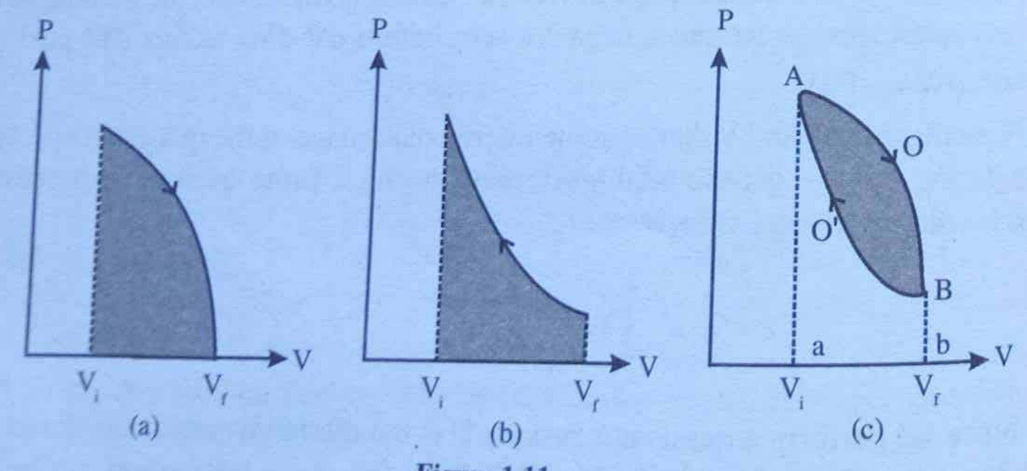


Figure 1.11

In figure 1.11(a), dV is positive since $V_f > V_i$ so the work done is negative indicating work is done by the system.

In figure 1.11(b), dV is negative since $V_f < V_f$ so the work done is positive means work is done on the system.

In figure 1. 11(c), when the system goes from A to B, dV is positive, work done is negative. So work is done by the system given by the area AOBba. When the system moves from B to A, dV is negative, work done is positive, so work is done on the system given by BO'Aab. Since area AOBba is greater than BO'Aab network done is negative. This is given by the area of the shaded portion so in this closed path network is done by the system.

Note : Any two independent thermodynamic variables such as (P, V), (T, V) (P, T) and (T, S) can be chosen to draw diagrams. In general these diagrams are called indicator diagrams.

Hydrostatic work depends on the path

Consider a hydrostatic system taken from state A to state B as shown in figure 1.2. Let the coordinates of state A and B be (P_1, V_1) and (P_2, V_2) respectively where P_1 and V_1 represent pressure and volume of state A and P_2 and V_2 that of state B. The system can move from A to B in different ways. We choose different paths such as AB, ADB and ACB. Our aim is to calculate the work done along these different paths which starts from A and ends at B in all cases.

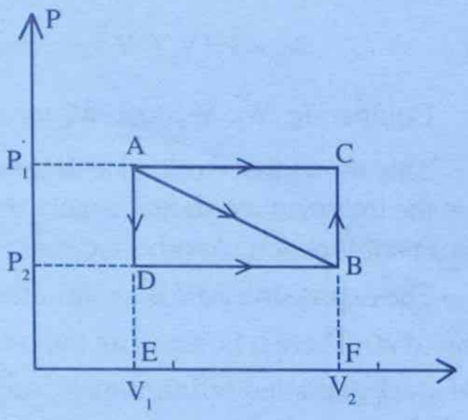


Figure 1.12

(a) Starting from point A, the pressure is continuously decreased from P_1 to P_2 along the line AB so that the volume increases from V_1 to V_2. The work done by the system is given by

$$W_1 = \int_{V_1}^{V_2} PdV = \text{Area of the trapezium ABFE} = \frac{1}{2}(P_1 + P_2)(V_2 - V_1)$$

(b) Starting from point A, the volume V_1 is kept constant in going from A to D, the pressure decreases from P_1 to P_2 and then P_2 is kept constant from D to B. The work done in this process (along the path ADB) is given by

$$W_2 = \text{Area under DBFE}$$

$$= \text{Area of the rectangle DBFE}$$

$$W_2 = P_2(V_2 - V_1)$$

[Remember that along the path AD, the process is isochoric hence work done along AD is zero. Along the path DB, the process is isobaric and the corresponding work done is $P_2(V_2 - V_1)$]

(c) Now we start from point A, the pressure P_1 is kept constant in going from A to C and then the volume V_2 is kept constant from C to B.

The work done along the path $AC = P_1(V_2 - V_1)$ since the process is isobaric.

The work done along the path $CB = 0$ since the process along this path is isochoric.

$\therefore$ The total work done along the path ACB,

$$W_3 = \text{work done along AC + work done along CB}$$

i.e. $W_3 = P_1(V_2 - V_1) =$ Area under ACFE

Comparing W_1, W_2 and W_3 we can see that $W_1 \neq W_2 \neq W_3$.

This shows that work done depends not only on the initial and final states but also on the intermediate states, namely on the path of integration. Thus we say that work is a path function. Another example for path function is heat.

The expression PdV is an infinitesimal amount of work and has been represented by ($đW$). There is however an important distinction between an infinitesimal amount of work and other infinitesimals, such a dP or dV. An infinitesimal amount of thermodynamic work is an inexact differential that $đW$ is not the differential of an actual function of the thermodynamic coordinates. To indicate that an infinitesimal amount of work is not a mathematical differential of a function W and to emphasise at all times that it is an inexact differential it is written as $đW$

Calculation of work for quasi-static process

Work done during quasi-static isothermal process

Consider a hydrostatic system (ideal gas) undergoes a quasi-static isothermal process from volume V_i to V_f.

The work done is given by

$$W = -\int_{V_i}^{V_f} PdV$$

The equation of state for an ideal gas is

$$PV = nRT$$

or

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

Substituting for P we get

$$W = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} dV \qquad (\therefore \text{ T is constant})$$

$$W = -nRT \ln \frac{V_f}{V_i} \qquad \text{..... (11)}$$

(See examples 5 and 6)

Work done can also be expressed in terms of P_i and P_f.

For isothermal process, we have

PV = constant

i.e.,

$$P_iV_i = P_fV_f$$

or

$$\frac{V_f}{V_i} = \frac{P_i}{P_f}$$

Now equation 11 becomes

$$W = -nRT \ln \frac{P_i}{P_f} \qquad \text{..... (12)}$$

or

$$W = nRT \ln \frac{P_f}{P_i}$$

Work done during isothermal increase of pressure on a solid

Consider a hydrostatic system (solid) undergoes an isothermal process from pressure P_i to P_f. The work done is given by

$$W = -\int_{P_i}^{P_f} PdV \qquad \text{..... (13)}$$

This integral cannot be performed since it is a two variable integration. Fixing the path of integration we can proceed. Here the path of integration is determined by isothermal compressibility. V is a function of P and T

i.e.,
$$V = V(P, T)$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Since the process is isothermal, the second term goes.

$$\therefore \qquad dV = \left(\frac{\partial V}{\partial P}\right)_T dP$$

or
$$dV = -kVdP \qquad \text{..... (14)}$$

$\because \quad k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, k is the isothermal compressibility.

Substituting eq 14 in eq 13 we get

$$W = \int_{P_i}^{P_f} PkVdP$$

At constant temperature, k and V are almost constant, thus

$$W \approx kV\int_{P_i}^{P_f} PdP = kV\frac{P^2}{2}\Bigg|_{P_i}^{P_f}$$

$$W \approx \frac{kV}{2}(P_f^2 - P_i^2) \qquad \text{..... (15)}$$

(see examples 7 and 8)

Work done during a quasi-static adiabatic process

Consider a hydrostatic system (ideal gas) undergoes an quasi-static adiabatic process where system goes from initial state (P_i, V_i) to final state (P_f, V_f). The work done is given by

$$W = -\int P dV$$

For an adiabatic process the equation of state of an ideal gas

$$PV^{\gamma} = K, \quad \text{K is a constant}$$

or $$P = \frac{K}{V^{\gamma}}$$

$$\therefore \qquad W = -\int_{V_i}^{V_f} \frac{K}{V^{\gamma}} dV = -K \int_{V_i}^{V_f} V^{-\gamma} dV$$

$$W = -K \frac{V^{-\gamma+1}}{-\gamma+1} \Bigg|_{V_i}^{V_f} = \frac{K}{\gamma-1}\left(V_f^{-\gamma+1} - V_i^{-\gamma-1}\right)$$

Using $P_i V_i^{\gamma} = K$ and $P_f V_f^{\gamma} = K$

We get

$$W = \frac{1}{\gamma-1}\left[K V_f^{-\gamma+1} - K V_i^{-\gamma+1}\right]$$

$$W = \frac{1}{\gamma-1}\left[P_f V_f^{\gamma} V_f^{-\gamma+1} - P_i V_i^{\gamma} V_i^{-\gamma+1}\right]$$

$$W = \frac{1}{\gamma-1}[P_f V_f - P_i V_i] \qquad \text{..... (16)}$$

(See example 9 and 10)

The above equation can also be written in terms of temperatures. For ideal gas, the gas law can be applied to all processes.

We have PV = nRT

$$P_i V_i = nRT_i$$

and $$P_f V_f = nRT_f$$

Thus equation 16 becomes

$$W = \frac{nR}{\gamma - 1}(T_f - T_i) \qquad \text{..... (17)}$$

(See problem - 16)

Example 5

Two moles of an ideal gas kept at a constant temperature of 20°C changes its volume from 4 litres to 1 litre. Calculate the work done.

Solution

$$n = 2 \quad T = 20 + 273 = 293\text{K}$$

$$V_i = 4 \times 10^{-6}\text{m}^3 \qquad V_f = 1 \times 10^{-6}\text{m}^3$$

Using $W = -nRT\ln\frac{V_f}{V_i} = -2 \times 8.315 \times 293\ln\left(\frac{1}{4}\right)$

$$= 6753\text{J}$$

Positive work indicates that work is on the gas.

Example 6

Calculate the work done when one mole of an ideal gas expands isothermally at 27°C to double its original volume. $R = 8.315\,\text{J K}^{-1}\text{mol}^{-1}$.

Solution

$$n = 1,\ T = 27 + 273 = 300\text{K}$$

$$V_i = V,\ V_f = 2V$$

Using $W = -nRT\ \ln\ \frac{V_f}{V_i}$

$$W = -1 \times 8.315 \times 300 \times \ln\frac{2V}{V}$$

$$W = -8.315 \times 300 \times 0.693$$

$$W = -1728.7\text{J}$$

Negative work indicates that work is done by the system.

Example 7

The pressure on 10 gram of solid copper is increased quasistatically and isothermally at 20°C from 0 to 1000 atm calculate the work done. $\rho = 8.96 \times 10^3 \text{kgm}^{-3}$, $k = 7.16 \times 10^{-12} (\text{Pa})^{-1}$ and 1 atm $= 1.01 \times 10^5$ Pa.

Solution

$$m = 10\text{g} = 10 \times 10^{-3}\text{kg} = 10^{-2}\text{kg}$$

$$T = 20 + 273 = 293\text{K}$$

$$P_i = 0,\ P_f = 100 \times 1.01 \times 10^5 = 1.01 \times 10^8 \text{Pa}$$

Using $W \approx \frac{kV}{2}(P_f^2 - P_i^2)$

$$W \approx \frac{km}{2\rho}(P_f^2 - P_i^2)$$

$$W \approx \frac{7.16 \times 10^{-12} \times 10^{-2}}{2 \times 8.96 \times 10^3}[1.01 \times 10^8)^2 - 0]$$

$$W \approx 4.076\text{J}$$

Positive work done indicates that work is done on the copper.

Example 8

The pressure on 100g of nickel is increased quasistatically and isothermally from 0 to 500 atm. Assuming the density and isothermal compressibility to remain constant at values of 8.90×10^3 kgm^{-3} and 6.75×10^{-12} (Pa)$^{-1}$ respectively. Calculate the work.

Solution

$$m = 100\text{g} = 100 \times 10^{-3} = 10^{-1}\text{kg}$$

$$P_i = 0,\ \ P_f = 500 \times 1.01 \times 10^5 \text{Pa}$$

Using $W \approx \frac{kV}{2}(P_f^2 - P_i^2)$

$$W \approx \frac{km}{2\rho}(P_f^2 - P_i^2)$$

$$W \approx \frac{6.75\times10^{-12}\times10^{-1}}{2\times8.90\times10^{3}}(5\times1.01\times10^{7})^{2}$$

$$W \approx 9.671\times10^{-2}\,\text{J}$$

Positive work indicates that work is done on the nickel.

Example 9

A diatomic ideal gas of volume 10^{-3}m^3 at a pressure of 10^6Pa undergoes quasi static adiabatic process until the pressure drops to 2×10^5 Pa and volume drop to $3.16\times10^{-3}\text{m}^3$ calculate the work.

Solution

$$\gamma = 1.4,\ V_i = 10^{-3}\,\text{m}^3,\ V_f = 3.16\times10^{-3}\,\text{m}^3$$

$$P_i = 10^6\,\text{Pa},\ P_f = 2\times10^5\,\text{Pa}.$$

Using $$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

$$W = \frac{2\times10^5\times3.16\times10^{-3} - 10^6\times10^{-3}}{1.4-1}$$

$$W = \frac{6.32\times10^2 - 10^3}{0.4}$$

$$W = -920\text{J}$$

Negative work indicates that work is done by the system.

Example 10

A mono atomic ideal gas of volume 1 litre at a pressure of 8 atmospheres undergoes quasi-static adiabatic expansion until the pressure drops to 1 atm. How much work is done. 1 atm = 10^5Pa.

Solution

$$V_i = 10^{-3}\,\text{m}^3,\ V_f = ?$$

$$P_i = 8\times10^5\,\text{Pa},\ P_f = 10^5\,\text{Pa}$$

$$\gamma = \frac{5}{3}\ \text{(For a mono atomic gas)}$$

For an adiabatic process

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\therefore \quad V_f = \left(\frac{P_i V_i^\gamma}{P_f}\right)^{\frac{1}{\gamma}}$$

$$V_f = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}} V_i$$

$$V_f = \left(\frac{8\times10^5}{10^5}\right)^{3/5} \cdot 10^{-3} = (8)^{3/5} \times 10^{-3}$$

$$V_f = 3.48\times10^{-3}\,m^3.$$

$\therefore$ Work done is

$$W = \frac{P_f\,V_f - P_i V_i}{\gamma - 1}$$

$$W = \frac{10^5 \times 3.48\times10^{-3} - 8\times10^5\times10^{-3}}{\frac{5}{3}-1}$$

$$W = \frac{3.48\times10^2 - 8\times10^2}{2/3}$$

$$W = \frac{348-800}{2/3} = -6785$$

Negative work indicates that work is done by the system.

Example 11

Calculate the work done upon expansion of one mole of a real gas quasistatically and isothermally from 10 litres to 22.4 litres at 20°C. $a = 1.4\times10^9\,Nm^4mol^{-1}$ and $b = 3.2\times10^{-5}\,m^{-3}mol$.

Solution

For one mole of real gas equation of state is

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

or $$P=\frac{RT}{V-b}-\frac{a}{V^2}$$

The work done, $W=-\int_{V_i}^{V_f} PdV$

$$W=-\int_{V_i}^{V_f}\frac{RT}{V-b}dV+\int_{V_i}^{V_f}\frac{a}{V^2}dV$$

$$W=-RT\ \ln(V-b)\Big|_{V_i}^{V_f}-\frac{a}{V}\Big|_{V_i}^{V_f}$$

$$W=-RT\ \ln\frac{(V_f-b)}{(V_i-b)}-a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)$$

Substituting the values, we get

$$W=-8.315\times 293\times \ln\frac{(10^{-2}-3.2\times 10^{-5})}{(22.4\times 10^{-3}-3.2\times 10^{-5})}$$

$$-1.4\times 10^{9}\left(\frac{1}{22.4\times 10^{-3}}-\frac{1}{10^{-2}}\right)$$

$$W=-2436.3\ \ln\frac{9.968\times 10^{-3}}{0.0224}-1.4\times 10^{9}(44.64-100)$$

$$W=-2436.2\ \ln(0.445)+1.4\times 10^{9}\times 55.36$$

$$W=-2436.2\times -0.81+77.5\times 10^{9}$$

$$W=1973.3+77.5\times 10^{9}$$

$$W\approx 77.5\times 10^{9}\,J$$

Work and heat

In the last section we found that a system can change its state by performing work done. But there are other means of changing the state of the system that do not involve performance of work. For example water containing in a heater with diathermic bottom is heated, the state of the system (water) changes. This happens because heater is at higher temperature and water is at a lower temperature. The temperature of a body has been assigned a meaning similar to level of a liquid. If there is a level difference liquid flows. Similarly if there is a temperature difference something flows. This something is called heat. In other words temperature is a measure of heat level. For example when two differently heated bodies are put in contact heat flows from one to the other. We know that it is because of temperature difference between the two bodies heat flows. Heat flows from a higher temperature to lower temperature until the two bodies attain a common temperature. Thus **we define temperature as the thermal state of a body with reference to its ability to communicate heat to other bodies.**

Heat is defined as something which flows from one body at a higher temperature to the one at a lower temperature.

In our example heat flow is the agency which changes the state of our system (water). This agency (heat) cannot be described by as mechanical work. The above discussion shows that work and heat are different agencies that cause the system to changes.

Finally it may be noted that an adiabatic wall does not allow heat to pass through, where as a diathermic wall transmits heat. In the mechanics a rigid wall does the function of adiabatic wall in heat. Rigid wall does not allow work. Through where as adiabatic wall does not allow heat to pass. A movable wall allows to perform work in mechanics where as a diathermic wall allows heat flow.

Adiabatic work

Consider a closed system surrounded by adiabatic walls. For example a gas is enclosed in a cylinder with adiabatic walls provided with adiabatic piston. Since the system is surrounded by adiabatic walls no heat transfers from the system to the surroundings. However since it being a closed system it can exchange energy with the surroundings. i.e., the system experiences the process of working. This is called adiabatic work.

During adiabatic work the system moves from one state to another. The system can assume several paths to go from initial to final state. It has been experimentally verified by several experiments that the adiabatic work is same for all paths.

i.e., **If a closed system is caused to change from an initial state to final state by adiabatic means only, then the work done is the same for all paths connecting the two states.**

This statement enables us to draw an important conclusion. Recall from mechanics that when work done is independent of path, the force involves is said to be conservative, then there exits an associated function called potential energy function

$$F = -\frac{dU}{dr}$$

$$U_f - U_i = -\int_i^f \bar{F} \cdot d\bar{r}$$

In a similar way we can argue that our adiabatic work is independent of path but depends only on the initial state and the final state of the system then there exists a function called internal energy function denoted by U.

i.e., $W_{i \to f}$ (adiabatic) $= U_f - U_i$ ..... (18)

If W is positive then $U_f > U_i$

It may be noted that thermodynamic work in general is path dependent but adiabatic work is path independent.

Internal energy function

Experiments on adiabatic work brings us two informations one is that during an adiabatic process work done results in change of internal energy of the system. It is nothing but law of conservation of energy. The second is that adiabatic work introduces a new energy function associated with the system. The internal energy is a function which depends on many thermodynamic variables used to describe the system. For example a closed hydrostatic system is described by P, V and T. so U is also a function of P, V and T. But only two variables are required to specify a system, we keep the third one constant. In this situation W can be a function of (P, V), (T, V) and (T, P).

$$U = U(T, V)$$

$$U = U(T, P)$$

and $$U = U(P, V)$$

Taking the differentials, of first two we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

and
$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP.$$

The four partial derivatives have different physical meanings. $\left(\frac{\partial U}{\partial T}\right)_V$ and $\left(\frac{\partial U}{\partial T}\right)_P$ give the specific heat capacity of the system at constant volume and pressure respectively. This concept will be introduced soon. $\left(\frac{\partial U}{\partial V}\right)_T$ tells us how does the internal energy of a system change with respect to change in volume keeping temperature constant.

$\left(\frac{\partial U}{\partial P}\right)_T$ tells us how does the internal energy of a system change with change in pressure keeping temperature constant.

It may be noted that it is not possible to measure the internal energy of a system but change in internal energy can be measured indirectly by measuring heat and work.

Note : For $U = U(P, V)$ see example 15 and problem 13.

Mathematical formulation of first law

We found that a system undergoes a change in state through the performance of adiabatic work only. This experiment is used only to measure the change in internal energy (eq 18). This is not the usual process carried out in laboratories. For example gas enclosed in a cylinder provided with adiabatic walls and a adiabatic piston. The bottom of the cylinder is provided with a diathermic boundary. When the system is heated at the bottom with a burner, the system undergoes a change in state by absorbing heat from the burner and does diathermic work (W). This is not equal to the adiabatic work $U_f - U_i$. Now we combine the two experiments firstly calculate $U_f - U_i$ by doing adiabatic work, the system goes from state i to state f. Secondly perform the diathermic work such that the system goes from the same state i to the same state f.

Combining the effect of two experiments and use of law of conservation of energy we can define thermodynamic heat. It is defined as the **difference between the change in internal energy and diathermic work when a closed system undergoes a process in which diathermic work is done.**

Heat is denoted by Q. Thus we have

$$Q = U_f - U_i - W$$

or

$$U_f - U_i = Q + W \qquad \text{..... (19)}$$

This is known as the mathematical formulation of the first law of thermodynamics.

Sign convention of Q

When heat enters a system Q is taken as positive and negative when heat leaves the system. Like U and W, heat is measured in joules.

Significance of first law

(i) It provides a method for determining the change in internal energy.

(ii) It embodies the law of conservation of energy and

(iii) it provides the definition of heat.

We found that heating is a process by which there is an exchange of energy between the system and the surroundings because of temperature difference. Now a fundamental question arises. What type of energy is exchanged. This can be precisely understood once the conditions of the processes are specified. Suppose we give heat to a system at constant volume it is called isochoric heat, which results in the transfer of internal energy. When heat is given to the system at constant pressure, it is called isobaric heat the heat (energy) transferred is known as enthalpy. It will be discussed later.

Concept of heat

Heat is the flow of energy from one system to the other. Depending upon the conditions specified it could be either internal energy or enthalpy. During the flow of heat thermodynamic variables cannot be assigned to the system as it goes on changing, Thus heat cannot be expressed in terms of thermodynamic variables so the calculation of heat depends on the path of integration. Thus heat is an inexact differential. An infinitesimal change in heat is designated by $đQ$. When heat flow stops the system attains a new state, in this context the system can be represented by thermodynamic variables.

Imagine two systems A and B in thermal contact with each other and the composite system is surrounded by adiabatic walls.

For the system A alone

$$U_f - U_i = = Q + W$$

For the system B along

$$U'_f - U'_i = Q' + W'$$

Adding we get

$$(U_f - U_i) + (U'_f - U'_i) = Q + W + Q' + W'$$

or $$(U_f + U'_f) - U_i + U'_i) = (Q + Q') + (W + W')$$

The equation represents the composite system. L.H.S represents the change in internal energy of the composite system. $Q + Q'$ is the heat transferred to the composite system and $W + W'$ is the work done for the composite system since the composite system is surrounded by adiabatic walls

$$Q + Q' = 0$$

i.e., $$Q = -Q'$$

It shows that within an adiabatic boundary heat lost (or gained) by the system A is equal to gained (or lost) by the system B. This is the basis of principle of method of mixtures. Experiments show that in general heat is not a conserved quantity but in an adiabatic container it is conserved.

Note : It is meaningless to say heat in a body or work in 'a body because both (Heat and work) are transient activities.

Differential form of first law

When a thermodynamic system undergoes an infinesimal process, the thermodynamic variables representing the system change infinitesimally. For such a process the first law of thermodynamics can be written as

$$dU = đQ + đW \qquad ..... (20)$$

This is the mathematical form of first law.

For an infinitesimall quasistatic process dU and $đW$ can be expressed in terms of thermodynamic coordinates only.

On the L.H.S of equation 20, dU is an exact differential where as on the R.H.S both are inexact differentials. It should be noted that dU refers to a property within the system where $đQ$ and $đQ$ are not related to the properties of the system rather they refer to the surroundings of the system and the interaction between the system and the surroundings.

For an infinitesimal quasistatic process of a hydrostatic system, we have $đW = -PdV$.

Now equation 20 becomes

$$dU = đQ - PdV$$

or
$$đQ = dU + PdV \qquad ..... (21)$$

Heat capacity and its measurements

According to first law of thermodynamics we have

$$U_f - U_i = Q + W$$

This shows that internal energy can be changed either by heat (Q) or work (W). As it is easier to produce heat rather than work, we go with measuring $U_f - U_i$ by supplying heat. Our aim is to measure the capability of a system to store internal energy by supplying heat to the system. Actually we are measuring internal energy capacity. Unfortunately this term had been miscoined as heat capacity.

Let ΔQ be the heat given to a system and the corresponding change in temperature is ΔT. Then, the average heat capacity is defined as

$$\text{Average heat capacity} = \frac{\Delta Q}{\Delta T}$$

In the limiting condition $\Delta Q \to 0$ and $\Delta T \to 0$, the ratio approaches a limiting value known as heat capacity denoted by C

i.e.,
$$C = \frac{đQ}{dT} \qquad ..... (22)$$

Its unit is JK^{-1}.

Remember that R.H.S is not a derivative of a function but simply a ratio.

The value of C depends on mass of the system because for a given $đQ, dT$ will be will be different for different masses of the same system. In other words C is an exentensive quantity. To make it intensive, we divide by mass m. Then the heat capacity is named as specific heat capacity denoted by c

$$C = \frac{1}{m}\frac{đQ}{dT} \qquad ..... (23)$$

Its unit is $Jkg^{-1}K^{-1}$.

The adjective specific means per unit mass.

When specific heats of different substances are compared, no regularities found to occur. However when the heat capacities are standardised to the same amount of substance called a mole, wonderful regularities found to occur.

The heat capacity per unit mole is called molar heat capacity. It is also denoted by c.

i.e., $$c = \frac{C}{n} = \frac{1}{n}\left(\frac{đQ}{dT}\right) \qquad \text{..... (24)}$$

Its unit is $\mathrm{J\,mol^{-1}K^{-1}}$.

The heat capacity can be negative, zero, positive or infinite depending upon the process of the system undergoes during heat transfer.

We have $C = \frac{đQ}{dT}$

For example, if a gas is compressed, it temperature rises, without supply any heat to it. i.e., $đQ = 0$

$$\therefore \qquad C = \frac{0}{dT} = 0$$

On the other hand if a gas is allowed to expand without any rise in temperature i.e., $dT = 0$, then

$$C = \frac{đQ}{0} = \infty$$

Thus in order to have a unique value of heat capacity of a hydrostatic system either by keeping pressure constant or volume constant.

Heat capacity at constant pressure is written as

$$C_P = \left(\frac{đQ}{dT}\right)_P$$

In general C_P is a function of P and T.

Heat capacity at constant volume is written as

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

In general C_V is a function of V and T.

Measurement of heat capacity

Measurement of heat capacities of solids, liquids and gases plays an important role in the realm of thermodynamics and statistical mechanics. In thermodynamics it enables us to categories the substances and also gives other properties exhibited by them. Statistical mechanics is based on somany assumptions and the validity of their predictions should come from experimental measurements. Heat capacity is one among them.

Here we explain one of the classic methods of measurement of heat capacity called electric method.

To find the heat capacity of a solid, solid is taken in the form of a block. Two vertical grooves are made in the block as shown in the figure below. Measure the mass of the block after making the groove let it be m. A sensitive thermometer is kept in one of the grooves and a heating coil is in the other groove. The heating coil is connected to a rheostat, an ammeter, a battery and a keep in series. A voltmeter is connected across the coil. The whole metal block is surrounded by thick cotton.

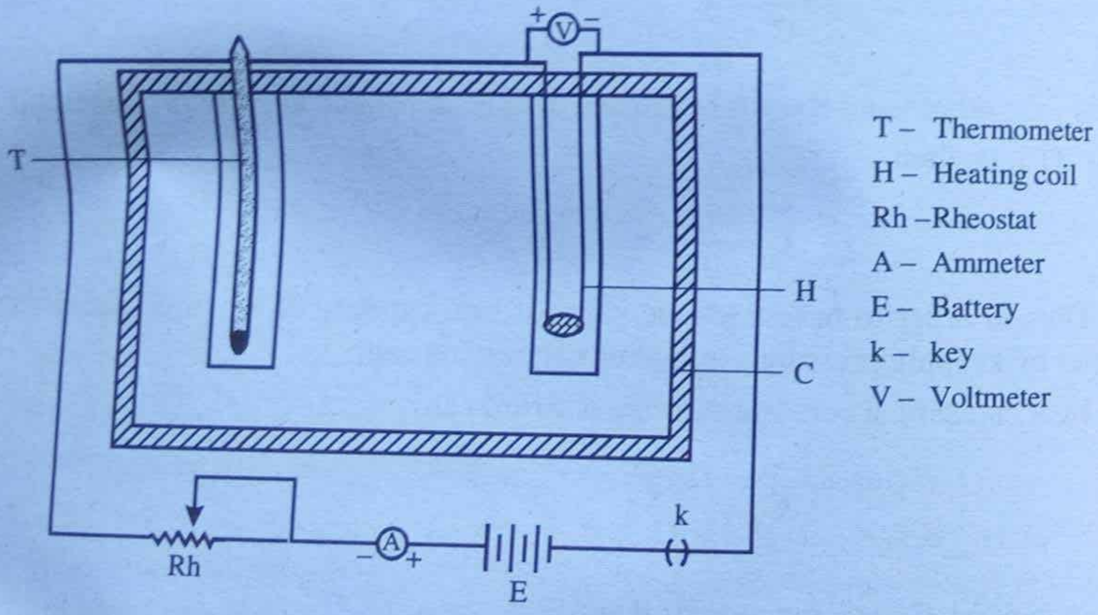


Figure 1.13

Pass a suitable constant current through the circuit. Measure the current from the ammeter and voltage from the voltmeter. Let it be I. Note the intial temperature as T_1 from the thermometer. Start a stop watch every definite interval of time t note down the thermometer reading each time as T_2.

Heat delivered by the heating coil in time interaval $t_2 - t_1 = t$ is

$$đQ = VIt$$

This heat will be absorbed by the metal and the temperature rises. From the definition of heat capacity we have

$$đQ = m\,c\,dT$$

Comparing the two equations, we get

$$m\,c\,dT = V\,I\,t$$

or
$$dT = \frac{V\,I}{mc}\,t$$

Finally draw a graph between time interval on the horizontal axis and temperature difference along the vertical axis we get a straight line graph. The slope of the graph gives $\frac{dT}{t}$

i.e.,
$$\frac{dT}{t} = \frac{V\,I}{mc}$$

or
$$c = \frac{V\,I}{m} \cdot \frac{1}{\text{slope}}$$

knowing V, I, m and slope, we can calculate the specific heat capacity of the solid.

Specific heat of water. The calorie

In olden days heat was measured in units of calorie (cal). One calorie is defined as the amount of heat required to raise the temperature by 1°C in a system of one gram of water. Later it was discovered that heat required to change the temperature of one gram of water from 0 to 1°C was different from the heat required to go from 35° to 36° (say). Calorie was then redefined as the heat required to raise the temperature of one gram of water from 14.5 to 15.5°C. Calorie is the unit of heat and unit of work is joule. They were considered as separate entitities. Experiments showed that one can produce the other.

i.e.,
$$W \propto H$$

or
$$W = JH$$

Where J was called as the mechanical equivalent of heat. It was defined as the amount work done per unit mass of water in going from 14.5° to 15.5°C. The mechanical equivalent of heat was measured to be 4.186 J cal^{-1}. Later it was realised that mechanical equivalent of heat was nothing but specific heat of water, with joule as the unit of work. Now a days we never use mechanical equivalent of heat instead we use specific heat of water. Then 1 calorie = 4.186 joules. The variation of specific heat of water with temperature is shown in figure below.

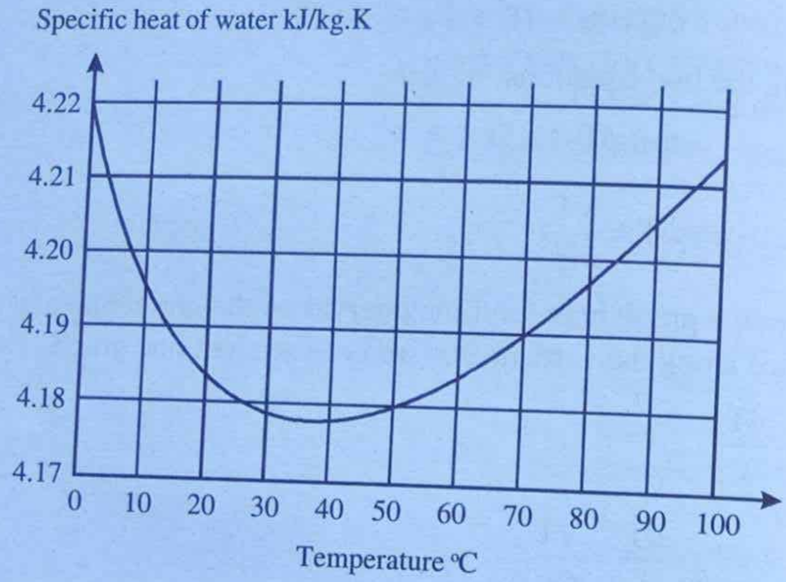


Figure 1.14 : Variation of specific heat capacity of water

Quasistatic flow of heat: Heat reservoirs

In this section we shall explain how to accomplish quastistatic flow of heat. We found that when a system is not in thermodynamic equilibrium, it passes through several non equilibrium states hence system cannot be handled by thermodynamic coordinates. Likewise similar situation arises when there is a finite temperature difference between the system and the surroundings. As a result a non-uniform temperature distribution is set up in the system and handling this type of system is more complicated. However during a quasistatic process the difference between the temperature and the surrounding is infinitesimally small, system changes infinitesimally slow. The flow of heat is also infinitesimally small and the calculation can be performed in a simple way in terms of thermodynamic coordinates specifying the system.

To achieve a quasi-static flow of heat the system is put in contact with a heat reservoir. A heat reservoir is a body having infinite heat capacity and it may absorb or reject any amount of heat without changing its temperature appreciably. For example an ice cube is thrown into ocean will not produce a drop in temperature of the ocean. Another example is atmosphere. A flow of heat from a camp fire into the air will not produce a rise of temperature of the atmosphere. The ocean and atmosphere are examples of reservoirs.

Any system in contact with a reservoir undergoing quasi-static process is said to be isothermal and there is no flow of heat. To describe a quasi-static flow of heat involving a change of temperature the system has to be placed in contact successively with a series of reservoirs. Thus we imagine a series of reservoirs ranging in temperature from T_i to T_f placed successively in contact with a system at constant pressure in such a way that the difference in temperature between the system and the reservoir with which it is in contact is infinitesimal. The flow of heat will be quasi-static and can be calculated from the definition of heat capacity at constant pressure.

i.e.,
$$C_P = \left(\frac{\text{đ}Q}{dT}\right)_P$$

or
$$Q = \int_{T_i}^{T_f} C_P\, dT$$

If C_P is constant

$$Q = C_P(T_f - T)_i$$

For a quasi-static isochoric process

$$C_V = \left(\frac{\text{đ}Q}{dT}\right)_V$$

or
$$Q = \int_{T_i}^{T_f} C_V\, dT$$

If C_V is constant, $Q = C_V(T_f - T_i)$.

In terms of specific heat capacity we have

$$Q = m\, c_P(T_f - T_i)$$

$$Q = m\, c_V(T_f - T_i)$$

A very familiar result to us.

Example 12

From the first law of thermodynamics show that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Solution

According to first law, we have

$$đQ = dU + PdV$$

U is function of either (T, V) or (T, P)

Take

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\therefore \quad đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

Dividing throughout by dT we get

$$\frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + P\frac{dV}{dT}$$

At constant volume, we have

$$\left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

By definition L.H.S is the heat capacity at constant volume C_V

$$\therefore \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Example 13

Assuming that internal energy of a hydrostatic system is a function of T and P, show that $\left(\frac{\partial U}{\partial T}\right)_P = C_p - PV\beta.$

Solution

$$U = U(T, P) \text{ given}$$

Taking differentials on both sides, we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

From first law of thermodynamics, we have

$$đQ = dU + PdV$$

or $$đQ = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP + PdV$$

Dividing throughout by dT and keep P constant

$$\left(\frac{đQ}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

i.e., $$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

Using $$\beta = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$$

$$\therefore \quad \left(\frac{dV}{dT}\right)_P = \beta V$$

Thus $$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\beta V$$

or $$\left(\frac{\partial U}{\partial T}\right)_P = C_P - P\beta V$$

Example 14

Taking U to be a function of P and V, show that $\left(\frac{\partial U}{\partial P}\right)_V = C_V \frac{k}{\beta}$

Solution

$U = U(P, V)$ given

Taking diffentials on bothsides, we get

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

Using first law of thermodynamics

$$đQ = dU + PdV$$

or
$$đQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + PdV$$

Dividing throughout by dP and keep V constant, we get

$$\left(\frac{đQ}{dP}\right)_V = \left(\frac{\partial U}{\partial P}\right)_V \qquad \text{..... (0)}$$

L.H.S can be written as

$$\left(\frac{đQ}{dP}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{đQ}{dP}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V \qquad \text{..... (1)}$$

From the definition of k and β

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta V = \left(\frac{\partial V}{\partial T}\right)_P \qquad \text{..... (2)}$$

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

or
$$kV = -\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{..... (3)}$$

$$\frac{\text{eq 3}}{\text{eq 2}} \text{ gives } \frac{k}{\beta} = -\left(\frac{\partial V}{\partial P}\right)_T \div \left(\frac{\partial V}{\partial T}\right)_P$$

or
$$\frac{k}{\beta} = -\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial T}{\partial V}\right)_P$$

$$\frac{k}{\beta} = \left(\frac{\partial T}{\partial P}\right)_V$$

Put this in equation (1), we get

$$\left(\frac{\text{đ}Q}{dP}\right)_V = C_V \frac{k}{\beta}$$

∴
$$\left(\frac{\partial U}{\partial P}\right)_V = C_V \frac{k}{\beta}.$$

IMPORTANT FORMULAE

1. Boyle's law: $PV = \text{constant}$
2. Ideal gas equation : $PV = nRT$
3. Expression for real gas temperature

$$\theta = 273.16\text{K} \frac{P}{P_{TP}}$$

4. Ideal gas temperature

$$T = 273.16\text{K} \underset{\text{Lt}\, P_{TP} \to 0}{\text{lt}} \frac{P}{P_{TP}}$$

5. Vander Waals equation of state

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

6. The coefficient of volume expansion

$$\beta = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$$

7. Bulk modulus and compressibility

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T ; \; k_T = \frac{1}{B}$$

8. Theorems on partial derivative

(i) $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y / \partial x)_z}$

(ii) $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$

9. Relation between β and k

$$\frac{\beta}{k} = \left(\frac{\partial P}{\partial T}\right)_V$$

10. Work done during a finite quasi-static process : $W = -\int_{V_i}^{V_f} PdV$

If the work is positive work is done on the system.

If the work is negative work is done by the system.

11. Work done during an quasi-static isothermal process

$$W = -nRT \ln \frac{V_f}{V_i}$$

or $\quad W = -nRT \ln \frac{P_i}{P_f}$

12. Work done during isothermal increase of pressure on a solid

$$W \approx \frac{kV}{2}(P_f^2 - P_i^2)$$

13. Work done during a quasi-static adiabatic process

$$W = \frac{1}{\gamma - 1}[P_f V_f - P_i V_i]$$

or $\quad W = \frac{nR}{\gamma - 1}(T_f - T_i)$

14. $W_{i \to f}$ (adiabatic) $= U_f - U_i$

15. First law of thermodynamics

$$U_f - U_i = Q + W$$

$$dU = \text{đ}Q + \text{đ}W \quad \text{Differential form}$$

16. Heat capacity

$$C = \frac{\text{đ}Q}{dT} \, JK^{-1}$$

17. Specific heat capacity

$$c = \frac{1}{m}\left(\frac{\text{đ}Q}{dT}\right) Jkg^{-1}K^{-1}$$

18. Molar heat capacity

$$c = \frac{1}{n}\left(\frac{\text{đ}Q}{dT}\right) Jmol^{-1}K^{-1}$$

19. Heat capacity at constant volume

$$C_V = \left(\frac{\text{đ}Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

20. Heat capacity at constant pressure

$$C_P = \left(\frac{\text{đ}Q}{dT}\right)_P$$

21. Heat in terms of C_P and C_V

$$Q = mc_V (T_f - T_i)$$

$$Q = mc_P (T_f - T_i)$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answwer questions in two or three sentences)

Short answer questions

1. What does thermodynamic deal with?
2. Define (i) system (ii) surroundings.
3. Define the following
   (i) open system (ii) closed system
   (iii) Isolated system.
4. Which are the two points of view adopted to study a system?

5. What is meant by macroscopic point of view?
6. What is meant by microscopic point of view?
7. What are macroscopic coordinates?
8. What are the properties of macroscopic coordinates?
9. What are the properties involved in the microscopic description of a system?
10. Define (i) Mechanical coordinates.
    (ii) Thermodynamic coordinates.
11. What is meant by equilibrium state of a system?
12. Define thermal equilibrium of a system.
13. Define thermal equilibrium of two systems separated by a diathermic wall.
14. What is an a diabatic wall? Give two examples.
15. What is a diathermic wall? Give an example.
16. State zeroth law of thermodynamics.
17. Define temperature.
18. Define triple point of water.
19. Write down the relation between real gas temperature (θ) and thermodynamic temperature (T).
20. What is the principle of ideal gas thermometer?
21. Draw the labelled diagram of constant volume gas thermometer.
22. What are the advantages of using helium in constant volume gas thermometer? Under what conditions.
23. Under what conditions the ideal gas temperature and real gas temperature coincide.
24. A thermodynamic system is said to undergo change when?
25. What is meant by mechanical equilibrium of a system?
26. What is meant by chemical equilibrium of a system?
27. When a system is said to be in thermodynamic equilibrium?
28. Define a non-equilibrium state.
29. What is an equation of state?
30. What is the limitation of equation of state?
31. Write down any two equations of state and explain the symbols.
32. What is a hydrostatic system?
33. Define average
    (i) coefficient of volume expansion
    (ii) isothermal bulk modulus.

34. What is meant by compressibility of a system? What is its unit?
35. What is the importance of coefficient of volume expansion?
36. What is the importance of isothermal compressibility in thermodynamics?
37. What are intensive and extensive variables?
38. Distinguish between external work done and internal work done.
39. Write down the sign convention of work in consistent with mechanics.
40. What is a quasi-static process?
41. Write down an expression for work done by an hydrostatic system.
42. What is a PV diagram?
43. What are the indications of PV diagram?
44. Define temperature.
45. Define heat.
46. Distinguish between work and heat
47. Define (i) adiabatic wall and (ii) diathermic wall.
48. What is meant by adiabatic work?
49. Distinguish between adiabatic work and thermodynamic work.
50. What is meant by internal energy of a thermodynamic system?
51. What is the relation between adiabotic work and internal energy function?
52. Distinguish between diathermic work and adiabatic work.
53. State first law of thermodynamics.
54. What are the significance of first law of thermodynamics?
55. Define thermodynamic heat.
56. What are the sign conventions used in connection with first law of thermodynamics?
57. Change of heat is an in exact differential. Justify.
58. Why it is meaningless to say heat in a body or work in a body?
59. Write down the differential form of first law for a quasi-static process of a hydrostatic system.
60. What is meant by heat capacity?
61. Define average heat capacity and heat capacity.
62. Define specific heat capacity. What is its unit?
63. Define molar heat capacity. What is its unit?
64. Define the specific heat of a gas at (i) constant pressure and (ii) constant volume.
65. Explain why $C_P > C_V$ for a gas.
66. Define 1 calorie of heat.

67. Define specific heat of water.
68. Show graphical variation of specific heat of water with temperature.
69. How to achieve quasi-static flow of heat?
70. What is a reservoir? Give two examples.

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. What are the properties of macroscopic coordinates and microscopic system?
2. Distinguish between macroscopic and microscopic points of view.
3. How equilibrium of two separate systems (X, Y) and (X′, Y′) be defined?
4. Establish the concept of temperature on the basis of zeroth law of thermodynamics.
5. Explain how do you check whether or not two beakers of water are in equilibrium using zeroth law of thermodynamics.
6. Explain an hydrostatic system and classify it.
7. Show that hydrostatic work depends on paths.
8. Derive an expression for work done during an isothermal process.
9. Derive an expression for work done during isothermal increase of pressure on a solid.
10. Derive an expression for work done during quasi-static adiabatic process.
11. Derive an expression for work done during quasi-static isobaric process.
12. Show that work done during a quasi-static isochoric process is always zero.
13. Distinguish between heat and work.
14. Show that adiabatic work done is equal to the change in internal energy.
15. For an ideal gas show that $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{kV}$ where k is the compressibility.
16. The equation of state of a Vander Waals gas is given as

$$\left(P+\frac{a}{v^2}\right)(v-b) = RT, \ v=\frac{V}{vn}$$

whre a, b and R are constants. Calculate

(a) $\left(\frac{\partial P}{\partial v}\right)_T$ (b) $\left(\frac{\partial P}{\partial T}\right)_V$

From parts a and b calculate $\left(\frac{\partial v}{\partial T}\right)_P$

17. (a) A block of copper at a pressure of 1 atm (10^5Pa) and a temperature of 5°C is kept at constant volume. If the temperature is raised to 10°C, what will be the final pressure (4.02 × 10^7Pa)

(b) If the vessel holding the block of copper has a negligible thermal expansivity and can withstand a maximum pressure of 1000 atm, what is the heighest temperature to which the system may be raised.

$\beta = 4.95\times10^{-5}\text{K}^{-1}$, $k = 6.17\times(10^{-12}(\text{Pa})^{-1}$ (17.45°C)

18. From the first law of thermodynamics show that $\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P.$

19. Assuming internal energy of a hydrostatic system is a function of T and P derive

$$\left(\frac{\partial U}{\partial P}\right)_T = PVk - (C_P - C_V)\frac{k}{\beta}.$$

20. Taking U to be a function of P and V show that $\left(\frac{\partial U}{\partial V}\right)_P = \frac{C_P}{V\beta} - P.$

Section C

(Answer question in about two pages)

Long answer type questions - essays

1. Explain how do you find ideal gas temperature using a constant volume gas thermometer.
2. Explain the electrical method of measuring heat capacity.
3. Starting from the quasistatic flow of heat explain how will you measure heat.

Hints to problems

15. Using $\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$ ..... (1)

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{k}$ from example 1 ..... (2)

From the definition of β, we have

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

or $\left(\frac{\partial V}{\partial T}\right)_P = \beta V$ ..... (3)

Substituting eqs 2 and 3, we get the result

16. We have $\left(P+\frac{a}{v^2}\right)(v-b)=RT$

$$P+\frac{a}{v^2}=\frac{RT}{v-b}$$

$$P=\frac{RT}{v-b}-\frac{a}{v^2}$$

a) Differentiate with respect to v, keeping T constant

$$\left(\frac{\partial P}{\partial v}\right)_T=-\frac{RT}{(v-b)^2}-\frac{2a}{v^3}$$

b) Differentiate with respect to T, keeping v constant

$$\left(\frac{\partial P}{\partial T}\right)_v=\frac{R}{v-b}$$

Using $\left(\frac{\partial P}{\partial T}\right)_v\cdot\left(\frac{\partial T}{\partial v}\right)_P=-\left(\frac{\partial P}{\partial v}\right)_T$

$$\left(\frac{\partial P}{\partial v}\right)_P=+\frac{\frac{RT}{(v-b)^2}-\frac{2a}{v^3}}{R/v-b}$$

$$\left(\frac{\partial T}{\partial v}\right)_P=\frac{T}{(v-b)}-\frac{2a(v-b)}{Rv^3}$$

Usually product ab is negligibly small

$$\left(\frac{\partial T}{\partial v}\right)_P=\frac{T}{v-b}-\frac{2a}{v^2R}$$

$$\left(\frac{\partial T}{\partial v}\right)_P=\frac{v^2RT-2a(v-b)}{(v-b)\,v^2R}$$

$$\left(\frac{\partial T}{\partial v}\right)_P=\frac{v^2RT-2aV}{(v-b)\,v^2R}$$

Inverting we get the required result.

17. a) Use $P_f-P_i=\frac{\beta}{k}(T_f-T_i)$, get the result

b) $$\frac{\beta}{k} = \frac{4.95 \times 10^{-5}}{6.17 \times 10^{-12}} = 80.23 \times 10^{5}\,\text{Pa}$$

$$(1000 - 1) = 80.23(T_f - 278)$$

$$T_f - 278 + \frac{999}{80.23} = 12.45$$

$$T_f = 278 + 12.45 = 290.45$$

$$T_f = 17.45^{\circ}\text{C}$$

18. From example 12, we have

$$\text{đ}Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial U}\right)_T dV + PdV$$

Dividing throughout by dT keeping P constant

$$\left(\frac{\text{đ}Q}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_P + P\left(\frac{dV}{dT}\right)_P$$

i.e., $$C_P = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P)\right)\left(\frac{dV}{dT}\right)_P \qquad \text{..... (1)}$$

From the definition β

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting for $\left(\frac{\partial V}{\partial T}\right)_P$ in eq (1) we get

$$C_P = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\beta V$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P$$

19. See example 14, only a slight change

20. See example 15, only slightly different.

UNIT TWO

IDEAL GAS

Equation of state of a gas

In unit 1 we could see that to measure temperature precisely gas thermometer was chosen as the standard reference. This is because gas as the working substance of thermometer is far superior than mercury or platinum as the working substance. When we use mercury or platinum as the working substance of a thermometer, depending upon the quality, purity and impurity different thermometers show different temperatures. When gas is used as the working substance, in the limiting case $\underset{P_{TP}\to 0}{Lt}\frac{P}{P_{TP}}$, it approaches a value independent of the nature of the gas. To measure temperature we used the equation

$$T = 273.16 \underset{P_{TP}\to 0}{Lt}\frac{P}{P_{TP}} \qquad \text{..... (1)}$$

It shows that whatever be the gas that we used in gas thermometers measurement is independent of the nature of the gas and gives the same value. By studying the above said behaviour of the gas experimentally in a different ways, we can arrive at the equation state of ideal gas which is the aim of this section.

Consider n moles of real gas system. Keeping its temperature constant measure the pressure P and volume V over a wide range of values. It has been found the relation between $P\upsilon\left(\upsilon = \frac{V}{n}\right)$ and P may be expressed as a power series of the form

$$P\upsilon = A(1 + BP + CP^2 + DP^3 + ...) \qquad \text{..... (2)}$$

This series expansion is called virial expansion and the constants A, B, C, D..... etc. are called first, second, third, fourth .... etc. virial coefficients respectively. The virial coefficients depend on the temperature and on the nature of the gas. It is seen experimentally that when pressure changes from 0 to 40 atm, the relation between $P\upsilon$ and P is linear, hence virial expansion becomes

$$P\upsilon = A(1 + BP)$$

When pressure goes to higher ranges of values large number of virial coefficients will come into play.

The virial expansion gives us a very important property exhibited by the gas. To see this draw a graph between pressure on the horizontal axis and $P\upsilon$ along the vertical axis at a constant temperature for various gases. A typical graph of $P\upsilon$ versus P at boiling point of water (constant) for various gases O_2, air, N_2 and H_2 are drawn in figure below.

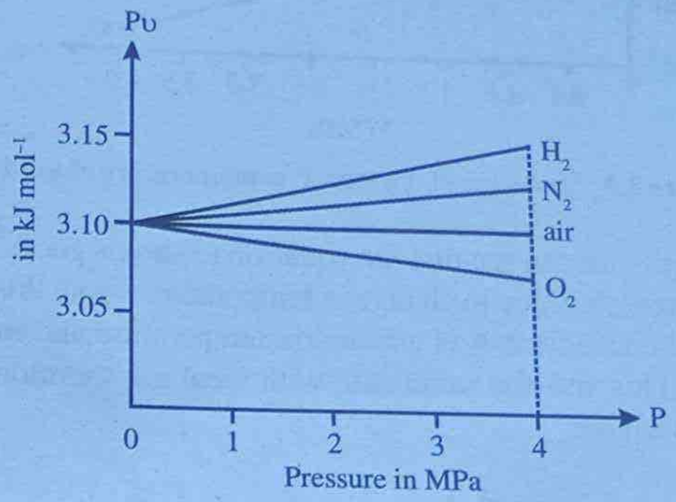


Figure 2.1 : Variation of $P\upsilon$ with P at boiling point of water

From the graph it is seen that for all gases as the pressure approaches zero, the product $P\upsilon$ approaches the same value.

Now the virial expansion becomes

$$\underset{P\to 0}{\mathrm{Lt}}\,(P\upsilon) = A \qquad \text{..... (3)}$$

Where all other terms goes to zero since P goes to zero. The value of A is 3.10 kJ mol^{-1}. It shows that A is same for all gases in other words A is independent of the nature of the gases. Now repeat the same experiment for the same four gases but at different temperatures say one graph at triple point of water another at temperature at solid CO_2. Two graphs are given between.

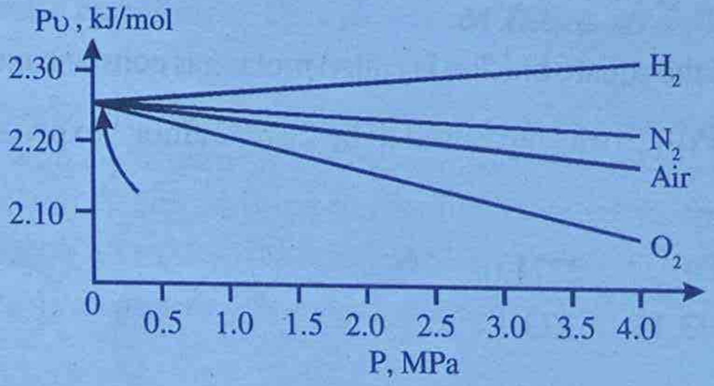


Figure 2.2 : Variation of $P\upsilon$ with P at triple point of water

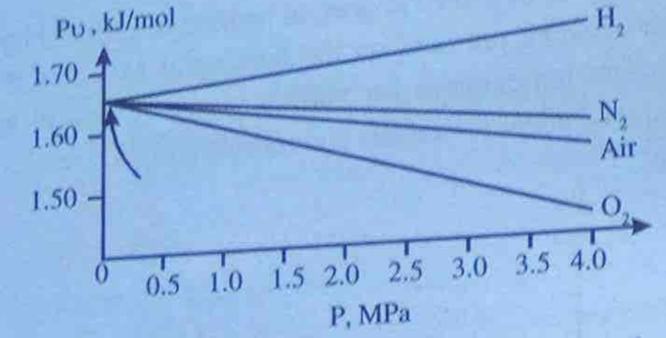


Figure 2.3 : Variation of $P\upsilon$ with P at temperature of solid CO_2

In all three graphs we can see that the equation (3) holds good. In each graph the value of A is different. It is due to change in temperature. From this we can conclude that the first virial coefficient A is a function temperature and independent of the nature of the gas. This was the same case with ideal gas thermometer. From ideal gas temperature, we have

$$T = 273.16 \underset{P_{TP}\to 0}{Lt}\left(\frac{P}{P_{TP}}\right) \text{ at constant volume V.}$$

Rewriting this equation as

$$T = 273.16 \underset{P_{TP}\to 0}{Lt}\left(\frac{P\upsilon}{P\upsilon_{TP}}\right)$$

or

$$T = 273.16 \frac{Lt_{P_{TP}\to 0}(P\upsilon)}{Lt_{P_{TP}\to 0}(P_{TP}\upsilon)}$$

$$\therefore \quad Lt_{P_{TP}\to 0}\,(P\upsilon) = \frac{Lt(P_{TP}\upsilon)}{273.16}T \qquad \text{..... (4)}$$

The term inside the square bracket is called molar gas constant and is denoted by R.

The value of $(P\upsilon)_{0^\circ C}$ was measured to be 227.02 $Jmol^{-1}$ experimentally for oxygen

Thus we get $\frac{(P\upsilon)_{0^\circ C}}{273.15} = \frac{2271.02}{273.15}$

$$= 8.314\,Jmol^{-1}K^{-1}$$

This is the value molar gas constant. Now equation 4 becomes

$$\text{Lt}\,(P\upsilon) = RT \qquad \text{..... (5)}$$

That is we evaluated the virial coefficient A.

$$A = RT$$

or

$$\text{Lt}\; P\frac{V}{n} = RT$$

$$\text{Lt}\; PV = nRT$$

i.e., in the limit of low pressures, we have

$$PV = nRT \qquad \text{..... (6)}$$

This is the equation state of an ideal gas.

Putting the value of A in the virial expansion, we get

$$P\upsilon = RT\,(1 + BP + CP^2 + ...)$$

or

$$\frac{P\upsilon}{RT} = 1 + BP + CP^2 + ... \qquad \text{..... (7)}$$

This plays an important role in theoretical and experimental realm of thermodynamics.

Note : It must be remembered that at low pressures real gases behave like ideal gases.

Internal energy of a real gas

In this section our aim is to find the dependence of internal energy on temperature and pressure. For this we have to perform a free expansion experiment.

Free expansion

When a fixed mass of gas is allowed to expand without doing any external work under adiabatic conditions. This process is called adiabatic free expansion.

For example consider a thermally insulated vessel with rigid walls divided into two compartments with a partition wall. One compartment is filled with gas other compartment is vacuum. If the partition is removed, the gas under goes adiabatic free expansion in which no work is done and no heat is transferred.

According to first law of thermodynamics we have

$$U_f - U_i = Q + W$$

In the adiabatic free expansion $Q = 0$ and $W = 0$ implies $U_f - U_i = 0$ i.e., in free expansion there is no change in internal energy. Then what happens to temperature and pressure. First experimental attemp in this was made by Joule in 1843. He tried to measure $\left(\frac{\partial T}{\partial V}\right)_V$ which is called the Joule coefficient. Joule coefficient tells us how does the temperature of system change with volume during adiabatic free expansion.

Joules experiment

Experimental arrangement consists of two flasks A and B connected by a tube and fitted with a stop cock S as shown in figure below. A was filled with a gas at higher pressure and B was perfectly evacuated. The whole system was immersed in a water bath. The temperature of water bath was measured with a sensitive thermometer. The stop-cock was opened and the gas rushed from A to B. The temperature of water bath was again measured.

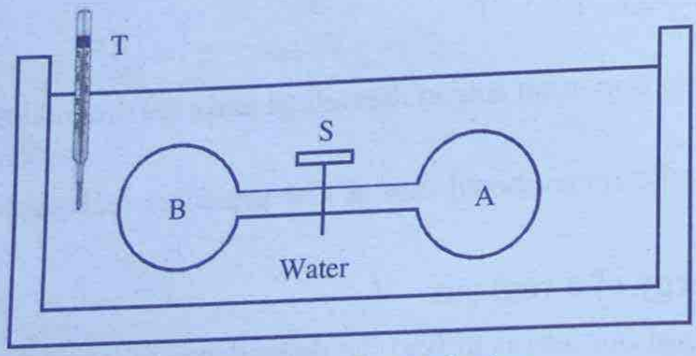


Figure 2.4 : Joules experimental setup

The idea was to measure the drop in temperature of the gas by measuring the temperature of water bath. Since the pressure and volume of the gas change normally we expect a drop in temperature. But in this experiment no temperature drop was measured. Joule could point out the draw back of his experiment and the difficulty in measuring $\left(\frac{\partial T}{\partial V}\right)_V$ · Thus a new method was suggested, instead of measuring a temperature change during free expansion for which the internal energy is constant, consider measuring a change of internal energy at constant temperature.

We know that internal energy U is a function of any two of the three thermodynamic coordinates P, V and T.

If U is a function of (T, V), we have

$$U = U(T, V)$$

Taking differentials, we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

When no temperature change ($dT = 0$) occurs in free expansion ($dU = 0$)

We get $$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad ..... (8)$$

It shows that U is independant of volume

If we consider U is a function of T and P

$$U = U(T, P)$$

Then $$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

When there is no temperature change ($dT = 0$) occurs in free expansion in which $dU = 0$, we get

$$\left(\frac{\partial U}{\partial P}\right) = 0 \cdot \qquad ..... (9)$$

It shows that U is independent of pressure. Clubbing the statements of the two equations 8 and 9 U is independent of V and P. Therefore U is a function of T only.

Now we have to conduct an experiment to prove that U is a function of temperature only. In this experiment we want to verify that

$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$ at constant temperature.

Experimental setup

This experiment was firstly conducted by Rossini and Frandsen in 1932 after 90 years of Joules experiment.

The experimental arrangement consists of a bottle B containing n moles of gas at pressure P. The gas communicates with the atmosphere through a long coil wrapped around the bottle as shown in figure. The whole apparatus is immersed in water bath whose temperature is maintained constant at exactly the same value as that of the surroundings.

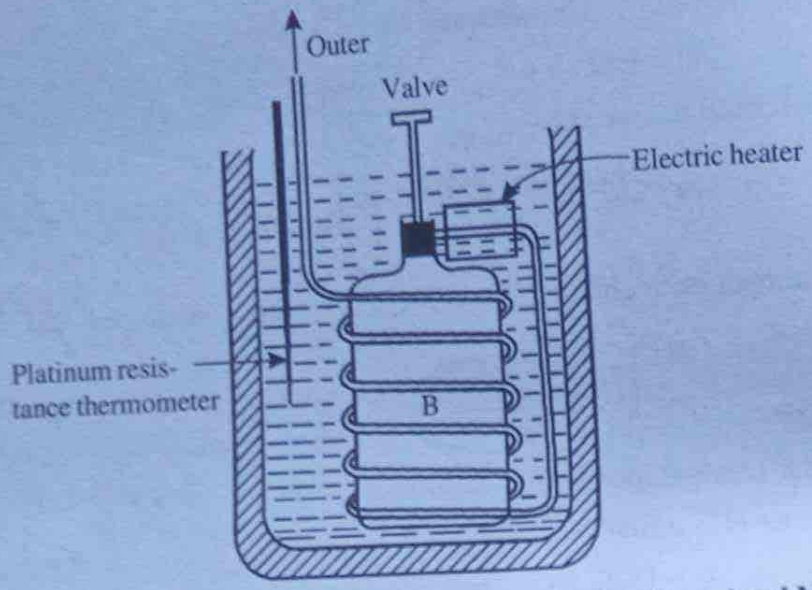


Figure 2.5 : Apparatus for measuring $(\partial u/\partial P)_T$ of a gas. (F.D. Rossini and M Frandsen)

To begin the experiment the valve attached to the bottle is opened slightly. The gas will escape to air slowly through the coil. At the same time the temperature of the gas, the bottle, the coils and the water is maintained constant by an electric heating coil immersed in the water. The electrical energy supplied to the water is equal to the heat Q absorbed by the gas during the expansion. The work done by the gas is (whole gas is leaked out)

$$W = -PdV$$

i.e.,
$$W = -P_0(n\upsilon_0 - V)$$

where P_0' is the atmospheric pressure, υ_0 is molar volume at atmospheric pressure and temperature and V is the volume of the bottle.

If u(P, T) is the molar energy at pressure P and temperature T and if $u(P_0, T)$ is the molar internal energy at atmospheric pressure and the same temperature. Using firs law of thermodynamics

$$U_f - U_i = Q + W$$

i.e.,
$$nu(P, T) - nu(P_0, T) = Q + W$$

or
$$u(P, T) - u(P_0, T) = \frac{Q+W}{n}$$

The change in internal energy Δu for various values of P are measured. A graph is plotted between Δu on the vertical axis and P on the horizontal axis, a straight line graph gas obtained as shown in figure below. Since $u(P_0, T)$ is a constant, the slope of the resulting curve is equal to $\left(\frac{\partial u}{\partial P}\right)_T$, at any value of P. Within the pressure change of 1 to 40 standard atmospheres the slope $\left(\frac{\partial u}{\partial P}\right)_T$ is the same for all pressures. It shows that $\left(\frac{\partial u}{\partial P}\right)_T$ is independent of the pressure, depending only on the temperature. Thus, we have $\left(\frac{\partial u}{\partial P}\right)_T = f(T)$. This implies that u is a function of both pressure and temperature. The experiments were repeated for various gas such as air, oxygen, and mixtures of oxygen and carbondioxide they obtained the same result.

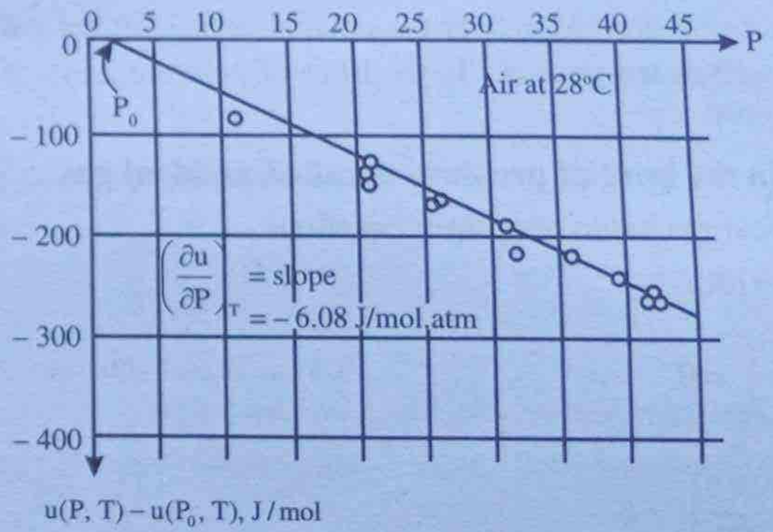


Figure 2.6 : Dependence of change of molar internal energy of a real gas on pressure, where P_0 is atmospheric pressure

They also found no pressure or temperature range in which $\left(\frac{\partial U}{\partial P}\right)_T = 0$

i.e., $\left(\frac{\partial U}{\partial P}\right)_T \neq 0$

writing $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial V}\right)_T$

For free expansion at constant temperature $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$ and we proved that $\left(\frac{\partial U}{\partial P}\right)_T \neq 0\cdot$

The above equation shows that $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. For a real gas $\left(\frac{\partial U}{\partial P}\right)_T \neq 0$ and $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$ For a perfect gas we will prove that $\left(\frac{\partial U}{\partial P}\right)_T = 0$ and $\left(\frac{\partial U}{\partial V}\right)_T = 0$

At the same time we know that a real gas behaves like an ideal gas in the limit of pressure. In our experiment since limiting pressure is not reached the gas behaved as such.

Ideal gas

We found that a real gas whose pressure $P \rightarrow 0$, the equation of state assumes a simple form $PV = nRT$. Moreover the internal energy of real gas is a function of pressure as well as temperature. In the limit of pressure, U is only a function of temperature only.

A real gas in the limit of pressure is called an ideal gas

Thus an ideal gas has to obey three equations

(i) $PV = nRT$

(ii) $\left(\frac{\partial U}{\partial P}\right)_T = 0$

(iii) and $\left(\frac{\partial U}{\partial V}\right)_T = 0$

The third equation follows from equation (ii).

i.e.,
$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

For an ideal gas

$$PV = nRT$$

Differentiating the above with respect to V, keeping T constant, we get

$$P + V\left(\frac{\partial P}{\partial V}\right)_T = 0$$

or $$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$$

since $\left(\frac{\partial U}{\partial P}\right)_T = 0$ and $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$, we can very well write $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

From (ii) and iii, we can write

(iv) $U = f(T)$ only

Note: Limiting pressure means very low pressure.

Ideally $P \to 0$. Pressure is very low even at about 2 atmospheres real gas behaves like ideal gas without much error.

Mayers relation

Consider an hydrostatic system (ideal) which undergoes an infinitesimal quasi-static process, according to first law.

$$đQ = dU + PdV \qquad \text{.....}(10)$$

Using $$\left(\frac{\partial P}{\partial T}\right)_V = C_V$$

For ideal gas U is a function of only T.

i.e., $$\frac{dU}{dT} = C_V$$

or $$dU = C_V dT$$

Now equation 10 becomes

$$đQ = C_V dT + PdV \qquad \text{.....}(11)$$

From the ideal gas equation, we have

$$PV = nRT$$

For infinitesimal quasi-static process

$$PdV + VdP = nRdT$$

or $$PdV = nRdT - VdP$$

put this in equation 11, we get

$$đQ = C_V dT + nRdT - VdP \qquad \text{..... (12)}$$

Dividing by dT,

$$\frac{đQ}{dT} = C_V + nR - V\frac{dP}{dT}$$

At constant pressure

$$\left(\frac{đQ}{dT}\right)_P = C_V + nR$$

By definition

$$\left(\frac{đQ}{dT}\right)_P = C_P$$

$\therefore$ $$C_P = C_V + nR$$

or $$C_P - C_V = nR \qquad \text{..... (13)}$$

This is called Mayers relation. The equation 13 tells us that C_P is always greater than C_V. This is because when heat is supplied to a gas and allowed to expand at constant pressure heat is used for two purposes.

(i) It raises the temperature of the gas (i.e., increase in internal energy) and

(ii) it does work in expanding the gas against the external pressure we have

$$đQ = dU + PdV.$$

On the other hand, when gas is heated at constant volume, no work is done (i.e., $đW = 0$) and hence whole of heat supplied is used to raise its temperature.

i.e., $$đQ = dU = C_V dT$$

Thus $C_P > C_V$

One more useful equation can be obtained from equation 12

i.e., $$đQ = C_V dT + nRdT - VdP$$

or $$đQ = (C_V + nR)dT - VdP$$

From Mayers relation

$$C_P - C_V = nR$$

or $$C_P = C_V + nR$$

$\therefore$ $$đQ = C_P dT - VdP \qquad ..... (14)$$

Experimental determination of heat capacities

Heat capacities of real gases are usually measured by the electric method.

Measurement of C_V

The gas whose C_V to be measured is taken in a thin walled steel flask with a heat ing coil wound around it. Measure the initial temperature of the gas as T_i by a sensitive thermometer. Pass a suitable current I for a time t.

The heat supplied by the heat coil. Q = VIt, where V is the potential difference given to the heating coil. This heat is transferred to the gas and temperature of the gas rises. Let it be T_f. The heat absorbed by the gas is

$$Q = C_V(T_f - T_i)$$

Using law of conservation of energy we have $VIt = C_V(T_f - T_i)$

$\therefore$ $$C_V = \frac{VIt}{(T_f - T_i)}$$

knowing V, I, t and $T_f - T_i$, C_V can be calculated.

To measure C_P the gas is allowed to flow at constant pressure through a calorimeter where it receives heat (VI) per second. From the initial (inlet) and the final (outlet) temperatures the value of C_P can be calculated as before. Use C_P instead of C_V.

Since the measurements are done at low pressure C_P and C_V measured are those of ideal gas. The following may be worth noting.

1. For all ideal gases
   a) C_V is a function of T
   b) C_P is a function of T
   c) $C_P > C_V$
   d) $C_P - C_V = R$, independent of T

e) $\frac{C_P}{C_V} = \gamma$ is a function of T and greater than 1

2. For a monatomic gases such as He, Ne and Ar

   a) C_V is constant over a wide range of temperature and its value $C_V = \frac{3}{2}R$ (nearly)

   b) C_P is constant over a wide range of temperature and its value $C_P = \frac{5}{2}R$ (nearly)

   c) $\frac{C_P}{C_V} = \gamma$ is constant over a wide range and is nearly equal to $\frac{5}{3}$.

3. For diatomic gases such as air, H_2, O_2, N_2, NO, CO etc.,

   a) $C_V = \frac{5}{2}R$, constant for ordinary temperatures and increases as the temperature is raised

   b) $C_P = \frac{7}{2}R$, constant at ordinary temperatures and increases as the temperature is raised.

   c) $\frac{C_P}{C_V} = \frac{7}{5}$, constant at ordinary temperatures and decreases as the temperature is raised.

4. For polyatomic gases such as CO_2, NH_3, CH_4, Cl_2, Br_2 etc. C_P, C_V and $\frac{C_P}{C_V}$ vary with temperature, the variation is different for each gas.

Note: The behaviour of H_2 is exceptional. H_2 is diatomic hence $C_P = \frac{7}{2}R$. But very low temperature $C_P = \frac{5}{2}R$ i.e., behaves like monatomic gas. For all diatomic gases except hydrogen, $\frac{C_P}{R}$ can be written as

$$\frac{C_P}{R} = \frac{7}{2} + f(T)$$

form of f(T) is $\left(\frac{b}{T}\right)^2 \frac{e^{b/T}}{(e^{b/T}-1)^2}$

Quasi-static adiabatic process

When an ideal gas undergoes a quasi-static adiabatic process pressure P, volume V and temperature T may change. But to write down equation of state we require only any two combinations (P, V), (T, V) and (P, T).

Equation of state

Recall equation 11 and 14

$$đQ = C_V dT + PdV$$

$$đQ = C_P dT - VdP$$

In an adiabatic process $đQ = 0$

$\therefore$ $$C_V dT = -PdV \qquad \text{..... (15)}$$

and $$C_P dT = -VdP \qquad \text{..... (16)}$$

$\frac{\text{Eq 16}}{\text{Eq 15}}$ gives $$\frac{C_P}{C_V} = -\frac{VdP}{PdV}$$

or $$\gamma = -\frac{VdP}{PdV}$$

or $$\frac{\gamma dV}{V} = -\frac{dP}{P}$$

The equation cannot be integrated as γ depends on temperature. But most of the adiabatic processes temperature change is moderate. Assume that γ is constant and integrate, we get

$$\gamma \ln V = -\ln P + C$$

or $$\ln P + \ln V^\gamma = C$$

$$\ln PV^\gamma = C$$

or $$PV^\gamma = \text{constant} \qquad \text{..... (17)}$$

This is the equation of state of a quasi-static adiabatic process in terms of P and V

Equation of state in terms of P and T

We have $PV = nRT$

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

Putting this in equation 17, yields

$$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant}$$

or $$\frac{T^{\gamma}}{P^{\gamma-1}} = \text{constant}$$

or $$\frac{P^{\gamma-1}}{T^{\gamma}} = \text{constant} \qquad \text{..... (18)}$$

Equation of state in terms of T and V

From $PV = nRT$

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

Put this in equation 17, yields

$$\frac{nRT}{V}V^{\gamma} = \text{constant}$$

or $$TV^{\gamma-1} = \text{constant} \qquad \text{..... (19)}$$

Note: It may be noted that an adiabatic free expansion process is not quasistatic, hences equations 17, 18 and 19 are not valid for this process.

Slopes of adiabatics and isothermals

In an isothermal process

$PV = \text{a constant}$

Taking the differential an both sides we get

$PdV + VdQ = 0$

or $$\frac{dP}{dV} = -\frac{P}{V}$$

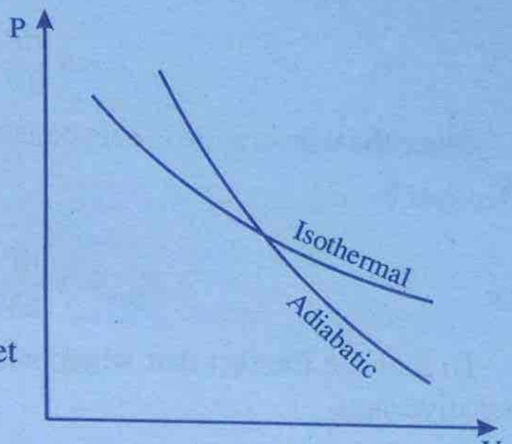


Figure 2.7

$\frac{dP}{dV}$ is the slope

i.e., $$\left(\frac{dP}{dV}\right)_{iso} = -\frac{P}{V}.$$

In an adiabatic process

PV^{γ} = a constant

Taking the differential on both sides, we get

$$P\gamma V^{\gamma-1}dV + V^{\gamma}dP = 0$$

or $$\frac{dP}{dV} = -\frac{\gamma P}{V}$$

i.e., $$\left(\frac{dP}{dV}\right)_{adi} = -\frac{\gamma P}{V}$$

Comparing the slopes of isothermal and adiabatic, we get

$$\left(\frac{dP}{dV}\right)_{adi} = \gamma\left(\frac{dP}{dV}\right)_{iso}$$

i.e., slope of adiabatic is γ times the slope of the isorthermal. Hence adiabatic curve is steeper than the isothermal cure. See figure above

Isothermal and adiabatic elasticity of a gas

Isothermal elasticity (E_{iso})

Suppose we have a certain mass of gas enclosed in a cylinder of a perfectly conducting material, fitted with a piston of the same material, so that its temperature throughout remains constant. Let its volume be V and its pressure P.

Now let the pressure P be increased slightly to P + dP, so that the volume of the gas is reduced to $V - dV$

Stress applied by the gas $= dP$

Strain produced $= \frac{\text{change in volume}}{\text{original volume}} = \frac{dV}{V}$

$\therefore$ Elasticity $= \frac{\text{stress}}{\text{strain}} = \frac{\frac{dP}{dV}}{V}$

$$= V\frac{dP}{dV}$$

Since the temperature is kept constant here, it is called isothermal elasticity and is denoted by E_{iso}

i.e. $$E_{iso} = V\frac{dP}{dV}$$

To indicate the fact that when pressure increases the volume deceases we put a negative sign.

$$\therefore \quad E_{iso} = -V\frac{dP}{dV} \qquad \text{..... (20)}$$

For an isothermal process, we have

$$PV = K$$

Taking differentials on both sides, we get

$$PdV + VdP = 0$$

or $$P = -V\frac{dP}{dV}$$

Thus $$E_{iso} = P \qquad \text{..... (21)}$$

This shows that isothermal elasticity of a gas is equal to its pressure.

Adiabatic elasticity (E_{adi})

We have $$E = -V\frac{dP}{dV}$$

Suppose the system undergoes an adiabatic process, then the elasticity is called adiabatic elasticity.

i.e. $$E_{adi} = -V\frac{dP}{dV}$$

During an adiabatic process, we have

$$PV^{\gamma} = K$$

Taking differentials on both sides, we get

$$P\gamma V^{\gamma-1}dV + dPV^{\gamma} = 0$$

Dividing throughout by $V^{\gamma-1}$, we get

$$P\gamma dV + dPV = 0$$

or
$$-V\frac{dP}{dV} = \gamma P$$

$\therefore$
$$E_{adia} = \gamma P \qquad \text{..... (22)}$$

This shows that adiabatic elasticity of a gas is equal to γ times its pressure.

Comparing eq (21) and eq (22) we get

$$E_{adi} = \gamma E_{iso} \qquad \text{..... (23)}$$

The reason for $E_{adia} > \gamma E_{iso}$ is that for similar change in pressure dP, there is a larger change in volume for the adiabatic process.

The microscopic point of view

Here we discuss the limitations of classical thermodynamics based on macroscopic point of view and need for microscopic point of view.

The first law of thermodynamics which is the relation connecting between work, heat and internal energy. This can be applied to class of systems such as solids, liquids, vapours, mixture of substances etc. The solution of the first law does not give properties of a particular system. For example we measure C_V of a system given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

This is true for all hydrostatic systems. If we know the internal energy we can calculate C_V, where C_V is a function of T and V. Thus the heat transferred during an isochoric process is

$Q_V = \int_{T_i}^{T_f} C_V dT$, provided C_V is known. But in classical thermodynamics nothing provides detailed information of U and C_V. This one of the major limitations.

Another limitation is that classical thermodynamics is unable to provide the equation of state of any desired system. To have an equation of state involving P, V, T and the derivatives $\left(\frac{\partial P}{\partial V}\right)_T$, $\left(\frac{\partial V}{\partial T}\right)_P$ and $\left(\frac{\partial T}{\partial P}\right)_V$ are required. These values must come from the experimental results. For each system we have to conduct experiments to evaluate those derivatives. Experimental datas for all systems are not available.

So to obtain informations regarding thermal properties of system without having to experimental measurements we go for analysing the system at microscopic level. We require calculations based on the properties and behaviour of particles of the system. There are two such theories developed. One is the kinetic theory and the other one is statistical mechanics. Using laws of mechanics and statistics kinetic theory deals with the average motion of particles and their collisions in order to calculate the equation of state for the ideal gas. But statistical mechanics deal with average value of energy of particles or ensemble of particles. Once the energy is obtained we can develop equation of state and thermodynamic variables and functions.

Kinetic theory of ideal gas

Here our aim is to formulate a microscopic theory of ideal gases limited to monatomic gases. To develop the theory several assumptions are made. The assumptions are called postulates.

Postulates of kinetic theory of gases

1. Any sample of gas consists of an enormous number of atoms N. For any gas all atoms are identical and inert. If m is the mass of each atom, the total mass is mN. If M be the molar mass, then the number of moles $n = \frac{Nm}{M}$. The number of atoms per mole is $\frac{M}{m} = \frac{N}{n}$ is called Avagadro's number denoted N_A. It value is calculated by Avagadro and is given by $N_A = 6.0221 \times 10^{23}$ atoms/mole.
2. The atoms are assumed to be small hard spheres and they are in ceaseless random motion. The average distance between neighbouring atoms is large compared to the size of the atom.

For example the size of the atom is of the order of 2 or 3×10^{-10} m. The average distance between atoms is about 50 times diameter under standard pressure and temperature.

3. It is due to the large distance between atoms it is also assumed that there are no interatomic force of attraction or repulsion between atoms. Forces come into play only when atoms collide with one another and also with walls. Between collisions they move with uniform rectilinear motion.

4. The walls of the container is assumed to be smooth and the collision is assumed to perfectly elastic. If v is the speed of an atom approaching a wall, the perpendicular component $v_\perp$ is retraced back with same velocity, therefore total change in velocity is $-2v_\perp$
5. When there is no external field of force, the atoms are distributed uniformly throughout the system. So that the number density $\frac{N}{V}$ is a constant. In any small element of volume dV, there are dN atoms, where

$$\frac{dN}{dV}=\frac{N}{V} \text{ or } dN=\frac{N}{V}dV$$

The infinesimal dV must satisfy two conditions of infinetismal in thermodynamics. dV must be small compared to V and large enough to make dN a large number.

6. Since the motion of atom is random there is no preferred direction for the velocity. All directions are equally probable.
7. Atoms moves with different speed varying from 0 to any value.

With these assumptions we can arrive at an interpretation for temperature in terms of kinetic energy

Consider cubical box ABCDEFGH of side l contains certain amount of ideal gas. The volume of the gas is l^3. Let m and N represent the mass of each atom and number of atoms respectively present in the box.

Consider an atom p moving in a random direction with a velocity c_1. This velocity can be resolved in to three components u_1, v_1 and w_1 along the X, Y and Z axis respectively (see figure).

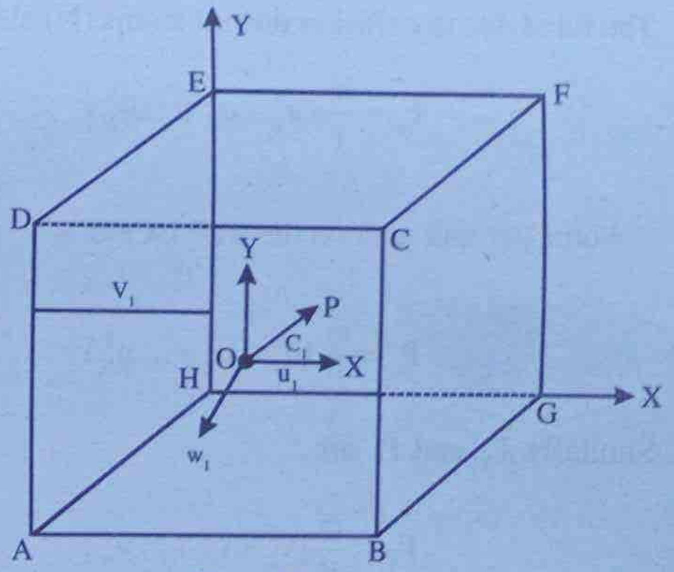


Figure 2.8

$$\therefore \qquad c_1^2=u_1^2+v_1^2+w_1^2$$

The velocity with which the atom P strikes the face BCFG is u_1 and the corresponding momentum is mu_1. It is due to elastic collision the atom is reflected with the same momentum.

The change in momentum due to the impact of collision

$$= mu_1 - (-mu_1) = 2mu_1$$

The atom reflected from BCFG travels a distance l towards ADEH strikes on this wall again reflected back to hit on BCFG. The total distance travelled by the atom when it collides with the wall BCFG is $2l$.

$\therefore$ The time interval between two successive collisions on the wall BCFG is

$$= \frac{\text{dis tan ce}}{\text{speed}} = \frac{2l}{u_1}$$

$\therefore$ Number of collisions per second $= \dfrac{1}{\dfrac{2l}{u_1}} = \dfrac{u_1}{2l}$

$\therefore$ Change in momentum produced in 1 second = $2mu_1 \cdot \dfrac{u_1}{2l} = \dfrac{mu_1^2}{l}$

The force due to collision due all atoms (N) along the X-direction is

$$F_x = \frac{m}{l}(u_1^2 + u_2^2 + ...u_N^2)$$

$\therefore$ Force per unit area on the wall BCFG is $P_x = \dfrac{F_x}{l^2}$

or $$P_x = \frac{m}{l^3}(u_1^2 + u_2^2 + ...u_N^2)$$

Similarly P_Y and P_Z are

$$P_Y = \frac{m}{l^3}(v_1^2 + v_2^2 + ...v_N^2)$$

and $$P_Z = \frac{m}{l^3}(w_1^2 + w_2^2 + ...w_N^2)$$

As the pressure is same in all directions the average pressure is

$$P = \frac{P_X + P_Y + P_Z}{3}$$

i.e., $P = \frac{m}{3l^2}\left[(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) + \ldots\ (u_N^2 + v_N^2 + w_N^2)\right]$

$$P = \frac{m}{3l^2}\,(c_1^2 + c_2^2 + c_n^2) \qquad \text{..... (24)}$$

Let c be the root mean square velocity of the atoms

$$c^2 = \frac{c_1^2 + c_2^2 + \cdots c_N^2}{N}$$

or

$$Nc^2 = c_1^2 + c_2^2 + \cdots c_N^2$$

Put this in equation 24 we get

$$P = \frac{m}{3l^2}\,Nc^2$$

or

$$P = \frac{mNc^2}{3V} \qquad (\because \quad l^3 = \text{volume})$$

or

$$PV = \frac{1}{3}mNc^2 \qquad \text{..... (25)}$$

From the experimental results of thermodynamics, we deducted the equation of state of ideal gas given by

$$PV = nRT \qquad \text{..... (26)}$$

Comparing equations 25 and 26, we get

$$nRT = \frac{1}{3}mNc^2 \qquad \text{..... (27)}$$

r

$$T = \frac{mN}{nR}\frac{1}{3}c^2$$

This can be re-written as

$$T = \frac{2N}{3R}\left(\frac{1}{2}mc^2\right) \qquad \text{..... (28)}$$

$\frac{1}{2}mc^2$ is the average kinetic energy of the atoms. Thus we have

$$\text{kinetic energy} \propto T$$

It provides an interpretation of temperature on the basis of kinetic theory. In kinetic theory of gases we assumed that there are no inter atomic forces. Hence particles posses no potential energy. So the entire energy is kinetic. Moreover we also assumed that atoms are in rectilinear motion. Thus this energy is purely translational kinetic energy. The monatomic gas possesses no rotational or vibrational energies. Therefore the internal energy (U) of a monatomic gas is the sum of the kinetic energies of all atoms.

i.e.,
$$U = \sum_i \frac{1}{2} m_i c_i^2$$

or
$$U = \frac{Nm}{2} \sum_i c_i^2$$

$$U = N\frac{1}{2} m \sum_i c_i^2 = N\frac{1}{2} mc^2$$

Substituting for $\frac{1}{2}mc^2$ from equation 27, we get

$$U = \frac{N}{2}\frac{3nRT}{N}$$

or
$$U = \frac{3n}{2}RT \qquad \text{..... (29)}$$

It shows that internal of ideal gas is proportional to temperature only which is in agreement with experimental results.

From equation 29 we can calulate C_V and C_P.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR \qquad \text{..... (30)}$$

Using $C_P - C_V = nR$

$$C_P - \frac{3}{2}nR = nR$$

or $$C_P = \frac{5}{2} nR \qquad \text{..... (31)}$$

Equations 30 and 31 show that C_V and C_P are independent of temperature.

Using $n = \frac{N}{N_A}$, the equation can be written as

$$U = \frac{3}{2} \frac{N}{N_A} RT$$

The term $\frac{R}{N_A} = 1.3807 \times 10^{-27} \, JK^{-1}$ is called Boltzmann's constant denoted by k.

$$U = \frac{3N}{2} kT \qquad \text{..... (32)}$$

∴ Average kinetic per atom is

$$\frac{U}{N} = \frac{3}{2} kT$$

or $$\frac{1}{2} mc^2 = \frac{3}{2} kT$$

∴ The rms velocity $c = \sqrt{\frac{3kT}{m}}$ ..... (33)

Note : In the case of diatomic and poly atomic gases they possess rotational and vibrational kinetic energies in addition to translational kinetic energy. As there is no interaction, potential energy is zero.

In general $U = \frac{nRT}{\gamma - 1}, \gamma = \frac{C_P}{C_V}$

The ideal gas equation PV = nRT is not obeyed by real gases, particularly at high pressures and low temperatures. In the derivation of the ideal gas equation on the basis of kinetic theory of gases two assumptions that have been made which do not hold good in case of real gases. They are (i) atoms are point masses and (ii) there are no interatomic forces. But in actual practice, at high pressure size of the atom becomes significant and cannot be neglected in comparison with the volume of the gas. Also at high pressure the atoms comes closer and interatomic forces are appreciable. Hence ideal gas equation needs modification. So in 1881, Vander Waal proposed an equation of state that accounted for the finite volume of the atoms and interaction between the atoms. The Vander Waals equation of state is

$$\left(P+\frac{n^2a}{V^2}\right)(V-b)=nRT$$

Where the constant a accounts for interatomic force between the atoms and b accounts for volume correction. It is due to the finite size of atoms, the actual volume available for the movement of atoms is less than the volume of V of the vessel. P appearing in Vander Waals equation is the observed pressure. It is due to correction observed pressure decreases.

Vander Waals equation of state is not valid for all real gas. After that several equations of state had been proposed such as claussius equation of state, Berthelot equation of state, Dieterici equation of state, Saba and Bose equation of state and so on. None was perfectly correct.

Example 1

Expand the Vander Waals equation of state, $\left(P+\frac{a}{\upsilon^2}\right)(\upsilon-b)=RT$ in virial series form.

Solution

$$\left(P+\frac{a}{\upsilon^2}\right)(\upsilon-b)=RT$$

$$P\left(1+\frac{a}{P\upsilon^2}\right)\upsilon\left(1-\frac{b}{\upsilon}\right)=RT$$

or $$P\upsilon=\frac{RT}{\left(1+\frac{a}{P\upsilon^2}\right)\left(1-\frac{b}{\upsilon}\right)}$$

i.e., $$P\upsilon=RT\left(1-\frac{b}{\upsilon}\right)^{-1}\left(1+\frac{a}{P\upsilon^2}\right)^{-1}$$

Since $\frac{b}{\upsilon}$ and $\frac{a}{P\upsilon^2}$ are very small we can apply Bionomial approximation

$$P\upsilon = RT\left(1+\frac{b}{\upsilon}\right)\left(1-\frac{a}{P\upsilon^2}\right)$$

$$P\upsilon = RT\left(1+\frac{b}{\upsilon}-\frac{a}{P\upsilon^2}-\frac{ab}{P\upsilon^3}\right)$$

The term $\frac{ab}{P\upsilon^3}$ is negligibly small

$$P\upsilon = RT\left(1+\frac{b}{\upsilon}-\frac{a}{P\upsilon}\right)$$

The second and third terms on the R.H.S are correction terms. There we can use $P\upsilon = RT$

In the second term put $\upsilon = \frac{RT}{P}$ and in the third term put $P\upsilon = RT$

$$\therefore \qquad P\upsilon = RT\left(1+\frac{bP}{RT}-\frac{a}{RT\upsilon}\right)$$

or

$$P\upsilon = RT\left(1+\frac{b}{RT}P-\frac{a}{R^2T^2}P\right)$$

$$P\upsilon = \left(1+\left(\frac{b}{RT}-\frac{a}{R^2T^2}\right)P\right)$$

This is the required form,

Example 2

Write down the Dieterici equation of state, $Pe^{\frac{a}{RT\upsilon}}(\upsilon-b) = RT$ in the virial form

Solution

$$Pe^{\frac{a}{RT\upsilon}}(\upsilon-b) = RT$$

$$P\upsilon - Pb = RTe^{-\frac{a}{RT\upsilon}}$$

$$P\upsilon = Pb + RTe^{-\frac{a}{RT\upsilon}}$$

Expanding the exponential term

$$P\upsilon = Pb + RT\left(1 - \frac{a}{RT\upsilon}\right)$$

Retained only linear term.

$$P\upsilon = RT\left[1 - \frac{a}{RT\upsilon} + \frac{Pb}{RT}\right]$$

If we substitute $\upsilon = \frac{RT}{P}$ for the second correction term, we get

$$P\upsilon = RT\left[1 - \frac{aP}{R^2T^2} + \frac{Pb}{RT}\right]$$

or
$$P\upsilon = RT\left[1 + \left(\frac{b}{RT} - \frac{a}{R^2T^2}\right)P\right]$$

Note : Look at the answers of example (1) and (2), they are same.

Example 3

If the pressure of an ideal gas varies according to the equation $P = P_0 - aV^2$, where P_0 and a are constants find the maximum attainable temperature.

Solution

$$P = P_0 - aV^2$$

Using $PV = nRT$, $V = \frac{nRT}{P}$

$$\therefore \quad P = P_0 - \frac{an^2R^2T^2}{P^2}$$

$$P^3 = P_0P^2 - an^2R^2T^2 \qquad ..... (1)$$

Differentiating with respect to P we get

$$3P^2 = 2P_0P - an^2R^2 2T\frac{dT}{dP}$$

For maximum temperature $\frac{dT}{dP} = 0$

$$\therefore \quad 3P = 2P_0$$

$$P = \frac{2}{3}P_0$$

Put this in equation (1), we get

$$\left(\frac{2}{3}P_0\right)^3 = P_0\left(\frac{2}{3}P_0\right)^2 - an^2R^2\,T_{max}^2$$

$$an^2R^2\,T_{max}^2 = \frac{4}{9}P_0^3 - \frac{8}{27}P_0^3$$

$$an^2R^2\,T_{max}^2 = \frac{4}{27}P_0^3$$

$$\therefore \quad T_{max} = \frac{2}{3\sqrt{3}}\frac{P_0^{3/2}}{\sqrt{a}nR}$$

$$T_{max} = \frac{2}{3}\left(\frac{P_0}{nR}\right)\sqrt{\frac{P_0}{3a}}$$

It may be checked that $\frac{d^2T}{dP^2}$ is negatiave.

Example 4

Find the minimum attainable pressure of ideal gas in the process $T = T_0 + aV^2$, where T_0 and a are constant

Solution

$$T = T_0 + aV^2 \text{ given}$$

Using $PV = nRT$, $T = \frac{PV}{nR}$

$$\frac{PV}{nR} = T_0 + aV^2$$

or $$P = \frac{nT_0R}{V} + anRV \qquad \text{..... (1)}$$

so $$\frac{dP}{dV} = -\frac{nT_0R}{V^2} + anR$$

For minimum pressure $\frac{dP}{dV} = 0$, yields

$$\frac{nT_0R}{V^2} = anR$$

$$V = \sqrt{\frac{T_0}{a}} \text{ put this in equation (1)}$$

$$P_{min} = \frac{nT_0R}{\sqrt{\frac{T_0}{a}}} + anR\sqrt{\frac{T_0}{a}}$$

$$P_{min} = nR\sqrt{aT_0} + nR\sqrt{T_0a}$$

$$P_{min} = 2nR\sqrt{aT_0}$$

It may be checked that $\frac{d^2P}{dV^2}$ is positive.

Example 5

Prove that the work done by an ideal gas with constant heat capacity C_V during a quasi-static adiabatic expansion is $W = -C_V(T_f - T_i)$

Solution

We have $đQ = dU + đW$

or $$đQ = C_VdT + đW$$

For an adiabatic process $đQ = 0$

$\therefore$ $$đW = -C_VdT$$

integrating $W = -\int_{T_i}^{T_f} C_V dT = -C_V (T_f - T_i)$

Example 6

Show that the heat transferred during and infinitesimal quasi-static process of a an ideal gas can be written as

$$đQ = \frac{C_V VdP}{nR} + \frac{C_P}{nR} \cdot PdV$$

Solution

We have $đQ = dU + PdV$

or $$đQ = C_V dT + PdV \qquad \text{..... (1)}$$

From ideal gas equation of state

$$PV = nRT$$

Take differentials on both sides, yields

$$PdV + VdP = nRdT$$

or $$dT = \frac{PdV + VdP}{nR}$$

Put this in equation (1), we get

$$đQ = C_V \frac{(PdV + VdP)}{nR} + PdV$$

$$đQ = \frac{C_V VdP}{nR} + \frac{C_V PdV}{nR} + PdV$$

$$đQ = \frac{C_V VdP}{nR} + PdV\left(\frac{C_V}{nR} + 1\right)$$

or $$đQ = \frac{C_V VdP}{nR} + \frac{PdV}{nR}(C_V + nR)$$

Using $C_P - C_V = nR$, $C_P = C_V + nR$

$$\therefore \qquad đQ = \frac{C_V VdP}{nR} + \frac{PdV}{nR} C_P$$

Example 7

Calculate the internal energy of the air in your room of volume $40 m^3$. Assume that air behaves like ideal gas

Solution

We have $$U = \frac{nRT}{\gamma - 1}$$

For ideal gas $PV = nRT$

$$\therefore \qquad U = \frac{PV}{\gamma - 1} = \frac{1 \times 10^5 \times 40}{1.4 - 1} = 10^7 J$$

$$= 10 MJ$$

Example 8

If h is the height above sea level show that the decrease of atmospheric pressure due to rise of dh is given by

$$\frac{dP}{P} = -\frac{Mg}{RT} dh$$

where M is the molar mass of air, g is the acceleration of gravity and T is the temperature at height z.

Solution

Consider a layer of thickness of air dh at h height above the surface of the earth. The pressures acting on the two sides of the layer are shown in the figure. Equating the upward and downward forces, we get

$$Adh\rho g + (P + dP) A = PA$$

or $$dP = -\rho g dh$$

Using $PV = RT$

$$\frac{PM}{\rho} = RT \text{ gives } \rho = \frac{PM}{RT}$$

$$\therefore \qquad dP = -\frac{PMgdh}{RT}$$

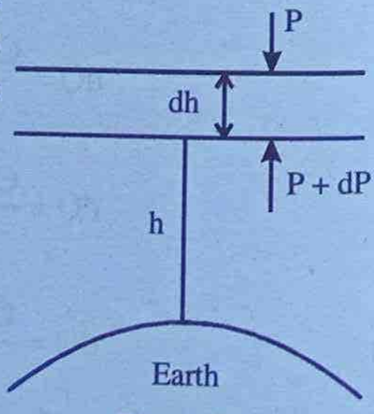


Figure 2.9

or
$$\frac{dP}{\rho} = -\frac{Mgdh}{RT}$$

Integrating this we get the variation of pressure with height

$$\int_{P_0}^{P} \frac{dP}{\rho} = -\frac{Mg}{RT}\int_{0}^{h} dh$$

$$\ln\frac{P}{P_0} = -\frac{Mgh}{RT}$$

$$P = P_0\, e^{-\frac{Mgh}{RT}}$$

In this derivation temperature is assumed to be constant.

Example 9

A horizontal cylinder closed at one end and is rotated with a constant angular velocity ω about a vertical axis passing through the open end of the cylinder. The outside pressure is P_0 and temperature T and the molar mass of air is M. Find the air pressure as a function of the distance r from the rotation axis. Assume that molar mass is independent of mass.

Solution

The centripetal force on the thin layer of thickness dr is

$$F = (P + dP)A - PA$$

$$mr\omega^2 = dPA$$

$$A\rho dr\, r\omega^2 = dPA$$

$$\therefore \quad dP = \rho\omega^2 rdr \qquad \text{..... (1)}$$

$$PV = RT$$

$$P = \frac{\rho}{M}RT \qquad \text{..... (2)}$$

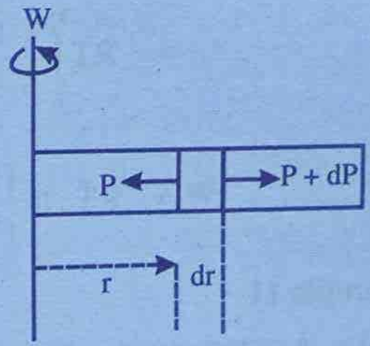


Figure 2.10

$\frac{\text{Eq 1}}{\text{Eq 2}}$ gives

$$\frac{dP}{P} = \frac{M\omega^2}{RT} rdr \text{ Integrating}$$

$$\int_{P_0}^{P} \frac{dP}{P} = \frac{M\omega^2}{RT} \int_{0}^{r} r\,dr$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{M\omega^2 r^2}{2RT}$$

$$P = P_0 e^{\frac{M\omega^2 r^2}{2RT}}$$

Example 10

Find the work performed by one mole of a Vander Waals gas during its isothermal expansion from the volume V_1 to V_2 at temperature T.

Solution

We have $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for 1 mole.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{Work done} \quad = -\int_{V_1}^{V_2} PdV$$

$$= -\int_{V_1}^{V_2} \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) dV$$

$$= -\,RT\int_{V_1}^{V_2} \frac{1}{V-b}\,dV + \int_{V_1}^{V_2} \frac{a}{V^2}\,dV$$

$$W = -\,RT\,\ln\frac{(V_2 - b)}{(V_1 - b)} - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Example 11

Air is compressed adiabatically to half its volume. Calculate the change in temperature. Initial temperature is 27°C.

Solution

Initial volume = V, Final volume = $\frac{V}{2}$

Initial temperature = $27^\circ C = 27 + 273 + 300\,K$

Using
$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$300(V)^{\frac{7}{5}-1} = T_2\left(\frac{V}{2}\right)^{\frac{7}{5}-1}$$

$$300V^{\frac{2}{5}} = T_2 2^{-\frac{2}{5}} . V^{\frac{2}{5}}$$

$$\therefore \quad T_2 = \frac{300}{2^{-\frac{2}{5}}} = 300 \times 1.319$$

$$= 395.85\,K$$

$\therefore$ Change in temperature $= 395.85 - 300 = 95.85K$

$= 95.85^\circ C.$

Note : Since air is diatomic, $\gamma = \frac{7}{5}$

Example 12

A quantity of air at 27°C and one atmospheric pressure is suddenly compressed half its original volume. Find the final pressure.

Solution

$P_1 = 1\,atm, \; V_1 = V, \; V_2 = \frac{V}{2}$

Using
$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$P_1V^{\gamma} = P_2\left(\frac{V}{2}\right)^{\gamma}$$

$$\therefore \quad P_2 = P_1 2^{\gamma}$$

$$P_2 = 1 \times 2^{1.4} = 1.263\,atm$$

Example 13

A tyre pumped to a pressure of 3 atm suddenly bursts. Calculate the fall in temperature due to adiabatic expansion. Initial temperature $27^\circ C$ and $\gamma = 1.4$

Solution

$P_1 = 3\text{atm},\ P_2 = 1\text{atm}$ and $T_1 = 27 + 273 = 300\,\text{K}$

$$\gamma = 1.4 = \frac{7}{5}$$

Using $$T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma}$$

or $$\left(\frac{T_2}{T_1}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\frac{T_2^\gamma}{300^\gamma} = \left(\frac{1}{3}\right)^{\gamma-1}$$

$$T_2 = \left(\frac{1}{3}\right)^{\frac{\gamma-1}{\gamma}} \cdot 300$$

$$T_2 = \left(\frac{1}{3}\right)^{\frac{2}{7}} \times 300 \qquad \because \frac{\gamma-1}{\gamma} = \frac{\frac{7}{5}-1}{\frac{7}{5}} = \frac{2}{7}$$

$$= 219.2\,\text{K}$$

$\therefore$ Fall in temperature $= T_1 - T_2$

$= 300 - 219.2$

$= 80.8$ K.

Example 14

The initial temperature of a gas is $27^\circ C$. Calculate the temperature when the gas is compressed suddenly to 8 times its original pressure $(\gamma = 1.5)$.

Solution

$$T_1 = 27^\circ C = 27 + 273 = 300\ \text{K}$$

$$P_2 = \frac{P_1}{8} \text{ and } \gamma = 1.5$$

Using
$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$$

or
$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\frac{8P_1}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{300}\right)^{\gamma}$$

$$8^{\gamma-1} = \left(\frac{T_2}{300}\right)^{\gamma}$$

$$8^{0.5} = \left(\frac{T_2}{300}\right)^{\frac{3}{2}}$$

or
$$8^{\frac{1}{3}} = \frac{T_2}{300}$$

$$(2^3)^{\frac{1}{3}} = \frac{T_2}{300}$$

or
$$T_2 = 600 \text{ K}$$

Example 15

A gas occupying 1 litre at 80 cm of Hg pressure is expanded adiabatically to 1190 cc. If the pressure falls to 60 cm of Hg in the process, deduce the value of γ.

Solution

$V_1 = 1 \text{ litre} = 10^3 \text{cc}, \; P_1 = 80$

$V_2 = 1190 \text{ cc}, \; P_2 = 60$

Using
$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$80 \times (10^3)^{\gamma} = 60(1190)^{\gamma}$$

or $$\frac{80}{60}=\left(\frac{1190}{1000}\right)^{\gamma}$$

$$\frac{4}{3}=(1.190)^{\gamma}$$

or $$\log\frac{4}{3}=\gamma\ \log 1.190$$

$$\gamma=\frac{\log\frac{4}{3}}{\log 1.19}=\frac{0.125}{0.0755}=1.66$$

$$\gamma=1.66$$

IMPORTANT FORMULAE

1. Temperature of ideal gas

$$T=273.16\ \underset{P_{TP}\to 0}{\mathrm{Lt}}\left(\frac{P}{P_{TP}}\right)$$

2. Virial expansion

$$P\upsilon=A(1+BP+CP^2+DP^3+.....)$$

A, B, C, D ...... etc. are virial coefficients

$$\underset{P\to 0}{\mathrm{Lt}}(P\upsilon)=A=RT$$

3. Molar gas constant

$$\mathrm{Lt}\frac{(P\upsilon)_{TP}}{273.16}=R=8.314\,\mathrm{J\,mol^{-1}K^{-1}}$$

4. Ideal gas equation

$$PV=nRT$$

5. For isothermal adiabatic free expansion

$$\left(\frac{\partial U}{\partial P}\right)_T=0 \text{ and } \left(\frac{\partial U}{\partial V}\right)_T=0,\ U=f(T)$$

6. For a real gas

$$\left(\frac{\partial U}{\partial P}\right)_T \neq 0 \text{ and } \left(\frac{\partial U}{\partial V}\right)_T \neq 0$$

7. Mayers relation: $C_P - C_V = nR$

8. Two important relations

$$đQ = C_V dT + PdV$$

$$đQ = C_P dT - VdP$$

9. Equation of state of quasi-static adiabatic process

   (i) $PV^{\gamma} = \text{constant}$

   (ii) $\frac{P^{\gamma-1}}{T^{\gamma}} = \text{constant}$

   (iii) $TV^{\gamma-1} = \text{constant}$

10. Slopes of adiabatics and isothermals

    (i) $\left(\frac{dP}{dV}\right)_{iso} = -\frac{P}{V}$

    (ii) $\left(\frac{dP}{dV}\right)_{adi} = -\frac{\gamma P}{V}$ or $\left(\frac{dP}{dV}\right)_{adi} = \gamma\left(\frac{dP}{dV}\right)_{iso}$

11. Isothermal and adiabatic elasticities

    (i) $E_{iso} = -V\left(\frac{dP}{dV}\right)_T = P$

    (ii) $E_{adi} = -V\left(\frac{dP}{dV}\right)_{adi} = \gamma P$ or $E_{adi} = \gamma E_{iso}$

12. Relation between temperature and kinetic energy

$$T = \frac{2N}{3R}\left(\frac{1}{2}mc^2\right)$$

13. Expression for internal energy and heat capacity of monatomic ideal gas.

$$U = \frac{3}{2}nRT, \quad C_V = \frac{3}{2}nR$$

or $U = \frac{3N}{2}kT \qquad C_V = \frac{3}{2}Nk$

14. Vander Waal's equation of state

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in about two or three sentences)

Short answer questions

1. What is the basis of arriving at equation of state of ideal gas?
2. Write down the virial series expansion of real gas and explain the symbols.
3. Draw $P\upsilon$ versus P graph at constant temperature in the range 0 to 4×10^6Pa.
4. Define molar gas constant. What is its unit and value.
5. Under what conditions ideal gas equation is valid.
6. What is meant by adiabatic free expansion?
7. Show that the internal energy of a system remains the same when it undergoes free adiabatic expansion.
8. Define the Joule coefficient.
9. In an isothermal, free expansion express internal energy in terms of pressure.
10. On what all thermodynamic coordinates the internal energy of a real gas depend.
11. Define ideal gas.
12. Write down three equations that ideal gas satisfy.
13. Write down Mayers relation and explain the symbols used.
14. Explain why $C_P > C_V$.
15. Why a gas has two heat capacities?
16. Write down the properties of molar heat capacities of ideal gases.
17. Write down C_P, C_V for a monatomic ideal gas.
18. Write down the temperature dependence of C_P, C_V and γ for a diatomic gas.
19. What is the exceptional behaviour of C_P of hydrogen atom?
20. Write down the three equations of state of quasi-static adiabatic process.
21. What are isothermals?
22. What are adiabatics?

23. Define (i) isothermal elasticity and (ii) adiabatic elasticity of a gas.
24. Mention two limitations of classical thermodynamics.
25. Write down the Vander Waals equation and explain the symbols used.
26. Write down an expression for the internal energy of a monatomic gas and obtain C_V.

Section B

(Answer questions in about half a page to one page)

Paragraph / problem type

1. Briefly explain Joule's experiment.
2. Show that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $\left(\frac{\partial U}{\partial P}\right)_T = 0$ for an isothermal free expansion.
3. Derive the relation $C_P - C_V = nR$
4. Briefly explain the experimental determination of C_V by electric method.
5. Derive the equation of state of a quasi-static adiabatic process.
6. Show that adiabatic slope is steeper than isothermal slope.
7. Show that adiabatic elasticity is γ times isothermal elasticity.
8. What are the limitations of classical thermodynamics?
9. What were the assumptions made in the kinetic theory of gases?
10. Explain the reason for the modification of ideal gas equation.
11. Write down the Berthelot equation of state $\left(P + \frac{a}{\upsilon^2 T}\right)(\upsilon - b) = RT$ in the virial form.
12. The pressure of an ideal gas varies according to the relation $P = P_0 e^{-\beta\gamma}$ where P_0 and are constants. Find the maximum attainable temperature $\left(T_{max} = \frac{P_0}{ne\beta R}\right)$
13. Prove that the work done by an ideal gas with constant heat capacities during a quasi-static expansion is equal to $W = \frac{P_f V_f}{\gamma - 1}\left[1 - \left(\frac{P_i}{P_f}\right)^{\frac{\gamma-1}{\gamma}}\right]$
14. An open glass tube of uniform cross section is bent in to the shape of an L. One arms is immersed a liquid of density ρ, the other arm of length remains in the air in a horizonal position. The tube is rotated with a constant angular speed ω about the axis of the vertical arm. Prove that the height h to which the liquid rises in the vertical arm is equal to $h = \frac{P_0}{\rho_g}\left(1 - e^{-\frac{\omega^2 L^2 M}{2RT}}\right)$.

15. A volume of a gas expands isothermally to 4 times its initial volume. Calculate the work done by the gas. [1.387 RT]

16. One mole of a monoatomic perfect gas $\left(\gamma=\frac{5}{3}\right)$ is adiabatically compressed from an initial pressure of 1 atmosphere to a final pressure of 150 atmospheres. Assuming the initial temperature of the gas to be 27°C. Calculate work done on the gas during compression $(1\,\text{atm}=10^5\,\text{Nm}^{-2})$ $[2.397\times10^4\,\text{J}]$

17. One mole of a gas at 127°C expands isothermally until its volume is doubled. Find the amount of work done. [2301J]

18. A sample of an ideal gas is expanded to twice its original volume of $1\,\text{m}^3$ in a quasi static process for which $P = KV^2$, where K is a constant whose value is 5 atm/m^6. Calculate the work done by the gas. $[11.78\times10^5\,\text{J}]$

19. A quantity of air $(\gamma=1.4)$ at 27°C is compressed suddenly to $\frac{1}{4}$th of its volume. Find the final temperature. [522.3K]

20. One mole of nitrogen expands isothermally at 20°C from a volume of 10 litre to 20 litre. Find how much heat must be supplied to keep the temperature from dropping. R = 8.3J/molK. [1685.7 J]

21. One mole of helium at 27°C is compressed adiabatically so that pressure becomes 32 times its initial value. Find the final temperature and work done $R=8.3\,\text{J}/\text{mol.K}$ and $\gamma=\frac{5}{3}$ [1200 K, 11205 J]

Section C

(Answer question in about two pages)

Long answer type questions-Essays

1. Describe Rossini and Frandsen experiment and prove that internal energy is a function of pressure, volume and temperature.
2. Based on the kinetic theory of gases arrive at the relation between temperature and kinetic energy.

Hints to problems

11. $\left(P+\frac{a}{T\upsilon^2}\right)(\upsilon-b)=RT$

$$P\left(1+\frac{a}{PT\upsilon^2}\right)\upsilon\left(1-\frac{b}{\upsilon}\right)=RT$$

$$P\upsilon = \frac{RT}{\left(1-\frac{b}{\upsilon}\right)\left(1+\frac{a}{PT\upsilon^2}\right)}$$

$$P\upsilon = RT\left(1-\frac{b}{\upsilon}\right)^{-1}\left(1+\frac{a}{PT\upsilon^2}\right)^{-1}$$

$$P\upsilon = RT\left[\left(1+\frac{b}{\upsilon}\right)\left(1-\frac{a}{PT\upsilon^2}\right)\right]$$

$$P\upsilon = RT\left[1+\frac{b}{\upsilon}-\frac{a}{PT\upsilon^2}\right]$$

Use $P\upsilon = RT$ on the correction terms

$$P\upsilon = RT\left(1+\frac{bP}{RT}-\frac{aP}{R^2T^3}\right)$$

$$P\upsilon = RT\left[\left(1+\frac{b}{RT}-\frac{a}{R^2T^3}\right)P\right]$$

12. $P = P_0e^{-\beta V}$ use $P = \dfrac{nRT}{V}$

$$\frac{nRT}{V} = P_0e^{-\beta V}$$

$$T = \frac{P_0V}{nR}e^{-\beta V} \text{ Find } \frac{dT}{dV} = 0 \quad \frac{d^2T}{dV^2} \text{ is –ve}$$

Find T_{max}. T is maximum at $V = \dfrac{1}{\beta}$.

13. We know that the adiabatic work done is

$$W = \frac{P_fV_f - P_iV_i}{\gamma - 1}$$

$$W = \frac{P_fV_f}{\gamma-1}\left[1-\frac{P_i}{P_f}\frac{V_i}{V_f}\right] \qquad \text{..... (1)}$$

In an adiabatic process the equation of state is PV^{γ} = constant

or $P_iV_i^{\gamma} = P_fV_f^{\gamma}$

$$\frac{V_i^\gamma}{V_f^\gamma} = \frac{P_f}{P_i}$$

$$\frac{V_i}{V_f} = \left(\frac{P_f}{P_i}\right)^{\frac{1}{\gamma}}$$

Put this in equation (1), we get the required result.

14. $h\rho g = P_0 - P$, P emerges from centripetal force is calculated in example 10.

15. $W = -RT \text{ lin}\frac{V_2}{V_1} = -RT\ln\frac{4V}{V} = -RT\ln 4$

$= -1.386RT$

Negative work indicates work is done by the system.

16. $\frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma}$ $P_1 = 1, P_2 = 150, T_1 = 300$

$\therefore \quad T_2 = 2226 \text{ K}$

Work done $W = \frac{R}{\gamma - 1}(T_2 - T_1)$

$R = 8.3 \text{J mol}^{-1}\text{k}^{-1}$

$W = 2.397 \times 10^4 \text{ J}$

Work done positive indicate work is done on the system.

17. $T = 127 + 273 > 300 \text{ K}$

$W = -RT \ln\frac{V_2}{V_1}, R = 8.3$

$W = -2301\text{J}$

Negative work done indicates work is done by the system.

18. Work done, $W = -\int_{V_1}^{V_2} PdV = -\int_1^2 KV^2 dV$

$K = 5 \times 10^5$

$\therefore \quad W = -11.78 \times 10^5 \text{J}$

Negative work done indicates work is done by the system.

19. $T_1 = 27 + 273 = 300\text{K}, V_2 = \frac{V_1}{2}$

Using $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_2 = 522.3\text{K}.$$

20. We have

$$đQ = dU + đW = dU + PdV = C_V dT + PdV$$

$$đQ = PdV \qquad (\because \ dT = 0)$$

$$Q = \int PdV = RT\ \ln\frac{V_2}{V_1}$$

$$= 1685.7\text{J}$$

21. $\dfrac{P_1^{\gamma-1}}{T_1^{\gamma-1}} = \dfrac{P_2^{\gamma-1}}{T_2^{\gamma-1}}$

$$P_1 = P,\ P_2 = 32P$$

$$T_1 = 300\,\text{K}$$

$$\therefore \quad T_2 = 1300\,\text{K}$$

Work done $W = \dfrac{R}{\gamma-1}[T_2 - T_1]$

$$= 11205\,\text{J}$$

Positive work indicates work is done on the system.

UNIT THREE

SECOND LAW OF THERMODYNAMICS

Conversion of work into heat and vice versa

First law of thermodynamics enables us to convert work into heat and vice versa in principle. How to achieve it experimentally is the discussion of this section.

Work into heat

According to first law of thermodynamics we have

$$Q = U_f - U_i + W$$

If a system is subjected to a process such that it is brought back to the initial state, then $U_f - U_i = 0$

$$\therefore \qquad W = Q$$

This shows that work can be completely converted into heat and the efficiency is 100%. The process can be continued indefinitely since in each process system comes back to the initial state. This indicates that work can be transformed into heat indefinitely.

How to achieve this in practice is our problem. For example when two stones are rubbed under water, it is due friction, heat is produced.

As a result temperature of water rises. If the mass of water is very large there will be no appreciable change of temperature of water. Here water acts like a reservoir. Since the state of system (stones) is same at the beginning and end. The net result of the process is the conversion of work into heat.

That is to convert work into heat we require three things (i) a system (ii) cyclic process and (iii) a reservoir.

Heat into work

Consider a gas enclosed in a cylinder provided with a movable piston. When it is heated the cylinder at the bottom, the gas expands and pushes the piston upward doing work. Our problem how to get work indefinitely without any changes in the system. One way is supply the heat at constant temperature. According to first law

$$Q = U_f - U_i + W$$

or $$Q = W \qquad (\because \quad U_f - U_i = C_V dT = 0)$$

i.e. heat is converted into work completely. But in this process, volume increases and pressure decreases. This process can continue only up to pressure reaches atmospheric pressure. i.e., the extraction of work stops. Therefore the process of isothermal expansion cannot be used to extract work indefinitely.

So to get work from heat we need a series of processes in which a system is brought back to its initial state (cyclic process). In each cycle work is done by absorbing heat. For this to takes place we require two reservoirs one at high temperature called source and the other at low temperature called sink.

Let Q_H be the heat exchanged between the source and the system and Q_L be the heat exchanged between the sink and the system. W be the work done during each cycle. To realise this in process heat must be extracted from the source by the system. The system performs work in each cycle then the remaining heat will be rejected by into sink. A device does this process is called heat engine.

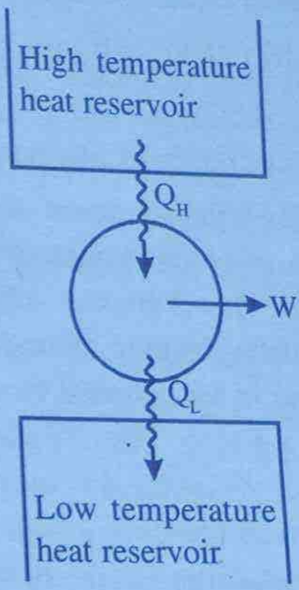


Figure 3.1: Schematic representation of heat engine

Heat engine

Any device which converts heat energy into mechanical energy is called heat engine.

Thermal efficiency of heat engine

The heat extracted (Q_H) from the source during each cycle is called the input whereas work obtained (W) during each cycle is called the output. The thermal efficiency (η) of the engine is defined as the ratio between the workout put (W) to the heat input Q_H.

i.e. $$\eta = \frac{\text{work output}}{\text{heat input}}$$

$$\eta = \frac{W}{Q_H} \qquad \text{..... (1)}$$

According to first law of thermodynamics

$$Q_H - Q_L = U_f - U_i + W$$

For a cyclic process

$$Q_H - Q_L = W$$

$$\therefore \quad \eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \qquad \text{..... (2)}$$

This equation shows that the efficiency of the engine is always less than one (100%). If $Q_L = 0$, $\eta = 1 = 100\%$

It shows that the efficiency of the heat engine is 100% only if engine works without rejecting any heat to the sink. This cannot be realised in actual practice.

The transformation of heat into work is usually accomplished in practice by two types of engines namely internal combustion engine, such as the gasoline engine and the diesel engine, and external combustion engine such as the steam engine and the stirling engine. In both the engines working is almost the same. In general a heat engine in its simplest form consists of a cylinder closed at one end and provided with a piston. The cylinder contains gas or mixture of gas the as the working substance. When the gas in the cylinder is ignited the temperature and pressure of the system increases to a high value. The high pressure provides force to perform work. In the gasoline and the diesel engines combustian takes inside the cylinder are called internal combustian engines, where as the combustian takes place outside the cylinder are called external combustian engines.

Heat engine : Kelvin-Planck statement of the second law

We found that there are different kinds of heat engines. Here we discuss the fundamental theory of operation of heat engines. The second law of thermodynamics is based upon the operations of heat engines. Though second law is an independent law stands by itself it emerges from the draw back of first law.

Second law of thermodynamics

The first law of thermodynamics gives the relation between heat and mechanical energy and that one of them can be converted into another. But it has two major limitations.

(i) It does not give information regarding the direction in which change will take place, and

(ii) it does not specify the limit to which heat can be converted to work.

To circumvent the difficulties not explained by first law, second law was formulated. It was not derived on any theoretical basis but on the basis of experiments.

There are number of ways in which the second law of thermodynamics can be stated. Here we explain four of them, one due to Lord Kelvin, other due to Clausius and third one due to Planck.

Kelvin's statement

"It states that it is impossible to get continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings".

Clausius's statement

"It states that it is impossible to transfer heat from a cold body to a hot body without doing external work".

This statement is based upon the performance of refrigerator (A heat engine working in reverse direction). This means that the natural flow of heat is always from a hot body to a cold body. If heat is to be transferred from a cold body to a hot body work will have to be done by an external agency.

Planck's statement

"It is impossible to construct an engine which working in a complete cycle will produce no effect other than the raising of a weight and cooling of a heat reservoir."

Thus, it is impossible to construct an engine which working in a complete cycle will produce no effect other than the absorption of heat from a reservoir and its conversion into an equivalent amount of work. i.e. perpetual motion of second kind is impossible. The engine must reject a part of the heat absorbed to a sink at lower temperature.

The statement of Kelvin and that of Planck can be combined into one equivalent statement known as Kelvin-Planck's statement of the second law of thermodynamics.

Kelvin-Planck statement

"It is impossible to construct an engine which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work".

It may be noted that second law is not a deduction from first law, it is a separate law of nature. The first law denies the possibility of creating or destroying energy. The second law denies the possibility of utilising energy in a particular way. The continuous operation of a machine that creates its own energy thus violates the first law is called perpetual motion machine of the first kind. The operation of a machine that utilises the internal energy of only one reservoir thus violating the second law is called perpetual machine of the second kind.

Refrigerator-Clausius' statement of second law

A heat engine is a device that takes a working substance through a cycle of operation during which some heat is absorbed by the system from a higher temperature heat reservoir and doing work by the system on the surroundings and the remaining heat is rejected to the lower temperature heat reservoir.

Refrigerator

A refrigerator is a heat engine working in the reverse order and works on the principle of second law. A device in which some heat is absorbed by the system from a heat reservoir at low temperature, a larger amount of heat is rejected to a reservoir at a high temperature by doing work on the system by the surroundings. A device that performs a cycle in this way is called a refrigerator. The working instance (system) is called a refrigerant. Refrigerators are used for climate control. Air conditioner and heat pump are the two examples.

Let Q_L be the amount of heat absorbed by the refrigerant from the lower temperature reservoir, Q_H be the amount of heat rejected by the refrigerant to the high temperature reservoir and W be the network done on the refrigerant by the surroundings. A schematic diagram of refrigerator is shown in figure 3.2.

According to first law, we have

$$Q_H - Q_L = U_f - U_i + W$$

As the refrigerant undergoes a cycle, change in internal energy is zero.

Thus $$Q_H - Q_L = W$$

or $$Q_H = Q_L + W$$

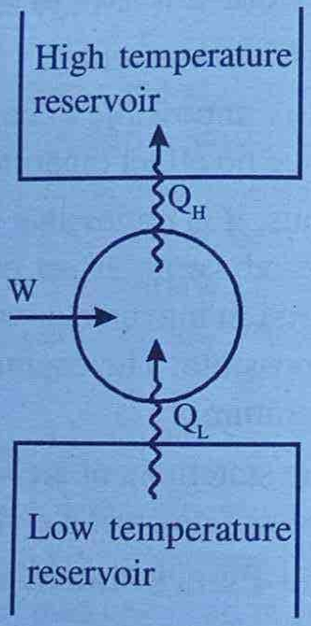


Figure 3.2: Schematic representation of the refrigerator

Here $Q_H > Q_L$, absorbing a small quantity of heat from the low temperature reservoir and rejecting large amount of heat to the reservoir at high temperature the above equation shows that work is to be done on the refrigerant. In other words work is necessary to transfer heat from cold body to a hot body. The negative statement of this leads us to the Clausius statement of second law. The statement is already given.

Equivalence of Kelvin-Planck and Clausius statement

Kelvin-Planck statement and Clausius statement are two different statements of second law. Two statements are said to be equivalent when the truth of one implies the truth of the second, and the truth of the second implies the truth of the first.

Let K represent the truth of Kelvin-Planck statement and C represent the truth of Clausius statement. We use two symbols $\equiv$ and $\supset$. The symbol $\equiv$ denotes equivalent. The symbol $\supset$ means to imply.

In symbolic language the equivalence of two statements can be put in the following way

$$K \equiv C$$

If $K \supset C$ and $C \supset K$.

The equivalence of two statements can be put in another way. Two statements are said to be equivalent when the falsity one implies the falsity of the second and the falsity of second implies falsity of the first.

Let –K represent the falsity of Kelvin-Planck statement and –C represent the falsity of Clausius statement

In symbolic language it can be put as

$$K \equiv C$$

If $-K \supset -C$ and $-C \supset -K$.

To demonstrate the equivalence of Kelvin-Planck statement and Clausius statement we will use the second definition of equivalence.

1. To prove that $-C \supset -K$

Consider a refrigerator. Let Q_L be amount of heat absorbed from the low temperature reservoir and Q_H be the amount of heat rejected to the higher temperature reservoir without doing work W on the refrigerant. (see schematic representation in Fig. 3.3). This violates the Clausius statement. Suppose a heat engine operates between the same two reservoirs such that the same Q_L is rejected to the low temperature reservoir.

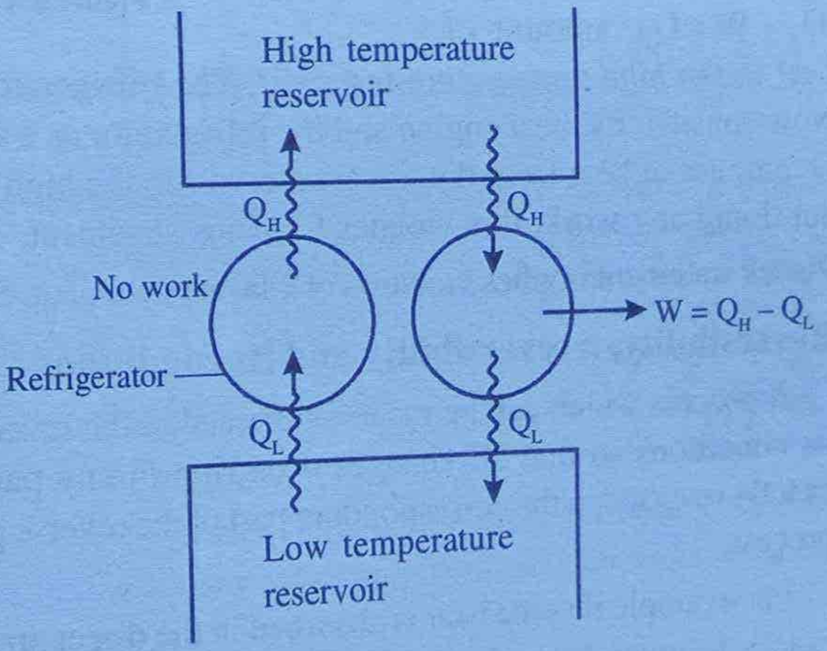


Figure 3.3

The heat engine does not violate any law. Now consider the heat engine and the refrigerator as a single machine that takes $Q_H - Q_L$ amount of heat from the high temperature reservoir and converts all this heat into work without producing any change in the low temperature reservoir. This violates Kelvin-Planck statement. So we proved that $-C \supset -K$.

2. To prove that $-K \supset -C$

Consider an engine working between high temperature reservoir and low temperature reservoir. Suppose the engine absorbs Q_H amount of heat from the high temperature reservoir and does W amount of work and no heat is transferred to low temperature reservoir. It violates Kelvin-Planck statement (see schematic representation in figure 3.4). Suppose a refrigerator operates between the same two reservoirs such that Q_L amount of heat is absorbed from the low temperature reservoir by using up the work done by the engine and rejects $Q_L + W = Q_H$ amount of heat to the high temperature reservoir. The refrigerator does not violate any law. Now consider the heat engine and the refrigerator as a single machine that transfers Q_L amount of heat from the lower reservoir to the high temperature reservoir without doing any work. this violates Clausius statement. That is violation of Kelvin-Planck statement implies violation of Clasius statement. So we proved that $-K \supset -C$.

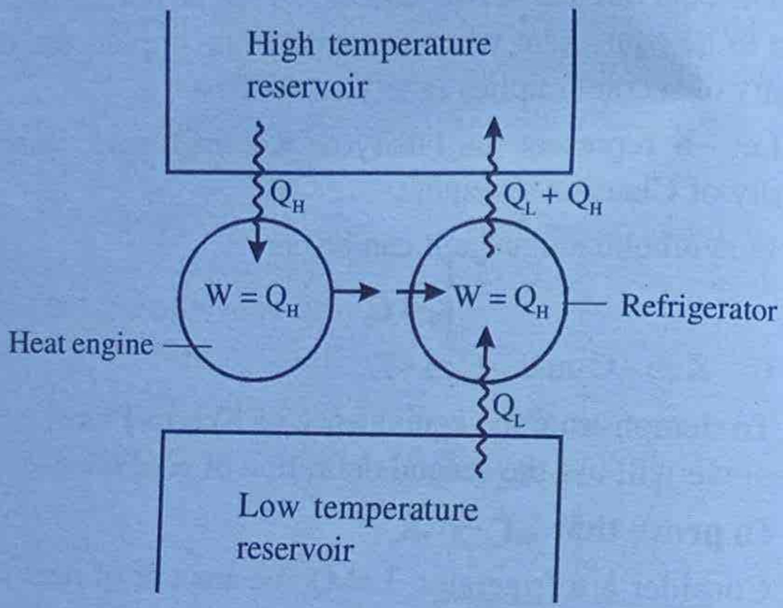


Figure 3.4

Reversibility, irreversibility and its conditions

A process which can be made to proceed in the reverse direction by variation in its conditions so that all changes occurring in any part of the direct process are exactly reversed in the corresponding part of the reverse process is called a reversible process.

For example if some heat is absorbed in the direct process the same amount must exactly be given out in the reverse process. If work is done by some substance during the direct process an equal amount of work must be done on it during the reverse process.

For a reversible process to take place,

(i) dissipative forces like friction, inelasticity, viscosity, electrical resistance etc., should be absent

(ii) the system should always be in mechanical and thermal equilibrium with the surroundings.

(iii) must be quasi-static.

1. Take some gas enclosed in an insulated cylinder fitted with well lubricated piston. Compress the gas very slowly by applying on the piston a pressure slightly exceeding the pressure exerted by the gas. Some work is done on the gas by compressing it. Now reduce the pressure on the piston so that it is slightly smaller than the pressure exerted by the gas. The gas will expand and do almost the same work during expansion as was done on it during compression.
2. Take an elastic spring. Compress it gradually by applying some force on it. Some work is done on the spring. Now reduce the force of compression. The spring will expand and so almost the same work as before.
3. The infinitesimally slow isothermal expansion and compression of a gas is a reversible process.

In fact all isothermal and adiabatic operations are reversible when carried out very slowly. It must be remembered that every reversible process must be a quasi-static process. The reverse of this is not true that is every quasi-static process need not be reversible.

Irreversible process

In nature all changes are irreversible because the conditions for the reversible process cannot be satisfied.

Any process which cannot be made to proceed in the reverse direction is called an irreversible process.

Examples

1. Transfer of heat between two bodies at different temperatures.
2. Two gases when left to themselves tend to mix together. But the reverse process, i.e. their mutual separation is not possible.
3. Rusting of iron is an irreversible process. Rusting is a chemical change during which iron gets converted into iron oxide. It cannot by itself come to its original state.
4. Spontaneous expansion of a gas into an evacuated space.

5. Transfer of electricity through a resistor.

Note: It may be noted that in a reversible process both the system and the local surroundings must be restored to their initial states without producing any changes in the rest of the universe. Here universe does not imply cosmic or celestial, simply means surroundings and auxillary surroundings of the system.

Carnot engine and Carnot cycle

Nicolas Leonard Sadi Carnot, a brilliant young French engineer (who died young at 26 in 1832) in the year 1824 proposed an ideal heat engine free from all imperfections of actual heat engine. It consists of a cycle of operations, hence the name Carnot's cycle. Though this can never be realised in practice it provides the best guide for the construction of actual heat engines and efficiency improvement. This ideal heat engine (Carnot engine) consists of four parts.

(i) Insulated cylinder

It is a cylinder with non-conducting walls and conducting bottom. A perfect gas is used as a working substance. The cylinder is fitted with a perfectly non-conducting and frictionless piston.

(ii) Source

It is a hot body of infinite thermal capacity at temperature T_1. Any amount of heat can be drawn from the source without changing its temperature T_1.

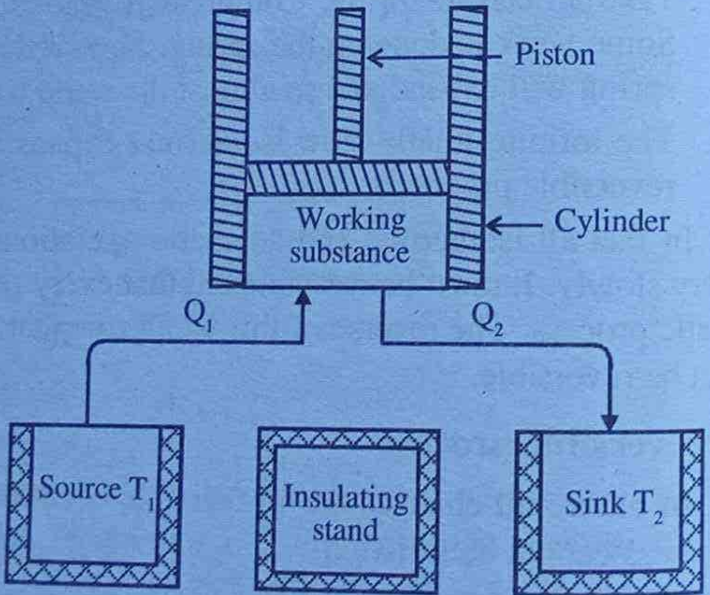


Figure 3.5

(iii) Sink

It is a cold body of infinite thermal capacity at temperature T_2. Any amount of heat can be added to it without changing its temperature T_2.

(iv) Insulating stand

This is a perfectly insulating stand so that the gas can undergo adiabatic changes when the cylinder is placed on it.

Working of Carnot engine

In order to obtain continuous supply of work, the working substance is subjected to the following cycle of operations known as Carnot's cycle.

Carnot's cycle of operations

Consider that the cylinder contains one mole of a perfect gas as the working substance.

1. Isothermal expansion

To start with the cylinder containing the gas at T_1K is placed on the source. The initial pressure and volume of the gas are P_1 and V_1 respectively. It is represented by the point A in the indicator diagram. The gas is allowed to expand isothermally at T_1K until its pressure becomes P_2 and volume V_2. It is represented by the point B in the indicator diagram. Let Q_1 be the amount of heat absorbed from the source during isothermal expansion. The work done by the gas during this expansion is given by

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = RT_1 \ln\frac{V_2}{V_1} = \text{Area ABGEA} \qquad ..... (3)$$

2. Adiabatic expansion

The cylinder is now removed from the source and is placed on the non-conducting platform until its temperature falls to T_2K. Let P_3 be the pressure and V_3 be the volume of the gas now. This is represented by the curve BC on the indicator diagram. The work done by the gas during this process (adiabatic) is given by

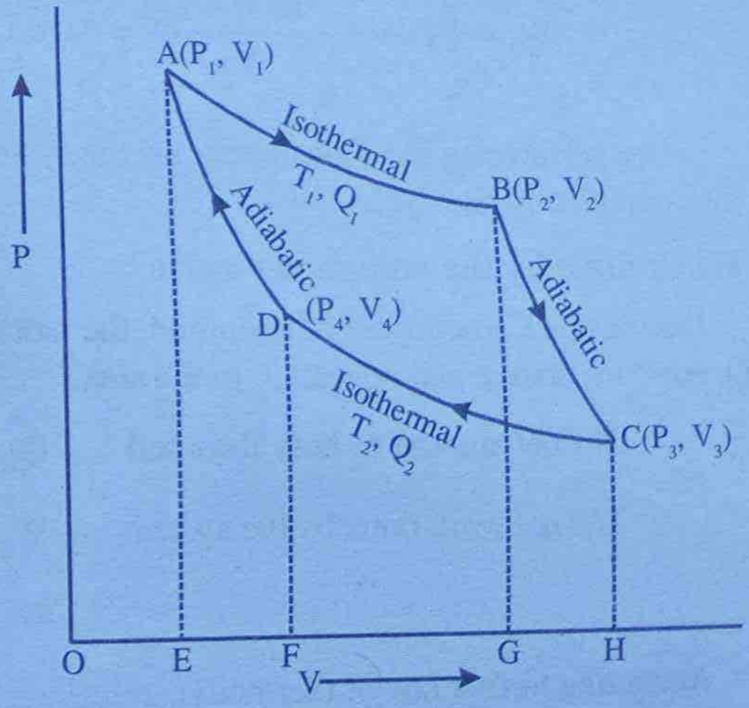


Figure 3.6

$$W_2 = \int_{V_2}^{V_3} PdV = \frac{R(T_1 - T_2)}{\gamma - 1} = \text{Area BCHGB} \qquad ..... (4)$$

3. Isothermal compression

The cylinder is now removed from the insulating stand and is placed over the sink at T_2K and the gas is compressed isothermally. Let P_4 be the pressure and V_4 be the volume of the gas after compression. The process is represented by the curve

CD. Let Q_2 be the quantity of heat rejected to the sink by the gas during isothermal compression. The work done on the gas is given by

$$Q_2 = W_3 = \int_{V_3}^{V_4} PdV = -RT_2 \ln \frac{V_3}{V_4} = \text{Area CHFDC} \quad \text{..... (5)}$$

–ve sign indicates that work is done on the gas.

4. Adiabatic compression

Finally the cylinder is removed from sink and is placed on the non-conducting platform and the gas is compressed adiabatically till the initial condition of the gas i.e. the state $A(P_1, V_1, T_1)$, is regained. This operation is represented by the curve (adiabatic) DA. In this process work done is represented by

$$W_4 = \int_{V_4}^{V_1} PdV = -\frac{R(T_1 - T_2)}{\gamma - 1} = \text{Area DFEAD} \quad \text{..... (6)}$$

After performing the four operations the system comes back to the initial state thus completing one cycle.

Work done by the engine per cycle

During one Carnot cycle of operation, the working substance absorbs an amount Q_1 from the source and rejects Q_2 to the sink.

∴ The net amount of heat absorbed $= Q_1 - Q_2$

The net work done by the system $= W_1 + W_2 + W_3 + W_4$

$$= W_1 + W_3 \quad (\because\ W_2 = -W_4)$$

According to first law of thermodynamics we have $đQ = dU + đW$

In a cyclic process $dU = 0$

∴ $$đQ = đW$$

i.e. Heat absorbed = work done

$$Q_1 - Q_2 = W_1 + W_3$$

or

$$Q_1 - Q_2 = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_3}{V_4} \quad \text{..... (7)}$$

Since the points A and D are at the same adiabatic DA

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

or
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \text{..... (8)}$$

Similarly, points B and C are at the same adiabatic BC

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

or
$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \text{..... (9)}$$

Comparing eqs 8 and 9, we get

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

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

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

Substituting this in eq 7, we get

$$Q_1 - Q_2 = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_2}{V_1}$$

$$Q_1 - Q_2 = R(T_1 - T_2) \ln \frac{V_2}{V_1}$$

$\therefore$ Work done $= Q_1 - Q_2 = R(T_1 - T_2) \ln \frac{V_2}{V_1}$ ..... (10)

Efficiency

By definition

$$\text{efficiency,} \quad \eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = \frac{R(T_1 - T_2)\ln\frac{V_2}{V_1}}{RT_1 \ln\frac{V_2}{V_1}}$$

$$\eta = \frac{T_1 - T_2}{T_1}$$

or $$\eta = 1 - \frac{T_2}{T_1} \qquad \text{.....(11)}$$

This shows that η depends only upon T_1 and T_2 i.e. independent of working substance. For 100% efficiency T_2 must be OK. i.e. the temperature of the sink must be at absolute zero. Since this is impossible, attaining 100% efficiency is impossible. When $T_1 = T_2$, we have $\eta = 0$ i.e. the engine does not work.

Example 1

Calculate the efficiency of an engine that absorbs heat at 600K and exhausts it at 400K.

Solution

$T_1 = 600K,\ T_2 = 400K$

$\therefore$ Efficiency, $$\eta = \frac{T_1 - T_2}{T_1} = \frac{600 - 400}{600}$$

$$\eta = \frac{2}{6} = \frac{1}{3}$$

$\therefore$ $$\eta = 33.33\%$$

Example 2

A carnot engine takes 200 calories of heat from a source at temperature 400K and rejects 150 calories of heat to the sink. What is the temperature of the sink. Also calculate the efficiency of the engine.

Solution

$Q_1 = 200$ calories, $Q_2 = 150$ calories, $T_1 = 400K$

Efficiency, $$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{200 - 150}{200}$$

$$\eta = \frac{1}{4}$$

i.e. $$\eta = 25\%$$

Using $$\eta = 1 - \frac{T_2}{T_1}$$

$$\frac{1}{4} = 1 - \frac{T_2}{400}$$

or $$\frac{T_2}{400} = 1 - \frac{1}{4} = \frac{3}{4}$$

$\therefore$ $$T_2 = 300\text{K}$$

Example 3

Three designs are proposed for an engine which is to operate between 500K and 300K. Design A is claimed to produce 3000J of work per kcal of heat input, B is claimed to produce 2000J and C, 1000J. Which design would you choose.

Solution

$T_1 = 500\text{K},\ T_2 = 300\text{K}$

$\therefore$ $$\eta = \frac{T_1 - T_2}{T_1} = \frac{500 - 300}{500} = 0.4$$

claimed efficiencies of the proposed engines are

$$\eta[A] = \frac{\text{Work output}}{\text{Heat input}} = \frac{3000}{4185} = 0.72$$

$$\eta[B] = \frac{2000}{4185} = 0.48$$

$$\eta[C] = \frac{1000}{4185} = 0.24$$

Since A and B claim efficiencies greater than that of the ideal engine which is not possible, we choose design C.

Example 4

A reversible engine converts one fifth of heat which it absorbs at source into work. When the temperature of the sink is reduced by 77°C, its efficiency is doubled.

Compute the temperature of the source and sink. $\eta = \frac{1}{5}$

Solution

We have $$\eta = 1 - \frac{T_2}{T_1}$$

$$\frac{1}{5} = 1 - \frac{T_2}{T_1} \qquad \text{..... (12)}$$

When T_2 is lowered by 77°C (77K), the efficiency is doubled.

$$\therefore \quad \frac{2}{5} = 1 - \frac{(T_2 - 77)}{T_1}$$

$$\frac{2}{5} = 1 - \frac{T_2}{T_1} + \frac{77}{T_1}$$

$$\frac{2}{5} = \frac{1}{5} + \frac{77}{T_1}$$

or $$\frac{1}{5} = \frac{77}{T_1}$$

$$T_1 = 77 \times 5 = 385\text{K}.$$

Putting this in eq 12, we get

$$\frac{1}{5} = 1 - \frac{T_2}{385}$$

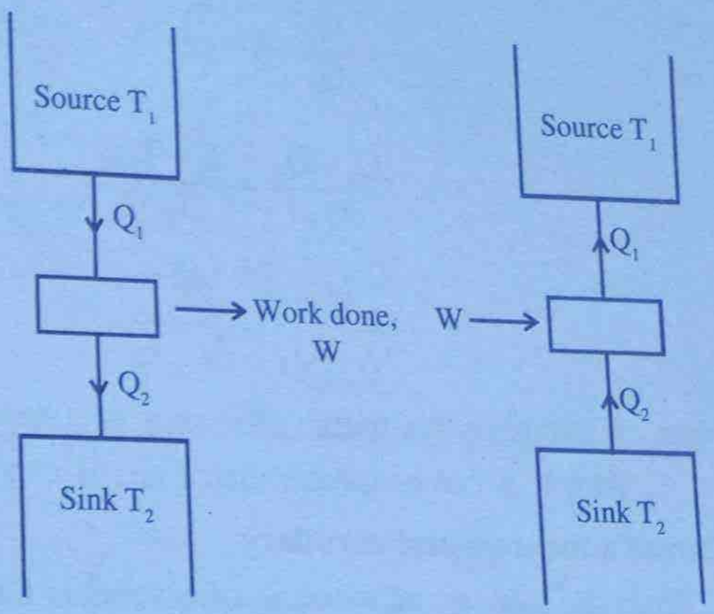
$$\frac{T_2}{385} = 1 - \frac{1}{5} = \frac{4}{5}$$

$$\therefore \quad T_2 = \frac{385 \times 4}{5} = 308\text{K}$$

Carnots refrigerator

Carnots cycle is perfectly reversible. It can work as a heat engine and also as a refrigerator.

When it works as a heat engine it absorbs Q_1 amount of heat from the source at temperature T_1, does an amount of work W and rejects Q_2 amount of heat to the sink at a lower temperature $T_2 (T_1 < T_2)$. See figure (a)



(a) (b)

Figure 3.7

Refrigerator

A refrigerator is a heat engine working in the reverse direction. It works on the principle of second law of thermodynamics. When it works as a refrigerator, it absorbs Q_2 amount of heat from the sink at temperature T_2 by doing W amount of work on the system by means of external agency then reject Q_1 amount of heat $(Q_1 = Q_2 + W)$ to the source at temperature $T_1 (T_1 > T_2)$. See figure above (b). In this case heat flows from lower temperature to higher temperature with the help of external work done. In each cycle Q_2 amount of heat is removed from the sink. This is the principle of refrigerator.

Coefficient of performance of a refrigerator (β)

The coefficient of performance (β) of a refrigerator is defined as the ratio of the amount of heat Q_2 removed from the sink in each cycle to the work W done in each cycle.

i.e.
$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

If the working substance is a perfect gas, we have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

or
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or
$$\frac{Q_1}{Q_2}-1=\frac{T_1}{T_2}-1$$

$$\frac{Q_1-Q_2}{Q_2}=\frac{T_1-T_2}{T_2}$$

$$\therefore \quad \frac{Q_2}{Q_1-Q_2}=\frac{T_2}{T_1-T_2}$$

Note : Remember that unlike efficiency of a heat engine which cannot be greater than 1, β can be greater than 1 i.e., β can be more than 100%.

Carnot's theorem and corollary

From the analysis of working of reversible Carnot's engine and second law of thermodynamics we can arrive at two conclusions. These two are taken together to constitute Carnot's theorem.

According to Carnot's theorem "No engine can be more efficient than a reversible carnot engine working between the same limits of temperature (source and sink) and all reversible engines operating between the same limits of temperature have the same efficiency".

Proof

Consider two engines one reversible (R) and the other one irreversible (I). Both the engines working between the temperatures T_1 (source) and T_2 (sink). Let the amounts of their working substances be so adjusted that the work performed per cycle by engine is the same say W.

If the engine R absorbs Q_1 amount of heat and rejects Q_2 amount of heat, then its efficiency

$$\eta=\frac{W}{Q_1}$$

If the engine I absorbs Q_1' amount of heat and rejects Q_2' amount of heat then its efficiency, $\eta'=\frac{W}{Q_1'}$

Suppose that engine I is more efficient that engine R

i.e.
$$\eta'>\eta$$

or $$\frac{W}{Q_1'} > \frac{W}{Q_1}$$

i.e. $$Q_1 > Q_1'$$

$\therefore$ $Q_1 - Q_1'$ is a positive quantity.

Let the two engines coupled together (see figure 3.8) such that engine I drives R backward. Then R performs as a refrigerator driven by I. Therefore engine R extracts $Q_1 - W$ amount of heat from the sink and work W being done on it by the engine I, transfers Q_1 amount of heat to the source.

The source thus loses Q_1' amount of heat and gains Q_1 amount of heat, therefore source gains $Q_1 - Q_1'$ amount of heat ($\because Q_1 > Q_1'$). The sink gains $Q_1' - W$ amount of heat and loses $Q_1 - W$ amount of heat so the sink loses $(Q_1 - W) - (Q_1' - W) = Q_1 - Q_1'$ amount of heat.

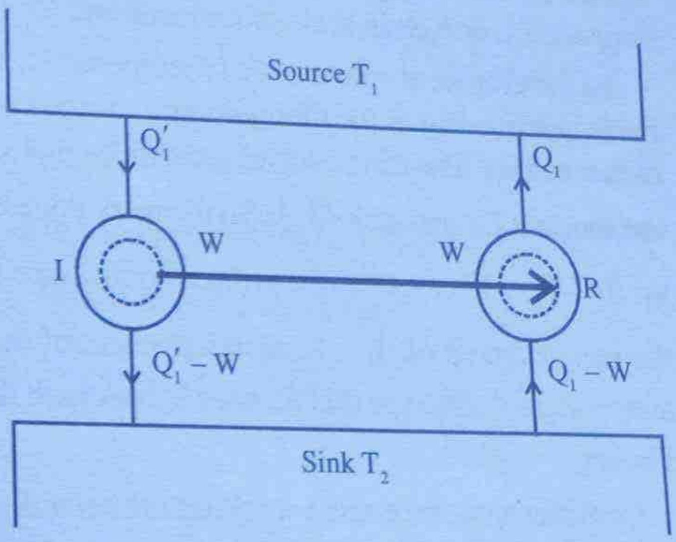


Figure 3.8

The above discussion shows that the heat gained by the source is equal to heat lost by the sink. Thus we can say that the coupling of engines R and I behaves like a self acting machine which requires no external agency to transfer heat from the sink to the source. This is against second law of thermodynamics. This implies that our basic assumption that the irreversible engine (I) is more efficient than the reversible engine (R) is wrong. In other words no engine operating between a given source and sink can be more efficient than a reversible engine operating between the same source and sink. This is the same thing as saying that the efficiency of a reversible engine operating between a given source and sink is maximum.

To prove the second part of the theorem we consider two reversible engines R_1 and R_2 and assume that R_2 is more efficient than R_1. Proceeding as before we can show that R_2 cannot be more efficient than R_1. Therefore all engines working between the same two temperatures have the same efficiency.

Thermodynamic scale of temperature

To measure temperature we make use of thermometers. In different thermometers different thermometric substances are used. Depending upon the nature of the substances used we get different scales of temperatures. Hence temperature measured with different thermometers do not agree with one another i.e., there is no ideal thermometric scale to measure temperature. To overcome this difficulty Lord Kelvin in 1848 suggested a new scale of temperature known as absolute scale of temperature or Kelvin scale of temperature.

To develop an absolute scale of temperature, the measuring temperature must be made independent of the thermometric substance. We have one such system. That is carnot engine. The efficiency of a carnot engine depends only on the temperature of the source (T_1) and sink (T_2). So the work done by the carnot's engine depends only on $T_1 - T_2$. This idea can be utilised to measure $T_1 - T_2$. Here it may be noted that the measurement of $T_1 - T_2$ is independent of the working substance. The scale of temperature defined in this manner agrees with the ideal gas scale.

Theory

Consider a carnot engine working between T_1 and T_2 temperature measured on any arbitrary scale. Let Q_1 be the amount of heat absorbed at T_1 and Q_2 be the amount of heat rejected at T_2.

We have $$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} = f(T_1, T_2)$$

$$\therefore \quad \frac{Q_2}{Q_1} = 1 - f(T_1, T_2)$$

or $$\frac{Q_1}{Q_2} = \frac{1}{1 - f(T_1, T_2)} = F(T_1, T_2) \qquad \text{..... (i)}$$

Where F is some other function of T_1 and T_2 similary, if the carnot engine working between T_2 and $T_3 (T_2 > T_3)$ absorbing a heat Q_2 and rejecting Q_3. We can write

$$\frac{Q_2}{Q_3} = F(T_2, T_3) \qquad \text{..... (ii)}$$

If it works between T_1 and $T_3 (T_1 > T_3)$, then

$$\frac{Q_1}{Q_3} = F(T_1, T_2) \qquad \text{..... (iii)}$$

eq (i) × eq (ii) gives

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = F(T_1, T_2) \times F(T_2, T_3)$$

i.e.,

$$\frac{Q_1}{Q_3} = F(T_1, T_2) \times F(T_2, T_3)$$

$$F(T_1, T_3) = F(T_1, T_2) \times F(T_2, T_3)$$

This is called function equation. In the above equation L.H.S contains no T_2. So R.H.S. should be independent of T_2. This is possible if we choose

$$F(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \text{and} \quad F(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

where ϕ is another function of temperature.

$$\therefore \qquad F(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_2)} \times \frac{\phi(T_2)}{\phi(T_3)} = \frac{\phi(T_1)}{\phi(T_2)}$$

since $T_1 > T_2$ and $T_1 > T_2$, the function $\phi(T_1) > \phi(T_2)$. This $\phi(T)$ is a linear function of T and can be used to measure temperature. Thus Lord Kelvin suggested that $\phi(T)$ should be taken proportional to T.

i.e.,

$$\phi(T_1) \times T_1 \text{ and } \phi(T_2) \propto T_2 .$$

Now we have

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

This equation shows that the ratio of the two temperatures on this scale is equal to the ratio of the heat absorbed to the heat rejected. This temperature scale is called Kelvin's thermodynamic scale of temperature.

Example 5

A Carnot's refrigerator takes heat from water at 0°C and rejects it to a room at temperature 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are rejected to the room. What is the work done by the refrigerator in this process. What is the coefficient of performance of the machine (1 calorie = 4.2J).

Solution

$$T_2 = 0^\circ C = 273K, \; T_1 = 27^\circ C = 300K$$

The latent heat of ice $= 80$ cal/g

$$= 80 \times 10^3 \text{cal/kg}$$

It means that 80×10^3 calories of heat is to be removed from 1 kg of water to make it ice at 0°C.

i.e.

$$Q_2 = 80 \times 10^3 \text{cal}$$

Heat rejected to the room $= Q_1$

Using

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$Q_1 = \frac{T_1}{T_2} Q_2 = \frac{300}{273} \times 80 \times 10^3$$

$$= 87900 \text{ cal}$$

Work done by the refrigerator

$$W = Q_1 - Q_2 = 87,900 - 80,000$$

$$= 7900 \text{ cal}$$

or

$$W = 7900 \times 4.2\text{J}$$

$$= 3.183 \times 10^4 \text{J}$$

Coefficient of performance $\beta = \dfrac{T_2}{T_1 - T_2}$

$$\beta = \frac{273}{300 - 273} = \frac{273}{27} = 10.11$$

Example 6

When a refrigerator is switched off, the ice stored in a cold storage melts at the rate of 36 kg/hour when the external temperature is 30°C. Find the minimum output power of the motor of the refrigerator required to prevent the ice from melting. L = 80 cal/g, 1 calorie = 4.2J

Solution

ice melts in one hour = 36 kg

∴ Heat released $= 36\times80\times10^3\,\text{cal}$

i.e. To prevent melting $36\times80\times10^3$ calories of heat must be removed.

i.e. $$Q_2=36\times80\times10^3\,\text{cal}$$

$$T_1=30^\circ\text{C}=303\text{K},\ T_2=273\text{K}$$

Using $$\frac{Q_1}{Q_2}=\frac{T_1}{T_2}$$

or $$Q_1=\frac{T_1}{T_2}Q_2=\frac{303}{273}\times36\times80\times10^3$$

$$Q_1=1.11\times36\times80\times10^3$$

∴ Work done, $$W=Q_1-Q_2=0.11\times36\times80\times10^3\,\text{cal}$$

$$W=31.68\times10^4\,\text{cal}$$

$$W=31.68\times10^4\times4.2\text{J}$$

$$W=133.056\times10^4\,\text{J}$$

This is the work done in one hour

∴ Work done in one second

$$P=\frac{133.056\times10^4}{60\times60}$$

$$P=369.6\text{ watt}$$

Example 7

An ideal refrigerator takes heat from a cold body and rejects to a hot reservoir at

300K. Calculate the amount of work which must be done in order to remove one calorie of heat when the cold body is at (i) 290K (ii) 100K (iii) 1K (iv) 10^{-4}K. What does this problem reveal?

Solution

$$T_1 = 300K,\ Q_2 = 1 \text{ calorie} = 4.2J$$

Work done $$W = Q_1 - Q_2$$

Using $$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or $$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$$

$\therefore$ $$W = Q_1 - Q_2 = \frac{T_1 - T_2}{T_2} Q_2$$

(i) $$W_1 = \frac{T_1 - T_2}{T_2} Q_2 = \frac{(300 - 290)}{290} \times 4.2$$

$$W_1 = 0.1448J$$

(ii) $$W_2 = \frac{T_1 - T_2}{T_2} Q_2 = \frac{(300 - 100)}{100} \times 4.2$$

$$W_2 = 8.4J$$

(iii) $$W_3 = \frac{T_1 - T_2}{T_2} Q_2 = \frac{(300 - 1)}{1} \times 4.2$$

$$W_3 = 1260J$$

(iv) $$W_4 = \frac{T_1 - T_2}{T_2} Q_2 = \frac{(300 - 10^{-4})}{10^{-4}} \times 4.2$$

$$W_4 = 125999995.8J$$

The problem reveals that when the temperature of the body becomes lower and lower, more and more work has to be done.

To complete the definition of the thermodynamical scale, we assign the arbitrary value of 273.16 K to the triple point of water T_{TP}.

Thus $$T_{TP} = 273.16\,\text{K}$$

For a Carnot engine working between reservoirs at the temperatures T and T_{TP} we have

$$\frac{Q}{Q_{TP}} = \frac{T}{T_{TP}}$$

$$\frac{Q}{Q_{TP}} = \frac{T}{273.16}$$

or $$T = 273.16\frac{Q}{Q_{TP}} \qquad \text{..... (A)}$$

From unit one recall that the equation for the ideal gas temperature, we have

$$T = 273.16\ \text{Lt}_{P_{TP}\to 0}\frac{P}{P_{TP}} \qquad \text{..... (B)}$$

Here pressure is the thermodynamics property used to measure ideal gas temperature. In the limiting case $P_{TP} \to 0$ temperature measurement is independent of the nature of the gas. Comparing equations A and B we can infer that Q takes the role of P. i.e. Q plays the role of thermometric property for a Carnot cycle and at the same time it is independent of the nature of the working substance. Thus thermodynamic scale of temperature is independent of the nature of the working substance. It is essential for a standard reference chosen. It will be soon proved that the thermodynamic scale of temperature and ideal gas temperature scale are numerically equal.

Absolute zero and Carnot efficiency

Recall the relation

$$T = 273.16\frac{Q}{Q_{TP}}$$

when Q is small, T is also small. The smallest possible value of Q is zero and the corresponding value of T is absolute zero.

When a system undergoes a reversible isothermal process without transfer of heat, the temperature at which this process takes place is called absolute zero.

The definition of absolute zero holds for all substances and is independent of specific properties of a substance arbitrarily chosen.

The efficiency of a reversible Carnot engine is given by

$$\eta_R = 1 - \frac{Q_L}{Q_H}$$

where Q_H is the heat absorbed from a hot reservoir and Q_L is the heat rejected to cold reservoir.

But we know that $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$

∴ The efficiency in terms of absolute temperature is

$$\eta_R = 1 - \frac{T_L}{T_H}$$

For η_R to be 100%, T_L must be zero. That is the low temperature reservoir must be at absolute zero in order to convert all heat into work. Since nature does not provide us with a reservoir at absolute zero, a heat engine with 100% efficiency is not possible

Equality of ideal gas and thermodynamic scale

Let θ represent the ideal gas temperature and T represent thermodynamic scale of temperature. Consider a P-V diagram of a Carnot cycle of an ideal gas.

During the isothermal expansion process $(1 \rightarrow 2)$ the heat absorbed Q_1 can be calculated from first law

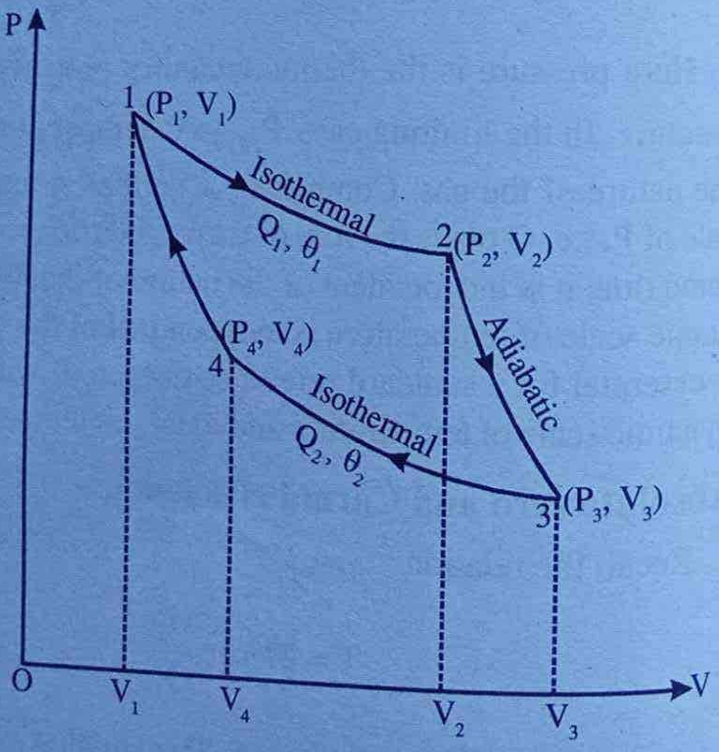


Figure 3.9

$$đQ = C_V d\theta + PdV \qquad (d\theta = 0 \text{ isothermal})$$

$$đQ = PdV$$

$$Q_1 = \int_{V_1}^{V_2} PdV$$

Using $PV = nR\theta_1$, gives $P = \frac{nR\theta_1}{V}$

$$\therefore \quad Q_1 = nR\theta_1 \ln\frac{V_2}{V_1} \qquad \text{..... (1)}$$

Similarly for the isothermal process $(3 \rightarrow 4)$, heat rejected is

$$Q_2 = nR\theta_2 \ln\frac{V_3}{V_4} \qquad \text{..... (2)}$$

$$\therefore \quad \frac{Q_1}{Q_2} = \frac{\theta_1 \ln\frac{V_2}{V_1}}{\theta_2 \ln\frac{V_3}{V_4}} \qquad \text{..... (3)}$$

For the adiabatic expansion process $(2 \rightarrow 3)$

$$đQ = C_V d\theta + PdV \qquad (đQ = 0 \text{ adiabatic})$$

$$C_V d\theta = -PdV$$

Using $PV = nR\theta$ gives $P = \frac{nR\theta}{V}$

$$\therefore \quad C_V d\theta = -\frac{nR\theta}{V} dV$$

or

$$C_V \frac{d\theta}{\theta} = -nR\frac{dV}{V} \text{ integrating}$$

$$\int_{\theta_1}^{\theta_2} \frac{C_V}{\theta} d\theta = -nR\int_{V_2}^{V_3} \frac{dV}{V}$$

or
$$\int_{\theta_1}^{\theta_2} C_V \frac{d\theta}{\theta} = -nR\ln\frac{V_3}{V_2} = nR\ln\frac{V_2}{V_3} \qquad \text{..... (4)}$$

Similarly for the adiabatic process $(4 \rightarrow 1)$

$$\int_{\theta_2}^{\theta_1} C_V \frac{d\theta}{\theta} = -nR\int_{V_4}^{V_1} \frac{dV}{V}$$

or
$$\int_{\theta_1}^{\theta_2} C_V \frac{d\theta}{\theta} = nR\ln\frac{V_1}{V_4} \qquad \text{..... (5)}$$

comparing equations 4 and 5, we get

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

or
$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad \text{..... (6)}$$

Substituting equation 6 in equation 3 yields

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2}$$

From thermodynamic scale of temperature we already have

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$\therefore$
$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2}$$

If θ_1 and T_1 refer to any temperature and θ_2 and T_2 refer to triple point of water

$$\frac{T}{T_{TP}} = \frac{\theta}{\theta_{TP}}$$

since $T_{TP} = \theta_{TP} = 273.16\text{ K}$, we get

$$\theta = T$$

This shows that the ideal gas temperature (θ) and the thermodynamic temperature scale (T) are numerically equal.

Example 8

In the PV diagram shown below, find the efficiency of the engine.

Solution

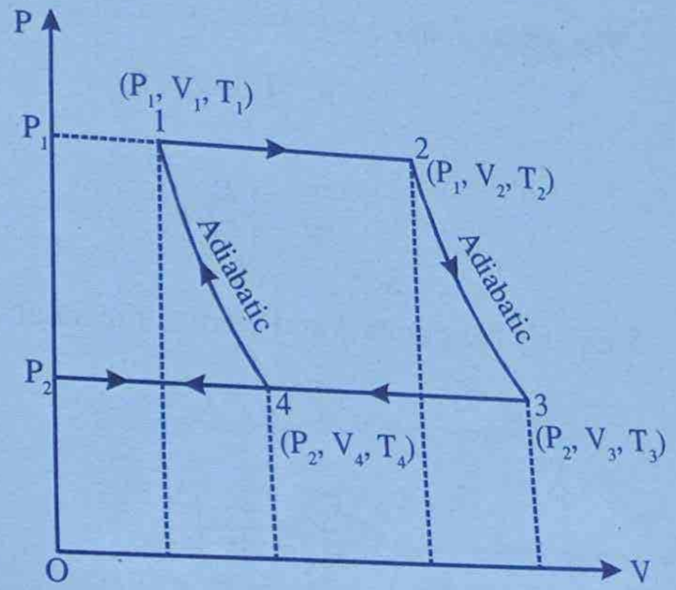


Figure 3.10

Heat is supplied only by isobaric processes.

During the isobaric process $(1 \rightarrow 2)$, $\frac{V}{T} =$ constant

when V increases T also increases

$$\therefore \quad dQ_1 = C_P(T_2 - T_1)$$

During the isobaric process $(3 \rightarrow 4)$ heat

$$dQ_2 = C_P(T_4 - T_3)$$

Work done by isobaric process $(1 \rightarrow 2)$

$$W_1 = P_1(V_2 - V_1) = R(T_2 - T_1)$$

Work done by isobaric process $(3 \rightarrow 4)$

$$W_2 = P_2(V_4 - V_3) = R(T_4 - T_3)$$

Work done by adiabatic process $(2 \rightarrow 3)$

$$W_3 = \frac{R}{\gamma - 1}(T_3 - T_2)$$

Work done in adiabatic process $(4 \rightarrow 1)$

$$W_4 = \frac{R}{\gamma - 1}(T_1 - T_4)$$

∴ Total work done

$$= W_1 + W_2 + W_3 + W_4$$

$$= R(T_2 - T_1) + R(T_4 - T_3) + \frac{R}{\gamma - 1}(T_3 - T_2) + \frac{R}{\gamma - 1}(T_1 - T_4) \qquad \text{..... (1)}$$

The points 2 and 3 are at the same adiabatic points.

$$P_1^{1-\gamma} T_2^{\gamma} = P_2^{1-\gamma} T_3^{\gamma}$$

$$\therefore \quad \frac{T_2}{T_3} = \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}} \qquad \text{..... (2)}$$

Similarly the points 4 and 1 are at the adiabatic points, we have

$$P_2^{1-\gamma} T_4^{\gamma} = P_1^{1-\gamma} T_1^{\gamma}$$

or

$$\frac{T_1}{T_4} = \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}} \qquad \text{..... (3)}$$

Comparing eqs 2 and 3, we get

$$\frac{T_2}{T_3} = \frac{T_1}{T_4} \quad \text{or} \quad \frac{T_1}{T_2} = \frac{T_4}{T_3}$$

Simplifying eq (1), we get

$$W = R\gamma(T_2 - T_1)\frac{\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}\right]}{\gamma - 1}$$

$$\eta = \frac{\text{work done}}{\text{heat input}} = \frac{R\gamma(T_2 - T_1)\frac{\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}\right]}{\gamma - 1}}{C_P(T_2 - T_1)}$$

put

$$C_P = \frac{R\gamma}{\gamma - 1}$$

$$\eta = 1 - \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}$$

Note: Do the entire problem in one step. Example 11.b.

Example 9

Assuming constant heat capacities, from the given PV diagram show that

$$\eta = 1 - (\gamma - 1)\frac{\left(\frac{V_1}{V_2} - 1\right)}{\left(\frac{P_3}{P_2} - 1\right)}$$

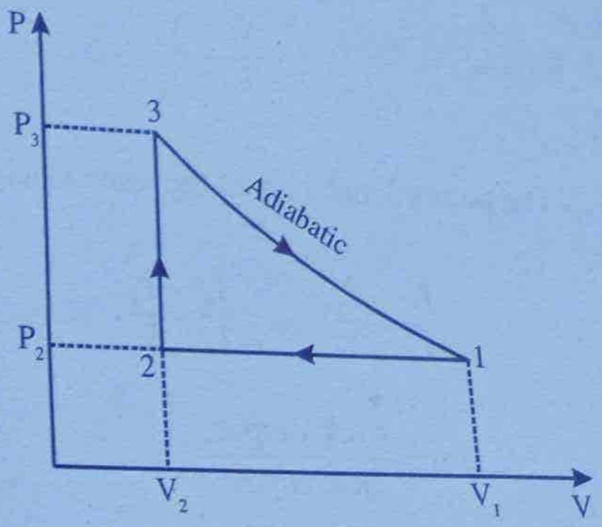


Figure 3.11

Solution

In the isobaric process $(1 \rightarrow 2)\frac{V}{T}$ = constant, as V decreases, T also decreases, so heat is rejected. Work done during this process

$$W_1 = C_P \cdot (T_2 - T_1)$$

During isochoric process $(2 \rightarrow 3)\frac{P}{T}$ = constant, as P increases, T also increases. So heat is absorbed by the system.

$$Q_1 = C_V(T_3 - T_2)$$

In the adiabatic process, $(3 \rightarrow 1)$ there is no change in heat. Work done by the system is

$$W_2 = \frac{R}{\gamma - 1}(T_3 - T_1)$$

$\therefore$ The network done $= W_1 + W_2$

$$= C_P(T_2 - T_1) + \frac{R}{\gamma - 1}(T_3 - T_1)$$

The points 1 and 2 are at the same isobaric points. Using $\frac{V}{T}$ = constant, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{T_1}{T_2} = \frac{V_1}{V_2}$$

The points 2 and 3 are at the same isochoric points. Using $\frac{P}{T}$ = constant

$$\frac{P_2}{T_2} = \frac{P_3}{T_3} \quad \text{or} \quad \frac{T_3}{T_2} = \frac{P_3}{P_2}$$

$$\eta = \frac{\text{work output}}{\text{heat input}}$$

$$\eta = \frac{C_P(T_2 - T_1) + \frac{R}{\gamma - 1}(T_3 - T_1)}{C_V(T_3 - T_2)}$$

$$\eta = \frac{\gamma(T_2 - T_1) + (T_3 - T_1)}{T_3 - T_2} \qquad \left(\because\ C_P = \frac{R\gamma}{\gamma - 1} \text{ and } C_V = \frac{R}{\gamma - 1}\right)$$

$$\eta = \frac{\gamma(T_2 - T_1) + (T_3 - T_2) + (T_2 - T_1)}{T_3 - T_2}$$

$$\eta = \frac{(T_2 - T_1)(\gamma - 1)}{T_3 - T_2} + 1$$

$$\eta = \frac{T_2\left(1 - \frac{T_1}{T_2}\right)(\gamma - 1)}{T_2\left(\frac{T_3}{T_2} - 1\right)} + 1$$

$$\eta=\frac{\left(1-\frac{T_1}{T_2}\right)(\gamma-1)}{\frac{T_3}{T_2}-1}+1$$

Substituting for $\frac{T_1}{T_2}=\frac{V_1}{V_2}$ and $\frac{T_3}{T_2}=\frac{P_3}{P_2}$

$$\therefore \qquad \eta=\frac{\left(1-\frac{V_1}{V_2}\right)(\gamma-1)}{\frac{P_3}{P_2}-1}+1$$

or

$$\eta=1-\frac{\left(\frac{V_1}{V_2}-1\right)(\gamma-1)}{\left(\frac{P_3}{P_2}-1\right)}$$

Example 10

Take an ideal monatomic gas $\left(\gamma=\frac{5}{3}\right)$ around the Carnot cycle, where $T_1=600K$ and $T_2=300K$.

Point 1 at the beginning of the adiabatic compression $P_1=P_0$ (atmospheric pressure) and volume 50 litres. Point 3 has a volume V_3 = 75 litres. Carnot cycle is shown in figure below. Calculate the values of volume and pressure at all four points.

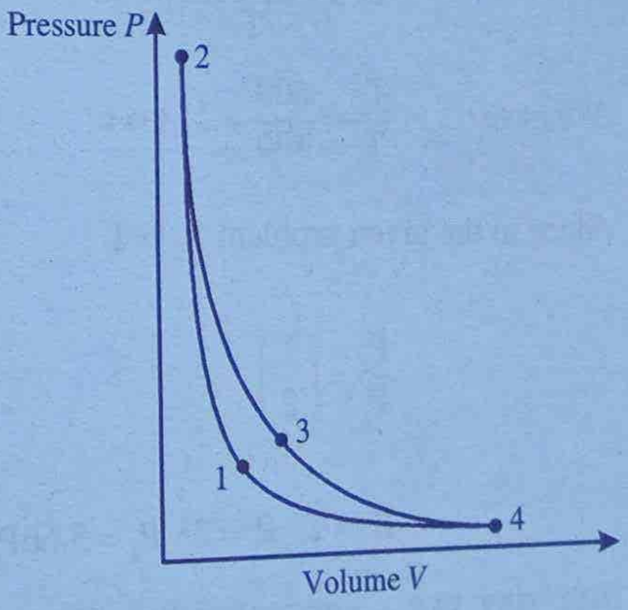


Figure 3.12

Solution

$P_1=P_0=1\,\text{atm}$, $\qquad V_1=50\,\text{litres}$, $V_3=75$ litres $\gamma=\frac{5}{3}$, $T_1=600\,K$ and $T_2=300\,K$

Points 1, 2, 3 and 4 are designated as follows

Point 1 as P_1, V_1, T_1

Point 2 as P_2, V_2, T_2

Point 3 as $P_3, V_3, T_3 = T_2$

(Since points 2 and 3 are isothermal points)

Point 4 as $P_4, V_4, T_4 = T_1$ (since points 4 and 1 are isothermal points)

The process $1 \rightarrow 2$ is adiabatic compression $T_2 > T_1$

Applying $P^{1-\gamma}T^{\gamma} =$ constant to the adiabatic points 1 and 2, we have

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

$$\left(\frac{P_2}{P_1}\right)^{1-\gamma} = \left(\frac{T_1}{T_2}\right)^{\gamma}$$

so
$$\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{1-\gamma}} \qquad \frac{\gamma}{1-\gamma} = \frac{5}{3\left(1-\frac{5}{3}\right)} = -\frac{5}{2}$$

$$\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{-\frac{5}{2}}$$

We have $\frac{T_2}{T_1} = \frac{600}{300} = 2$ given

Since in the given problem $T_2 > T_1$

$$\therefore \quad \frac{P_2}{P_1} = \left(\frac{1}{2}\right)^{-\frac{5}{2}} = 2^{\frac{5}{2}}$$

$$P_2 = 2^{\frac{5}{2}}\,P_1 = 2^{\frac{5}{2}}\,P_0 = 5.66P_0.$$

Applying $PV^{\gamma} =$ constant to the adiabatic points 1 and 2, we get

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$P_0 50^{\gamma} = 5.66P_0V_2^{\gamma}$$

$$V_2^{\gamma} = \frac{50^{\gamma}}{2^{\frac{5}{2}}} \text{ gives } V_2 = \frac{50}{\left(2^{\frac{5}{2}}\right)^{\frac{1}{\gamma}}}$$

$$V_2 = \frac{50}{2^{\frac{5}{2}}} = 17.677 \text{ litres.}$$

The process $2 \rightarrow 3$ is isothermal expansion. So points 2 and 3 are isothermal points.

Applying PV = constant to the points we get

$$P_2V_2 = P_3V_3$$

$$P_3 = \frac{P_2V_2}{V_3} = 2^{\frac{5}{2}}P_0 \cdot \frac{50}{2^{\frac{3}{2}}}\frac{1}{75}$$

$$P_3 = 2P_0 \cdot \frac{50}{75} = \frac{4}{3}P_0 = 1.33P_0.$$

The process $3 \rightarrow 4$ is adiabatic expansion, so points 3 and 4 are adiabatic points.

Applying $P^{1-\gamma}T^{\gamma} =$ constant to the points 3 and 4, we get

$$P_3^{1-\gamma}T_2^{\gamma} = P_4^{1-\gamma}T_1^{\gamma}$$

$$\therefore \quad \left(\frac{P_4}{P_3}\right)^{1-\gamma} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\frac{P_4}{P_3} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{1-\gamma}} = (2)^{\frac{\gamma}{1-\gamma}} = 2^{-\frac{5}{2}}$$

Thus $$P_4 = 2^{-\frac{5}{2}} \cdot P_3 = \frac{\frac{4}{3}P_0}{2^{\frac{5}{2}}} = 0.235\ P_0.$$

Finally applying $PV^\gamma =$ constant to the adiabatic points 3 and 4, we get

$$P_3V_3^\gamma = P_4V_4^\gamma$$

$$V_4^\gamma = \frac{P_3V_3^\gamma}{P_4}$$

$$V_4 = \left(\frac{P_3}{P_4}\right)^{\frac{1}{\gamma}} \cdot V_3 = \left[\frac{4\ P_0}{3(0.235)P_0}\right]^{\frac{3}{5}} \cdot 75$$

$$V_4 = \left(\frac{1.33}{0.235}\right)^{\frac{3}{5}} 75 = 212 \text{ litres.}$$

Example 11

A Carnot engine absorbs 100J of heat from a reservoir at the temperature of the boiling point of water and rejects heat to a reservoir at the temperature of the triple point of water. Find the heat rejected, the work done by the engine and the thermal efficiency.

Solution

$$Q_H = 100J$$

$$T_H = 100 + 273 = 373K$$

$$T_L = 273.16K$$

$\therefore$ Efficiency, $\eta = 1 - \dfrac{T_L}{T_H}$

$$\eta = 1 - \frac{273.16}{373} = 0.268$$

Using $\dfrac{Q_L}{Q_H} = \dfrac{T_L}{T_H}$

$$\therefore \quad Q_L = \frac{T_L}{T_H}Q_H = \frac{273.16}{373} \times 100$$

$$Q_L = 73.2\,J$$

Work done by the engine, $W = Q_H - Q_L$

$$W = 100 - 73.2 = 26.8\,\text{J}$$

Example 12

Hydrogen is used in a Carnot cycle as a working substance. Find the efficiency of the cycle if as a result of an adiabatic expansion.

(a) the gas volume increase by 2 times.

(b) the pressure decreases by two times.

Solution

(a) $$\eta = 1 - \frac{T_2}{T_1}$$

At the two adiabatic points

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

or $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{1}{2}\right)^{\gamma-1} = \left(\frac{1}{2}\right)^{1.4-1}$$

$$\frac{T_2}{T_1} = (0.5)^{0.4} = 0.7578$$

$\therefore$ $$\eta = 1 - 0.7578 = 0.24 = 24\%$$

(b) At the two adiabatic points

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

$\therefore$ $$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} = (2)^{\frac{1-1.4}{1.4}} = (2)^{-\frac{0.4}{1.4}}$$

$$\frac{T_2}{T_1} = 0.82$$

$\therefore$ $$\eta = 1 - 0.82 = 0.18 = 18\%.$$

IMPORTANT FORMULAE

1. Thermal efficiency of heat engine:

$$\eta = \frac{\text{work output}}{\text{heat input}} = \frac{W}{Q}$$

$$\eta = \frac{Q_H - Q_L}{Q_H}$$

$$\eta = \frac{T_H - T_L}{T_H}$$

2. Coefficient of performance of refrigerator:

$$\beta = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L}$$

3. Thermodynamic scale of temperature:

$$T = 273.16 \frac{Q}{Q_{TP}}$$

4. Ideal gas temperature:

$$T = 273.16\ \text{Lt}_{P_{TP} \to 0} \left(\frac{P}{P_{TP}} \right)$$

UNIVERSITY MODEL QUESTIONS

Section A

(*Answer questions in about* **two** *or* **three** *sentences*)

Short answer type questions

1. What are the three basic essential things required to convert work into heat?
2. What is heat engine?
3. What is the principle of heat engine?
4. Define the efficiency of a heat engine.
5. A heat engine cannot attain 100% efficiency. Explain why?
6. Distinguish between internal and external comustian engines.
7. Give two examples each of internal and external combusitan engines.
8. Give Kelvin's statement of second law of thermodynamics.
9. Give Planck's statement of second law of thermodynamics.
10. Give Kelvin-Planck statement of second law of thermodynamics.

11. Give Clausius' statement of second law of thermodynamics.
12. What are the limitations of first law of thermodynamics?
13. Distinguish between first and second law of thermodynamics.
14. What is perpetual motion machine of the first kind?
15. What is the perpetual motion machine of the second kind?
16. What is the principle of refrigerator?
17. When two statements are said to be equivalent?
18. What is a reversible process? Give two examples.
19. What are the conditions to be satisfied for a reversible process?
20. What is an irreversible process? Give two examples.
21. Define the coefficient of performance of refrigerator.
22. What is Carnot's theorem?
23. Define absolute zero of thermodynamic scale.

Section B

(*Answer questions in a* **paragraph** *of about half a page to one page*)

Paragraph / Problem type questions

1. Briefly explain how to convert work into heat.
2. Briefly explain how to convert heat into work.
3. Under isothermal process it is not possible to convert heat into work indefinitely. Explain.
4. Briefly explain the mechanism of refrigerator that leads to Clausius statement of second law.
5. Prove that the Kelvin-Planck and Clausius statements are equivalent.
6. Show that the efficiency of Carnot engine can never be 100%.
7. The efficiency of an ideal engine increases from 20% to 30% when the temperature of the sink is lowered by 40°C. Find the temperature of the source and sink.

   $[T_1 = 400\,\text{K},\ T_2 = 320\,\text{K}]$
8. A Carnot engine working between 127°C and 27°C. What is the efficiency [25%]
9. A Carnot engine whose temperature of the source is 400K takes 800 J of heat at this temperature and reject 600J of heat to the sink. What is the temperature of the sink and efficiency of the engine. $[T_2 = 300\,\text{K},\ \eta = 25\%]$
10. A Carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of high temperature reservoir be increased. [373.3]
11. The efficiency of a ideal engine is 0.2. If the temperature of the sink is lowered by 20°C, the efficiency becomes 0.25. Find the temperature of the source and sink.

   [400K, 320K]

12. A Carnot engine working between a source at 400K and a sink at T_2K has an efficiency of 50%. If the temperature of both source and sink are increased by 100K. What is the efficiency of the engine. [0.4]

13. In a refrigerator heat from inside at 277K is transferred to a room at 300K. How many joules heat will be delivered to the room for each joule of electrical energy consumed ideally. Also compute the coefficient of performance of this refrigerator. [13.04J, 12.04]

14. A Carnot engine working as a refrigerator between 260K and 300K receives 500 calories of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of work done in each cycle to operate the refrigerator. [576.9 cal, 323.1J]

15. An inventor claims to have developed an engine that takes 100000 J at temperature of 400 K rejects 40,000 J at a temperature of 200 K and delivers 15 Kwh of work. Would you advise investing money to put his on the market? [No]

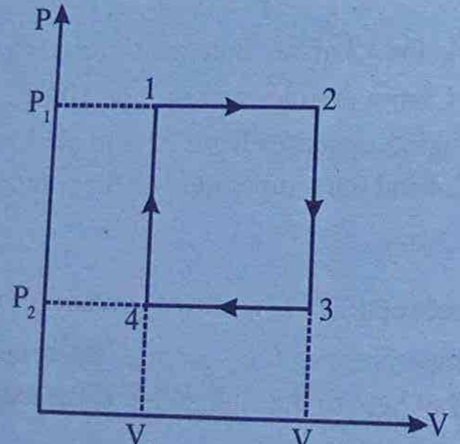
16. Which is the more effective way to increase the thermal efficiency of a Carnot engine to increase T_H keeping constant or to decrease T_L, keeping T_H constant? [Decrease T_L]

17. A Carnot engine whose efficiency is 10% is used as a refrigerator. Find the coefficient of performance.

18. What amount of heat is transferred to N_2 in the isobaric process to perform work 2J [7J]

19. In the PV diagram shown calculate the thermal efficiency. $T_2 \to nT_1$

$$\left[\eta = 1 - \frac{n+\gamma}{1+\gamma n}\right]$$



Section C

(*Answer questions in about* **two** *pages*)

Long answer type questions (Essays)

1. Describe Carnot's cycle and obtain an expression for the efficiency of an ideal heat engine in terms of temperatures.

2. State and prove Carnot's theorem.
3. Prove that ideal gas temperature and thermodynamic temperature scale are numerically equal.

Hints to problems

7. See example 4

8. $\eta = 1 - \frac{T_2}{T_1}$

9. $\eta = 1 - \frac{Q_2}{Q_1}, \quad \eta = 1 - \frac{T_2}{T_1}$

10. $T_2 = 280K, \ \eta_1 = \frac{1}{2}$ find $T_1 \cdot T_1 = 560K$

$$\eta_2 = 1 - \frac{T_2'}{T_1'} \qquad 0.7 = 1 - \frac{280}{T_1'} \qquad T_1' = 933.3K$$

$$\therefore \quad T_1' - T_1 = 933.3 - 560 = 373.3K$$

11. $\eta = \frac{T_1 - T_2}{T_1}$

$$0.2 = \frac{T_1 - T_2}{T_1}$$

$$0.25 = \frac{T_1 - (T_2 - 20)}{T_1}$$

$$0.25 = \frac{T_1 - T_2}{T_1} + \frac{20}{T_1}$$

$$0.25 = 0.2 + \frac{20}{T_1}$$

or $T_1 = 400K$ $\qquad \therefore \quad T_1 = 320K$

12. $\eta = 1 - \frac{T_2}{T_1}$

$$\frac{1}{2} = 1 - \frac{T_2}{400} \qquad \text{......(1)}$$

$$\eta = 1 - \frac{T_2 + 100}{500} \qquad \text{...... (2)}$$

From eq (1), we get $T_2 = 200\text{K}$. Put this in eq (2), we get $\eta = \frac{2}{5} = 0.4$

13. $T_2 = 277\text{K},\ T_1 = 300\text{K}$

$W = 1\text{J}$

Using $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{300}{277}$

or $\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$

$$\frac{W}{Q_2} = \frac{T_1 - T_2}{T_2}$$

or $Q_2 = \frac{T_2 W}{T_1 - T_2} = \frac{277 \times 1}{300 - 277} = \frac{277}{23} = 12.04$

$\therefore$ Heat transferred $Q_1 = Q_2 + W = 13.04$

$$\beta = \frac{T_2}{T_1 - T_2}$$

14. $T_1 = 300\text{K},\ T_2 = 260\text{K}$

$Q_2 = 500 \text{ cal}$

$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ or $Q_1 = \frac{T_1}{T_2} Q_2$

$$Q_1 = \frac{300}{260} \times 500 = 576.9$$

Work done $= Q_1 - Q_2 = 576.9 - 500$

$= 76.9 \text{ cal} = 76.9 \times 4.2$

$= 323.1 \text{ J}$

15. $T_H = 400\text{K},\ T_L = 200\text{K},\ W = 15 \times 10^4 \text{Wh}$

$$\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{200}{400} = 1 - \frac{1}{2} = \frac{1}{2} = 5\%$$

Work done = $Q_H - Q_L = 100000 - 40,000 = 60,000$

$$\therefore \quad \eta' = \frac{Q_H - Q_L}{Q_H} = \frac{60,000}{100000} = 0.6 = 60\%.$$

since $\eta' = \eta$, so impossible.

16. $\eta = \frac{T_H - T_L}{T_H}$, Let ΔT be the increase in T_H, keeping T_L constant

$$\therefore \quad \eta_1 = \frac{(T_H + \Delta T) - T_L}{(T_H + \Delta T)} = \frac{T_H - T_L}{T_H + \Delta T} + \frac{\Delta T}{T_H + \Delta T} \qquad \text{..... (1)}$$

Let ΔT be the decrease in T_L, keeping T_H constant

$$\eta_2 = \frac{T_H - (T_L - \Delta T)}{T_H} = \frac{T_H - T_L}{T_H} + \frac{\Delta T}{T_H} \qquad \text{..... (2)}$$

Comparing eqs 1 and 2

$$\eta_2 > \eta_1 .$$

So it is go for the second.

17. $\beta = \frac{T_2}{T_1 - T_2} = \frac{1}{\frac{T_1}{T_2} - 1}$

Using $\eta = 1 - \frac{T_2}{T_1}$ gives $\frac{T_2}{T_1} = 1 - \eta$

$$\therefore \quad \beta = \frac{1}{\frac{1}{1-\eta} - 1} = \frac{1-\eta}{\eta} = \frac{1-0.1}{0.1} = 9$$

18. $dW = PdV = nRdT$ ..... (1)

$dQ = nC_p dT$ ..... (2)

$$\therefore \quad \frac{dW}{dQ} = \frac{R}{C_P} = \frac{R(\gamma - 1)}{R\gamma} = \frac{\gamma - 1}{\gamma}$$

$$\therefore \quad dQ = \frac{\gamma}{\gamma - 1} dW = \frac{\frac{7}{5}}{\frac{7}{5} - 1} \times 2 = 7\ \text{J}$$

19. $1 \rightarrow 2$ heat supplied $Q_1 = C_p(T_2 - T_1)$

$4 \rightarrow 1$ heat supplied $Q_2 = C_V(T_1 - T_4)$

$\therefore$ Total heat supplied $C_P(T_2 - T_1) + C_V(T_1 - T_4)$

In the isobaric process $(1 \rightarrow 2)$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V_1}{T_1} = \frac{V_2}{nT_1} \qquad \therefore \qquad \frac{V_2}{V_1} = n \qquad \text{..... (0)}$$

In the isochoric process $(2 \rightarrow 3)$

$$\frac{P_1}{T_2} = \frac{P_2}{T_3}$$

$$\frac{P_1}{nT_1} = \frac{P_2}{T_3} \quad \text{gives} \quad \frac{P_1}{P_2} = \frac{nT_1}{T_3} \qquad \text{..... (1)}$$

In the isochoric process $(4 \rightarrow 1)$

$$\frac{P_1}{T_1} = \frac{P_2}{T_4} \quad \text{gives} \quad \frac{P_1}{P_2} = \frac{T_1}{T_4} \qquad \text{..... (2)}$$

Comparing eqs 1 and 2, $T_4 = \frac{T_1}{n}$

$$\eta = \frac{\text{work out}}{\text{heat input}} = \frac{\text{area}}{\text{heat input}} = \frac{(V_2 - V_1)(P_1 - P_2)}{C_P(T_2 - T_1) + C_V(T_1 - T_4)}$$

$$\text{Heat input} \quad = \frac{R\gamma}{\gamma - 1}(nT_1 - T_1) + \frac{R}{\gamma - 1}\left(T_1 - \frac{T_1}{n}\right)$$

$$= \frac{RT_1}{\gamma - 1}\left[\gamma(n-1) + \left(1 + \frac{1}{n}\right)\right]$$

$$= \frac{RT_1}{\gamma - 1}\left[\gamma(n-1) + \left(\frac{(n-1)}{n}\right)\right]$$

Work output $= P_1V_2 - P_1V_1 + P_2V_1 - P_2V_2$

$$= RnT_1 - RT_1 + \frac{RT_1}{n} - RT_1$$

$$= RT_1(n-1) - \frac{RT_1}{n}(n-1)$$

$$= \frac{RT_1(n-1)^2}{n}$$

$$\therefore \qquad \eta = \frac{RT_1(n-1)^2}{n\frac{RT_1}{\gamma-1}\left[\gamma(n-1) + \frac{(n-1)}{n}\right]}$$

$$\eta = \frac{(n-1)(\gamma-1)}{1+n\gamma} = 1 - \frac{(n+\gamma)}{(1+\gamma n)}$$

ENTROPY

Reversible part of the second law

So far we were dealing with PV diagrams, which is useful only for handling hydrostatic systems. In order to account all systems we generalise the PV diagram as work diagram. Any product of two variables giving work will do for this. These two variables are called generalised force and generalised displacement. Some combinations are given below.

System	Generalised force	Generalised displacement	Work done
Hydrostatic system	Pressure P	Volume V	PdV
Wire	Tension T	Length L	TdL
Surface film	Surfacetension S	Area A	SdA
Electrochemical cell	emf, ε	Charge q	εdq
Dielectric substance	Electric field E	Dipolement p	Edp

In work diagrams, generalised force is taken along the vertical axis (Y) and the generalised displacement is taken along the horizontal axis. In a work diagram the isothermal processes and adiabatic processes can be indicated by different curves for all systems.

Here we discuss how the reversible part of second law of thermodynamic leads to Clausius' theorem.

Consider a reversible process represented by the curve AB as shown in figure 4.1. The dashed curves through A and B represent adiabatic processes 1 and 2 respectively. Draw a line ab from the adiabatic curve 1

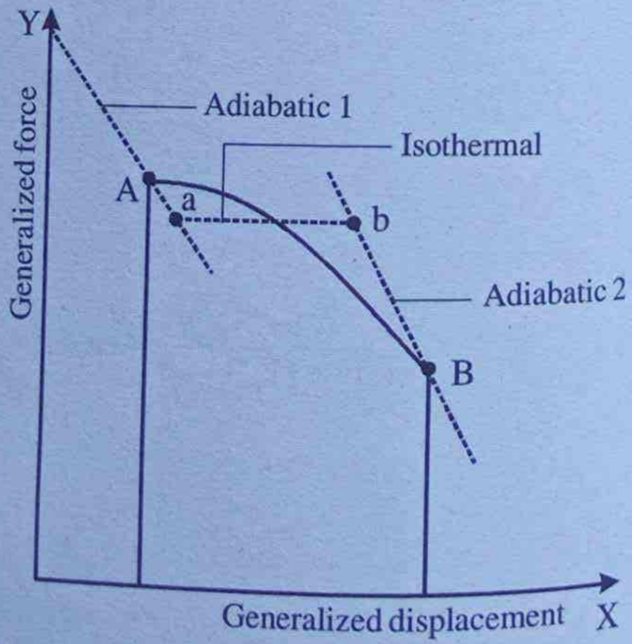


Figure 4.1

to adiabatic curve 2. The curve ab represents an isothermal process. This curve is drawn in such a way that the area under AB is equal to area under AabB. Then the work done in both the paths is the same.

Using first law of thermodynamics

$$Q_{AB} = U_B - U_A + W_{AB}$$

and

$$W_{AB} = W_{AabB}, \text{ we get}$$

$$Q_{AB} = Q_{AabB}$$

since no heat is transferred in transversing from A to a and b to B (adiabatic paths), we have

$$Q_{AB} = Q_{ab} \qquad \text{..... (1)}$$

This discussion shows that we can go from an initial state to a final state of a system in two ways such that heat transferred is the same, one along $A \rightarrow B$ (isothermal process) the other along $A \rightarrow a \rightarrow b \rightarrow B$ (adiabatic → isothermal → adiabatic). This reversible process enables us to develop a new concept.

Clausius' theorem

Consider a reversible cycle ABCDA on the work diagram. The closed curve can be divided into large number of Carnot cycles by drawing adiabatics and isothermals as shown in figure below. since no two adiabatic lines can intersect, a number of lines may be drawn, dividing the circle into a number of adjacent strips. A zigzag

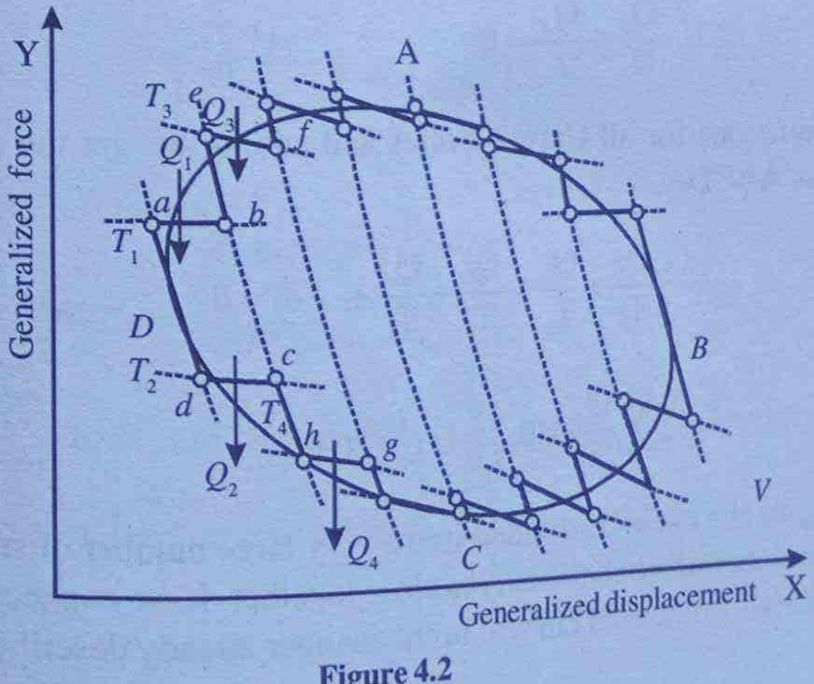


Figure 4.2

closed path may now be drawn consisting of alternate adiabatic and isothermal portions such that heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle.

Consider the Carnot cycle abcda. During the isothermal process ab at temperature T_1, heat Q_1 is absorbed, during the isothermal process cd at temperature T_2, heat Q_2 is rejected.

From the efficiency of the Carnot cycle we have

or
$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2}$$

∴
$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2} \qquad \text{..... (2)}$$

Applying the sign convention to Q, Q_1 is positive (absorbed) Q_2 is negative (rejected)

i.e.
$$\frac{Q_1}{T_1}=-\frac{Q_2}{T_2}$$

or
$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}=0$$

Similarly the Carnot cycle efghe, we can write

$$\frac{Q_3}{T_3}+\frac{Q_4}{T_4}=0$$

Writing equations for all Carnot cycles and adding we get the equation for the cyclic process ABCDA.

i.e.
$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{Q_3}{T_3}+\frac{Q_4}{T_4}+\cdots\cdots=0$$

or
$$\sum_i \frac{Q_i}{T_i}=0, \quad i=1,2,3,4,\ldots\ldots \qquad \text{..... (3)}$$

Now imagine the cycle be divided into a very large number of strips by drawing a very large number of adiabatic curves close together. If we connect these adiabatic curves with small isothermal curves, in the manner already described then a zigzag path may be traced that can be made to approximate the original cycle as close as we please. When these isothermal processes become infinitesimal, $\frac{Q}{T}$ becomes $\frac{\text{đ}Q}{T}$, the summation in the equation can be replaced by integral over a closed path. Thus we have

$$\oint_{R} \frac{\text{đ}Q}{T} = 0 \qquad \text{..... (4)}$$

R indicates that it is valid only for reversible cycle. this result is known as Clausius' theorem. This is one part of Clausius' mathematical statement of the second law of thermodynamics. The other part is for irreversible cycle.

Entropy

Consider a thermodynamic system taken from the initial state A to state B along the path ACB (say R_1) then from B to A along the path BDA (say R_2). The two paths together form a reversible cycle. According to Clausius' theorem

$$\oint_{R_1R_2} \frac{\text{đ}Q}{T} = 0 \qquad \text{..... (5)}$$

This can be written as

$$\int_{R_1A}^{B} \frac{\text{đ}Q}{T} + \int_{R_2B}^{A} \frac{\text{đ}Q}{T} = 0$$

or

$$\int_{R_1A}^{B} \frac{\text{đ}Q}{T} = -\int_{R_2B}^{A} \frac{\text{đ}Q}{T} = 0$$

Since path R_2 is reversible

$$\int_{R_1A}^{B} \frac{\text{đ}Q}{T} = \int_{R_2A}^{B} \frac{\text{đ}Q}{T} = 0 \qquad \text{..... (6)}$$

The paths R_1 and R_2 are chosen arbitrarily. It shows that $\int \frac{\text{đ}Q}{T}$ is independent of the reversible path connecting between A and B and depends only on the initial

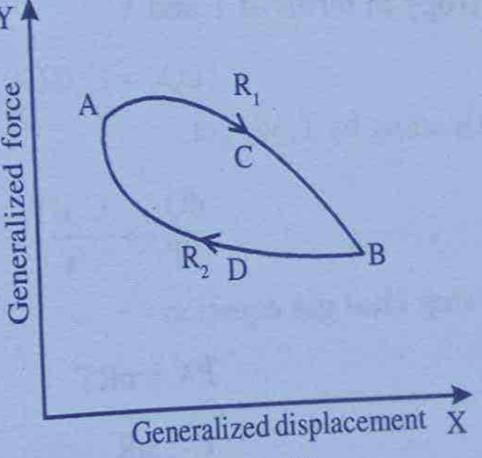


Figure 4.3

state A and the final state B. This integral indicates that there exists a function of thermodynamic coordinates of a system which depends only on the initial and final states. This is called entropy denoted by S. It may be noted that it is a state function. If S_A is the entropy at the initial state A and S_B is the entropy at the final state B given by

$$S_B - S_A = \int_{RA}^{B} \frac{đQ}{T} \qquad \text{..... (7)}$$

It may further be noted that heat entering a system depends on path whereas entropy is not.

If the states A and B are infinitesimally close, the change in entropy is also infinitesimal and is denoted by dS. Then equation 7 becomes

$$dS = \frac{đQ_R}{T} \qquad \text{..... (8)}$$

dS is an exact differential since it is the differential of an actual function, whereas $đQ$ and $đW$ are not. $đQ_R$ indicates that a small quantity of heat is transferred reversibly.

The unit of entropy is JK^{-1}.

Entropy of the ideal gas

Consider an ideal gas occupying volume V at pressure P and temperature T. Let $đQ_R$ be the infinitesimal amount of heat supplied to the gas. According to first law of thermodynamics, we have

$$đQ_R = dU + đW$$

Entropy in terms of T and V

$$đQ_R = C_V dT + PdV$$

Dividing by T, we get

$$\frac{đQ_R}{T} = \frac{C_V dT}{T} + \frac{PdV}{T}$$

Using ideal gas equation

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

$$\therefore \quad \frac{đQ_R}{T} = \frac{C_V dT}{T} + \frac{nRdV}{T} \qquad \text{..... (9)}$$

Now we calculate the entropy change when the system goes from an arbitrarily initial state T_r, V_r to other state T, V.

Integrating the above equation between these two states assuming C_V is a constant we get

$$\int \frac{đQ_R}{T} = \int_{T_r}^{T} C_V \frac{dT}{T} + nR\int_{V_r}^{V} \frac{dV}{V}$$

$$S - S_r = C_V \ln\frac{T}{T_r} + nR\ln\frac{V}{V_r}$$

$$S - S_r = C_V \ln T - C_V \ln T_r + nR\ln V - nR\ln V_r$$

$$S - S_r = C_V \ln T + nR\ln V - (C_V \ln T_r + nR\ln V_r)$$

or

$$S = C_V \ln T + nR\ln V - (-S_r + C_V \ln T_r + nR\ln V_r)$$

$$S = C_V \ln T + nR\ln V + S_0 \qquad \text{..... (10)}$$

where $S_0 = S_r - C_V \ln T_r - nR\ln V_r$

S_0 is called standard state entropy once the standard reference is chosen and the absolute entropy S can be calculated.

From equation 9, we have

$$dS = \frac{C_V dT}{T} + \frac{nRdV}{V}$$

Integrating this equation, we get

$$S = C_V \ln T + nR\ln V + S_0 \qquad \text{..... (11)}$$

comparing equations 11 and 10 the standard reference turns cut to be the constant of integration.

If C_V is not constant we have

$$\Delta S = \int_{A}^{B} C_V \frac{dT}{T} + nR\ln\frac{V_B}{V_A}$$

or
$$\Delta S = n\int_A^B c_V \frac{dT}{T} + nR\ln\frac{V_B}{V_A}$$

Entropy in terms of T and P

Recall the other form of first law of thermodynamics

$$đQ_R = C_P dT - VdP$$

Dividing by T, we get

$$\frac{đQ_R}{T} = C_P\frac{dT}{T} - \frac{VdP}{T}$$

Using $PV = nRT$

$$\frac{V}{T} = \frac{nR}{P}$$

$$\therefore \quad \frac{đQ_R}{T} = C_P\frac{dT}{T} - \frac{nRdP}{P} \qquad \text{..... (12)}$$

Suppose the system goes from an initial reference state (T_r, P_r) to another state (T, P).

Integrating the above equation by assuming C_P is a constant, we get

$$S - S_r = C_P\ln\frac{T}{T_r} - nR\ln\frac{P}{P_r}$$

or
$$S - S_r = C_P\ln T - nR\ln P - C_P\ln T_r + nR\ln P_r$$

or
$$S = C_P\ln T - nR\ln P + S_r - C_P\ln T_r + nR\ln P_r$$

$$S = C_P\ln T - nR\ln P + S_0 \qquad \text{..... (13)}$$

where $S_0 = S_r - C_P\ln T_r + nR\ln P_r$

called standard reference entropy once S_0 is chosen, the absolute entropy S can be calculated.

If C_p is not constant, we have

$$\Delta S = \int_A^B C_P\frac{dT}{T} - nR\ln\frac{P_B}{P_A}$$

or
$$\Delta S = n\int_A^B c_P \frac{dT}{T} - nR\ln\frac{P_B}{P_A}$$

where A is the initial state and B is the final state.

Entropy in terms of P and V

We have

$$đQ_R = dU + PdV$$

or
$$đQ_R = C_V dT + PdV \qquad \text{..... (14)}$$

Using $PV = nRT$

Take the differential on both sides

$$PdV + VdP = nRdT$$

Collect dT and put in equation 14, we get

$$đQ_R = \frac{C_V}{nR}(PdV + VdP) + PdV$$

Dividing by T

$$\frac{đQ_R}{T} = \frac{C_V PdV}{nRT} + \frac{C_V VdP}{nRT} + \frac{PdV}{T}$$

or
$$\frac{đQ_R}{T} = \frac{C_V PdV}{PV} + \frac{C_V VdP}{PV} + \frac{nRdV}{V}$$

$$\frac{đQ_R}{T} = C_V\frac{dV}{V} + C_V\frac{dP}{PV} + nR\frac{dV}{V} \qquad \text{..... (15)}$$

Combining first and the last terms then use $C_P = C_V + nR$

$$\frac{đQ}{T} = C_P\frac{dV}{V} + C_V\frac{dP}{P} \qquad \text{..... (16)}$$

Integrating we get

$$\Delta S = C_P \ln V + C_V \ln P + C \qquad \text{..... (17)}$$

where C is the constant of integration. Here we assumed that C_P and C_V are constants.

TS diagram

For every infinitesimal amount of heat transfer during an infinitesimal reversible process we have

$$\frac{\text{đ}Q_R}{T} = dS$$

or

$$\text{đ}Q_R = TdS$$

Suppose the system goes from initial state A to final state B. Integrating between the states A and B, we get

$$Q_R = \int_A^B TdS \qquad \text{..... (18)}$$

The integral on the L.H.S can be interpreted as the area under the curve $\left(\int ydx\right)$ in which T is plotted on the Y-axis and S along the X-axis. Such a diagram is called TS diagram.

This idea enriches our knowledge of understanding the thermodynamic system. To describe a thermodynamic system we require two independent variables. Among several possibilities like (P, V), (P, T), (V, T), we take the pairs (T, S). The value of T and S can completely specify the thermodynamic state of the system.

The thermodynamic changes in the state of a system can be graphically represented by plotting entropy (S) along the horizontal axis and temperature T along the vertical axis. Such a diagram is called Temperature-entropy (TS diagram) diagram. TS diagrams are convenient and useful in the case of reversible cycles. This is because an isothermal process will, on such a diagram, be represented by a horizontal line drawn parallel to the entropy axis. Similarly an adiabatic process will be represented by a vertical line parallel to the temperature axis. This is because, we have $\text{đ}Q_R = \frac{dS}{T}$, for an adiabatic process $\text{đ}Q = 0$ implies $dS = 0$. So S is a constant such a process is called isentropic process. For a reversible isobaric process the curve has a slope that can be obtained from

$$dS = C_P \frac{dT}{T} - nR\frac{dP}{P} \quad \text{see eq 12}$$

For an isobaric process, $dP = 0$

$$dS = C_P \frac{dT}{T}$$

∴

or

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P} \qquad \text{.....(19)}$$

$\left(\frac{\partial T}{\partial S}\right)_P$ is the slope of the TS diagram at constant pressure.

Similarly for a reversible isochoric process, the graph is curve which has a slope that can be obtained from

$$dS = \frac{C_V}{T} dT + nR\frac{dV}{V} \qquad \text{(see eq 9)}$$

For an isochoric process $dV = 0$

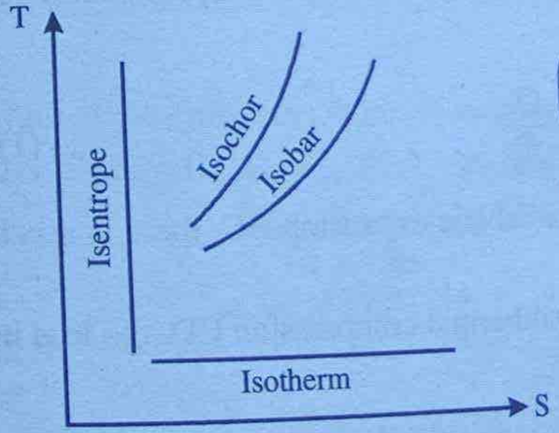
$$dS = \frac{C_V}{T} dT$$

∴

or

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \qquad \text{.....(20)}$$

$\left(\frac{\partial T}{\partial S}\right)_V$ is the slope of the TS diagram at constant pressure. The isochoric, isobaric, isentropic and isothermal curves are shown in figure below.



$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$$

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

Figure 4.4

TS diagram for a Carnot cycle

A carnot cycle consists of two isothermals and two adiabatics. When it is represented on a PV diagram we get a figure as shown below.

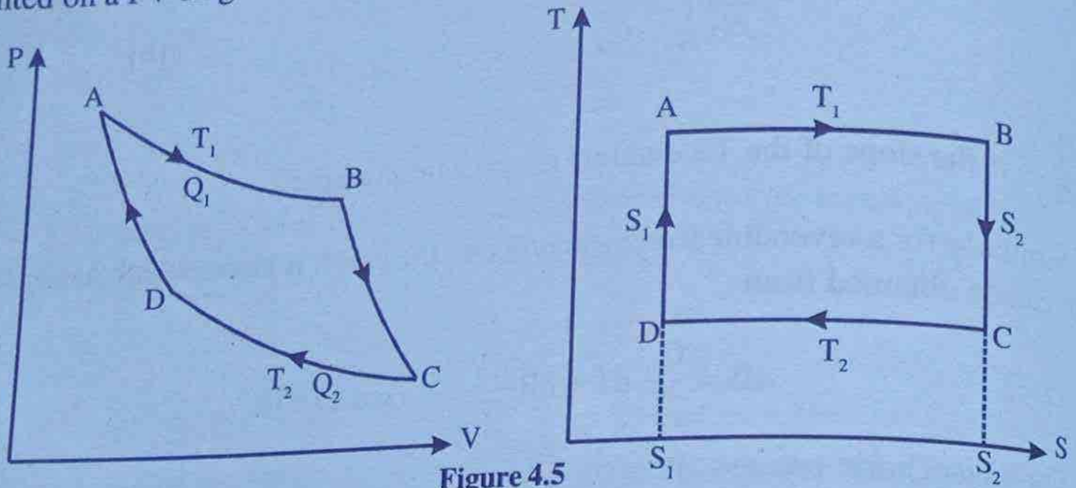


Figure 4.5

AB and CD are isothermals at temperatures T_1 and T_2 respectively. BC and DA are the adiabatics.

On the TS diagram the isothermals are two straight lines AB and CD parallel to S-axis and the adiabatic curves are also straight lines BC and DA parallel to T-axis. The resulting TS diagram is a rectangle ABCD.

Consider a carnots reversible cycle on TS diagram. Suppose S_1 be the entropy of working substance in state A, S_2 be the entropy in state B. Q_1 be the heat absorbed along AB i.e. isothermal expansion at constant temperature T_1 and Q_2 be the heat rejected in the isothermal compression at constant temperature T_2 along CD.

In going from A to B, along isothermal expansion AB, the gain in entropy of the working substance is given by

$$S_2 - S_1 = \frac{Q_1}{T_1} \qquad \text{..... (1)}$$

In going from B to C, along adiabatic expansion BC, there is no change in the entropy.

In going from C to D, along isothermal compression CD, the loss in entropy of the working substance is givenby

$$S_2 - S_1 = \frac{Q_2}{T_2} \qquad \text{..... (2)}$$

Along the adiabatic compression DA, there is no change in entropy.

From eqs (1) and (2) we get

$$Q_1 = T_1(S_2 - S_1)$$

and

$$Q_2 = T_2(S_2 - S_1)$$

$\therefore$

$$Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1)$$

The quantity $Q_1 - Q_2$ represents the external work done in the cycle and $(T_1 - T_2)(S_2 - S_1)$ is the area of the rectangle on the TS diagram. Thus the area of the rectangle on the TS diagram represents the external work done in a reversible carnot's cycle.

Efficiency of carnot's engine

We have

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = \frac{(T_1 - T_2)(S_2 - S_1)}{T_1(S_2 - S_1)}$$

$\therefore$

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

Example 1

Calculate the change in entropy when 100 grams of ice at 0°C is converted into water at the same temperature. Latent heat of ice = 80 cal/g.

Solution

When 1 gram of ice melts into water 80 calories of heat is absorbed.

$\therefore$ Heat absorbed by 100 grams of ice when melts = 100 × 80

i.e.

$$đQ = 8000 \text{ cals}$$

$\therefore$ Change in entropy,

$$dS = \frac{đQ}{T} = \frac{8000}{273}$$

$$= 29.3 \text{ cal/K}$$

Example 2

Calculate the change in entropy when 1 litre of water at 27°C is heated to 77°C.

Solution

Change in entropy $$dS = \int_{T_1}^{T_2} \frac{đQ}{T}$$

But $đQ = ms \cdot dT = 1000 \times 1 \times dT$

$m = 1000$ g, $T_1 = 27°C = 300K$

$s = 1$ $T_2 = 77°C = 350K$

$$\therefore \quad dS = \int_{300}^{350} 1000 \frac{dT}{T} = 1000 \ln\left(\frac{350}{300}\right)$$

$$= 154.15\,\text{cal}K^{-1}$$

Example 3

One mole of a gas expands isothermally to four times of its volume. Calculate the change in entropy. $R = 8.31\,J/molK$

Solution

$V_1 = V,\ V_2 = 4V$

Change in entropy, $$dS = \frac{đQ}{T}$$

During an isothermal process

$$đQ = đW$$

$$\therefore \quad dS = \frac{đW}{T}$$

Work done during an isothermal process, $đW = RT\ln\left(\frac{V_2}{V_1}\right)$

$$\therefore \quad dS = \frac{RT\ln\left(\frac{V_2}{V_1}\right)}{T}$$

$$= R\ln\left(\frac{V_2}{V_1}\right) = R\ln 4$$

or
$$dS = \frac{R \ln 4}{4.2} \text{ cal/K}$$

$$= \frac{8.31 \times \ln 4}{4.2} = 2.743 \text{ cal/K}$$

Example 4

Calculate the change in entropy of 5 kg water at 100°C when changes into vapour. $L = 540 \text{ cal/g}$

Solution

$m = 5\,\text{kg} = 5 \times 10^3\,\text{g}, \; L = 540\,\text{cal/g} \quad T = 100^\circ\text{C} = 373\ \text{K}$

Change in entropy $\quad dS = \frac{đQ}{T} = \frac{mL}{T}$

$$= \frac{5 \times 10^3 \times 540}{373} = 7.238 \times 10^3 \text{ cal/K}$$

Example 5

Calculate the change in entropy when 100 gram of water at 30°C is mixed with 50 gram of water at 80°C.

Solution

$$m_1 = 100\text{g} \qquad T_1 = 303\text{K}$$

$$m_2 = 50\text{g} \qquad T_2 = 353\text{K}$$

Let T be temperature after mixing

Using $\quad$ Heat gained = Heat lost

$$m_1 s(T - 303) = m_2 s(353 - T)$$

$$100 \times 1 \times (T - 303) = 50 \times 1 \times (353 - T)$$

$$2(T - 303) = 353 - T$$

$$2T - 606 = 353 - T$$

$$3T = 953$$

$$\therefore \quad T = 319.67\text{K}$$

Change in entropy when the temperature of 100 g of water changes from 303 K to 319.67 K

$$dS = \frac{đQ}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$$

$$dS_1 = 100\times 1\times \ln\left(\frac{319.67}{303}\right)$$

$$= 5.36\,\text{cal}/\text{K}$$

The change in entropy when 50 g of water changes 353 K to 319.67 K

$$dS_2 = ms\int_{353}^{319.67}\frac{dT}{T} = ms\ \ln\left(\frac{319.67}{353}\right)$$

$$dS_2 = 50\times \ln\left(\frac{353}{319.67}\right) = -4.96\,\text{cal}/\text{K} \qquad (\because\ \ s=1)$$

$\therefore$ Total gain in entropy

$$= 5.36 - 4.96$$

$$= 0.4\ \text{cal}/\text{K}$$

Example 6

Calculate the increase in entropy of 1kg of ice when it is converted into steam. Specific heat of water $1\,\text{k calkg}^{-1}\text{C}^{-1}$. Latent heat of ice 80 cal/g and Latent heat of steam 540 cal/g.

Solution

(a) Increase in entropy when 1 kg of ice at 0°C is converted into water at 0°C

$$dS = \frac{đQ}{T} = \frac{mL}{T} = \frac{1000\times 80}{273} = 293.04\ \text{cal}/\text{K}$$

(b) Increase in entropy when the temperature of 1 kg of water is raised from 0°C to 100°C·

$$dS = \int_{T_1}^{T_2}\frac{đQ}{T} = \int_{273}^{373} ms\frac{dT}{T} = ms\int_{273}^{373}\frac{dT}{T}$$

$$= 1\times10^3 \int_{273}^{373} \frac{dT}{T} = 10^3 \times \ln\left(\frac{373}{273}\right)$$

$$= 312.11 \text{ cal/K}$$

(c) Increase in entropy when 1kg of water at 100°C is converted into steam at 100°C

$$dS = \frac{đQ}{T} = \frac{mL}{T} = \frac{10^3 \times 540}{373}$$

$$= 1447.72 \text{ cal/K}$$

$\therefore$ Total increase in entropy $= 293.04 + 312.11 + 1447.72 = 2052.87$ cal/K

Example 7

Calculate the change of entropy on converting a mole of perfect gas occupying 20 litre at a pressure of $2\times10^5 \text{Nm}^{-2}$ to occupying 50 litre at a pressure of $5\times10^5 \text{Nm}^{-2}$. Given $R = 8.4 \text{Jmol}^{-1}\text{K}^{-1}$, $C_V = 21 \text{Jmol/K}$

Solution

$P_1 = 2\times10^5 \text{Nm}^{-2}$, $V_1 = 20$ litre

$P_2 = 5\times10^5 \text{Nm}^{-2}$, $V_2 = 50$ litre

Using $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore \quad \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{5\times10^5\times50}{2\times10^5\times20} = 6.25$$

The change in entropy $= C_V \times \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)$

$$= 21\times\ln(6.25) + 8.4\ln\left(\frac{5}{2}\right)$$

$$= 46.181 \text{ JK}^{-1}$$

Example 8

A mass m of water at temperature T_1 is isobarically and adiabatically mixed with an equal mass of water at temperature T_2. Show that the change in entropy of the universe is $2mC_P \ln\left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right)$

Solution

When equal amount of water are mixed, the temperature of the mixture is $\frac{T_1+T_2}{2}$.

Change in entropy of water at temperature T_1

$$dS = \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{đQ}{T} = m\,C_P \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{dT}{T}$$

$$dS = m\,C_P \ln\left(\frac{T_1+T_2}{2T_1}\right)$$

Change in entropy of water at temperature T_2

$$dS = \int_{T_2}^{\frac{T_1+T_2}{2}} \frac{đQ}{T} = m\,C_P \int_{T_2}^{\frac{T_1+T_2}{2}} \frac{dT}{T}$$

$$= m\,C_P \ln\left(\frac{T_1+T_2}{2T_2}\right)$$

Since the process is adiabatic, change in entropy of the universe

$$= m\,C_P \ln\left(\frac{T_1+T_2}{2T_1}\right) + m\,C_P \ln\left(\frac{T_1+T_2}{2T_2}\right)$$

$$= m\,C_P \ln\frac{(T_1+T_2)^2}{4T_1T_2}$$

$$= m\,C_P \ln\left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right)^2$$

$$= 2m\,C_P \ln\left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right)$$

Example 9

Compare the efficiencies of cycles A and B.

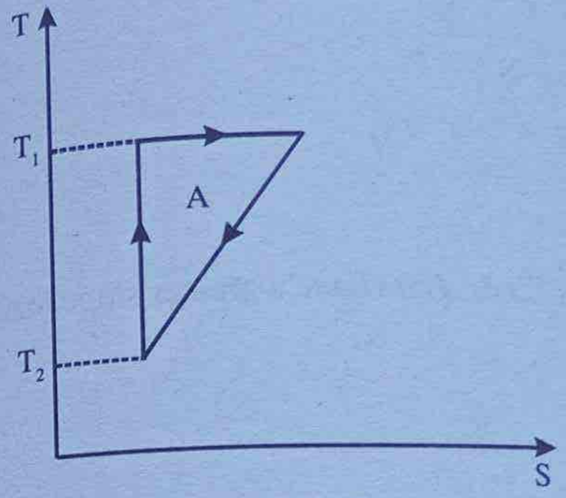


Figure 4.6(a)

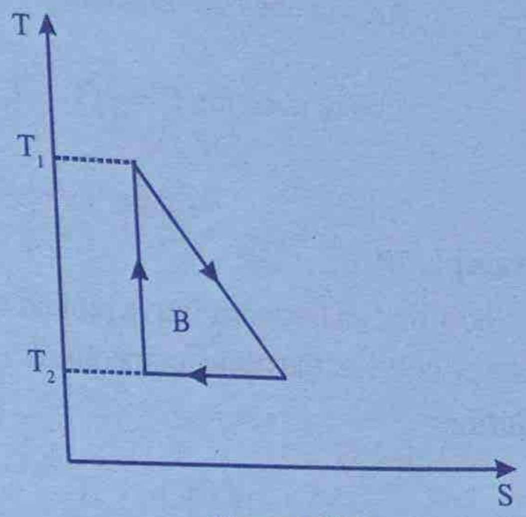


Figure 4.6(b)

Solution

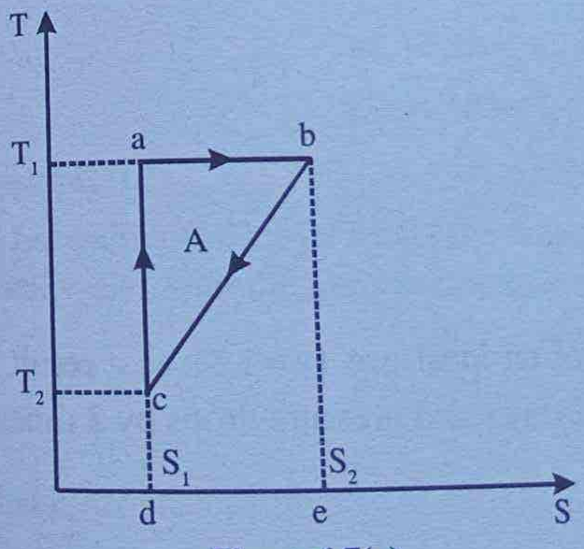


Figure 4.7(a)

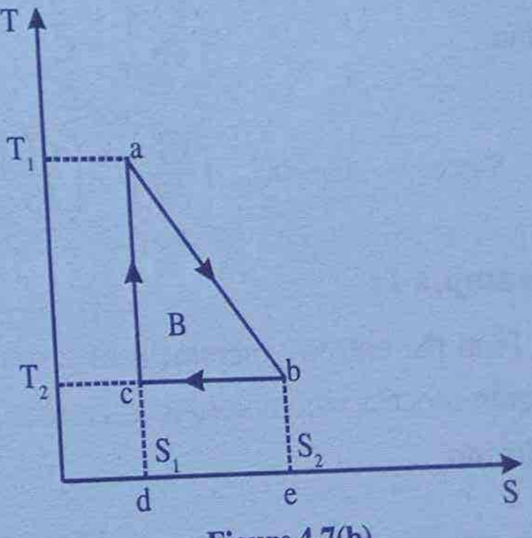


Figure 4.7(b)

Let Q_1 be the amount of heat absorbed during the process in which entropy increases and Q be the amount of heat rejected during the process in which entropy decreases.

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Area of abc}}{\text{Area of abed}}$$

Area of abc for figure A = Area of abc for figure B.

Area of abed for figure A > Area of abed for figure B

$\because$ Area of abed for $A = T_1(S_2 - S_1)$

Area of abed for $B = \frac{1}{2}(T_2 - T_1)(S_2 - S_1)$

$\therefore$ $\eta_A < \eta_B$

Example 10

Show that an isochoric curve plotted on a TS diagram have a greater slope than a isobaric curve at the same temperature.

Solution

We have $$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

and $$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$$

Since $C_V < C_P$, $\left(\frac{\partial T}{\partial S}\right)_V > \left(\frac{\partial T}{\partial S}\right)_P$

Example 11

Find the entropy increment of 2 moles of an ideal gas $(\gamma = 1.3)$ as a result of certain process where volume increases by 2 times and pressure drops by 3 times.

Solution

We have $$dS = C_V \frac{dT}{T} + \frac{PdV}{T}$$

$$dS = C_V \frac{dT}{T} + \frac{nRdV}{V}$$

Integrating,
$$\Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{nR}{\gamma - 1} \ln \frac{T_2}{T_1} + nR \ln \frac{2V_1}{V_1}$$

Using
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

∴
$$\frac{T_2}{T_1} = \frac{P_2}{P_1}\frac{V_2}{V_1} = \frac{1}{3} \cdot 2 = \frac{2}{3}$$

∴
$$\Delta S = \frac{2R}{1.3 - 1} \ln \frac{2}{3} + 2R \ln 2$$

$$\Delta S = \frac{2 \times 8.31}{0.3} \ln \frac{2}{3} + 2 \times 8.31 \times \ln 2$$

$$\Delta S = -22.46 + 11.52$$

$$\Delta S = -10.94\,\mathrm{J}$$

Example 12

According to Debye's law, the molar heat capacity at constant volume of a diamond varies with the temperature as

$$C_V = 3R \frac{4\pi^4}{5} \left(\frac{T}{\Theta} \right)$$

what is the entropy change in units of R of a diamond of 1.2 g mass when it is heated at constant volume from 10 to 350 K. The molar mass of diamond is 12 g and Θ is 2230 K.

Solution

We have
$$\Delta S = n \int C_V \frac{dT}{T} + nR \int \frac{dV}{V}$$

since volume is kept constant $dV = 0$

$$\therefore \quad \Delta S = n \int_{10}^{350} C_V \frac{dT}{T}$$

$$n = \frac{1.2}{12} = 0.10$$

$$\Delta S = 0.10 \int_{10}^{350} 3R \frac{4\pi^4}{5} \frac{T^3}{\Theta^3} \frac{dT}{T}$$

$$\Delta S = \frac{0.10 \times 12\pi^4}{5\Theta^3} R \int_{10}^{350} T^2 dT$$

$$\Delta S = \frac{2.4\pi^4 R}{\Theta^3} \left[\frac{T^3}{3} \right]_{10}^{350}$$

$$\Delta S = \frac{0.8\pi^4 R}{\Theta^3} \left(350^3 - 10^3 \right)$$

$$\Delta S = \frac{0.8\pi^4 R}{2230^3} \left(350^3 - 10^3 \right)$$

$$\Delta S = \frac{0.8\pi^4 R(42875000 - 1000)}{2230^3}$$

$$\Delta S = 0.3006\,R$$

Entropy and reversibility

When a system undergoes an entropy change, it may absorb heat from the surroundings or reject heat to the surroundings. Thus in order to understand the entropy change it is necessary to learn the entropy change of the system as well as that of the surroundings. Then only the study will be completed. If ΔS_1 be the entropy change of the system and ΔS_2 be that of surroundings, then $\Delta S_1 + \Delta S_2$ is known as the entropy change of the universe.

Suppose a system is in contact with a reservoir. The system may absorb heat or reject to the reservoir. Though the reservoir can absorb or reject any amount of heat without change of its temperature it is due to the flow of heat in or out of the reservoir, entropy change is accompanied. If Q be the amount of heat absorbed by the reservoir at constant temperature T, then the entropy change of the reservoir is $+\frac{Q}{T}$.

If the heat flows out of the reservoir, the entropy change is $-\frac{Q}{T}$.

Now consider a reversible process in which $đQ_R$ be the amount of heat transferred to the reservoir at temperature T.

Then

$$\text{change in entropy of the system} = -\frac{đQ_R}{T}$$

$$\text{change in entropy of the reservoir} = +\frac{đQ_R}{T}$$

$$\therefore \quad \text{Entropy change of the reservoir} = -\frac{đQ_R}{T} + \frac{đQ_R}{T} = 0$$

If $đQ_R$ be the amount of heat rejected by the reservoir at constant temperature T, then

$$\text{entropy change of the system} = -\frac{đQ_R}{T}$$

$$\text{entropy change of the reservoir} = +\frac{đQ_R}{T}$$

$$\therefore \quad \text{Total entropy change of the universe} = \frac{đQ_R}{T} - \frac{đQ_R}{T} = 0$$

It shows that **for a reversible process the total change in entropy of the universe is zero.**

Remember that all natural processes are irreversible and only ideal processes are reversible.

Note: It may be noted that when heat is absorbed entropy change is positive.

Example 13

Calculate the entropy change of the universe as a result of

a) A copper block of 0.4 kg mass and with heat capacity at constant pressure of 150 JK^{-1} at 100°C is placed in a lake at 10°C

b) The same block at 10°C is dropped from a height of 100 m into the lake.

c) Two such blocks at 100°C and 10°C are joined together.

Solution

a) Entropy $$dS = \frac{đQ}{T} = C_P \frac{dT}{T}$$

change of entropy of copper $$\Delta S_1 = \int_{373}^{283} C_P \frac{dT}{T} = C_P \ln\frac{283}{383}$$

$$\Delta S_1 = 150 \times \ln\frac{283}{383} = -41.42\ JK^{-1}$$

change of entropy of the reservoir (lake)

$$\Delta S_2 = \frac{Q}{T} = \frac{mc_P(T_f - T_i)}{T_i}$$

$$\Delta S_2 = \frac{150(373-283)}{283} = 47.70$$

$mc_p = C_P$.

$\therefore$ Entropy change of the universe $= \Delta S_1 + \Delta S_2 = 6.28\ JK^{-1}$

b) Work done when it touches water = mgh

$$W = 0.4 \times 9.8 \times 100 = 392\,J$$

$$\therefore \quad (\Delta S)_{cu} = 0$$

$$(\Delta S)_{lake} = \frac{W}{T} = \frac{392}{283} = 1.385\ JK^{-1}$$

$$\therefore \quad (\Delta S)_{universe} = (\Delta S)_{cu} + (\Delta S)_{lake} = 1.385\ JK^{-1}$$

c) Final temperature of the block $= \frac{373+273}{2} = 323K$

$$(\Delta S)_I = C_P \int_{373}^{323} \frac{dT}{T} = 150 \ln \frac{323}{373} = -21.59\ JK^{-1}$$

$$(\Delta S)_{II} = C_P \int_{273}^{323} \frac{dT}{T} = 150 \ln \frac{323}{273} = 25.23\ JK^{-1}$$

$$(\Delta S)_{universe} = (\Delta S)_I + (\Delta S)_{II} = 3.64\ JK^{-1}.$$

Entropy and irreversibility

When a system undergoes an irreversible process the entropy change of the universe is entirely different. Suppose a system undergoes an irreversible process from an equilibrium state A to another equilibrium state B the change in entropy is

$$S_B - S_A = \int_{A}^{B} \frac{\text{đ}Q}{T}$$

since the process is irreversible the path of integration is not known. Thus integration cannot be performed. Then what we do is as the initial and final states are in equilibrium, choose an arbitrary path and perform the integration without changing the initial and final equilibrium states. This gives the entropy change of an irreversible process

i.e.
$$S_B - S_A = \int_{RA}^{B} \frac{\text{đ}Q}{T} \qquad ..... (21)$$

If the initial and final states are not in equilibrium some special methods are used. Depending upon the process of irreversibility, calculations are different.

1. External mechanical irreversibility processes

a) **Processes involving the isothermal dissipation of work through a system (remains unchanged) into internal energy of a reservoir is called external mechanical irreversibility processes.**

Examples

(i) Friction from two solids in contact with a reservoir.

(ii) Irregular stirring of a viscous liquid in contact with a reservoir.

(iii) Transfer of charge through a resistor in contact with a reservoir.

(iv) Magnetic hysterisis of a material in contact with a reservoir.

Calculation of entropy

According to first law, during an isothermal process Q = W.

i.e. Q be the amount of heat flows into the reservoir.

$$\therefore \quad \text{Entropy change of the reservoir} = \frac{Q}{T} = \frac{W}{T} \qquad \text{..... (22)}$$

As the system remains unchanged the entropy change of the universe is equal to entropy change of the reservoir, which is $\frac{Q}{T}$. As it is positive quantity entropy of the universe increases.

b) Now we consider **processes involving the adiabatic dissipation of work into the internal energy of a system open to the atmosphere.**

Examples

(i) Friction from rubbing thermally insulated liquids

(ii) Irregular stirring of a viscous liquid inside thermally insulated walls.

(iii) Transfer of charge through a thermally insulated resistor.

(iv) Magnetic hysteresis of a thermally insulated material

Calculation of entropy change

As the process is adiabatic $đQ = 0$. Here work goes over into internal energy of the system, whose temperature rises from T_A to T_B at constant atmospheric pressure. As there is no heat transfer to or from the surroundings, there is no change in entropy of the surroundings. To calculate the entropy change of the system, the original irreversible path is replaced by a reversible path without changing the initial equilibrium state (P, T_A) and the final equilibrium state (P, T_B).

∴ The entropy change of the system

$$S_B - S_A = \int_{RT_A}^{T_B} \frac{đQ}{T}$$

For an isobaric process $đQ = C_p dT$

$$\therefore \quad S_B - S_A = \int_{T_A}^{T_B} C_P \frac{dT}{T}$$

If C_p is constant

$$S_B - S_A = C_P \ln\frac{T_B}{T_A} \qquad \text{..... (23)}$$

Thus, the entropy change of the universe is same as the entropy change of the system. This is a positive quantity.

2. Internal mechanical irreversibility processes

When a system undergoes a process in which the internal energy of a system enclosed by adiabatic walls transformed into mechanical energy and then back into internal energy is called internal mechanical irreversibility process.

Examples

(i) Ideal gas rushing into vacuum (free expansion)

(ii) Gas flowing through a porus plug (Throttling process)

(iii) Collapse of a soap film after it is punctured.

Calculation of entropy change

As the system is enclosed by adiabatic walls there is no heat transfer into or from the surroundings. Thus the entropy change of the surroundings is zero. To calculate the entropy change of this irreversible system the process is replaced by a reversible path without changing the initial equilibrium state (V_A, T) and the final equilibrium state (V_B, T) of the irreversible process.

∴ The change in entropy of the system is

$$S_B - S_A = \int_{V_A}^{V_B} \frac{đQ_R}{T}$$

For an isothermal process

$$đQ_R = PdV$$

or

$$\frac{đQ_R}{T} = \frac{PdV}{T} = nR\frac{dV}{V}$$

∴

$$S_B - S_A = \int_{V_A}^{V_B} nR\frac{dV}{V}$$

$$S_B - S_A = nR\ln\frac{V_B}{V_A} \qquad \text{..... (24)}$$

Thus the entropy change of the universe is $nR\ln\frac{V_B}{V_A}$. This is again a positive quantity.

3. External thermal irreversibility processes

A process in which heat transfers from the system to surroundings or vice versa by virtue of a finite temperature difference is called as external thermal irreversibility process

Examples

(i) Conduction or radiation of heat from a system to its cooler surroundings.

(ii) Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

Calculation of entropy change

Let Q be the amount of heat transferred from one end to the other end of the system (remains unchanged) from a hot reservoir at temperature T_1, a cooler reservoir at temperature T_2.

$$S_B - S_A \text{ of the system} = 0$$

$$S_B - S_A \text{ of the hotter reservoir} = -\frac{Q}{T_1}$$

$$S_B - S_A \text{ of the cooler reservoir} = +\frac{Q}{T_2}$$

$$\therefore \quad S_B - S_A \text{ of the universe} = \frac{Q}{T_2} - \frac{Q}{T_1} \qquad \text{..... (25)}$$

Here again the entropy change of the universe is positive since $T_1 > T_2$.

Chemical irreversibility processes

Processes involving a spontaneous change of internal structure, density, chemical composition etc. are called chemical irreversibility processes.

Examples

(i) Diffusion of two dissimilar inert ideal gases.

(ii) Mixing of alcohol and water

(iii) Osmosis

(iv) Dissolution of solid in water

(v) A chemical reaction.

Calculation of entropy change

Consider mixing of two inert gases initially in separate adiabatic enclosures with equal volume V. Let A be the initial equilibrium state of the system. When they are allowed to mix they come to another equilibrium state B. While mixing this can be considered as two separate free expansions in an adiabatic enclosure.

The change entropy one gas is

$$S_B - S_A = nR\ln\frac{V_B}{V_A} \qquad \text{(equation 24)}$$

The change in entropy of the second gas is

$$S_B - S_A = nR\ln\frac{V_B}{V_A}$$

Entropy change of the universe due to irreversible processes

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal through a system into internal energy of a reservoir.	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system.	$C_P\ln\frac{T_f}{T_i}$	0	$C_p\ln\frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas.	$nR\ln\frac{V_f}{V_i}$	0	$nR\ln\frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir.	0	$\frac{Q}{T}-\frac{Q}{T_1}$	$\frac{Q}{T_2}-\frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases.	$2nR\ln\frac{V_f}{V_i}$	0	$2nR\ln\frac{V_f}{V_i}$

$\therefore$ change in entropy of the system (two gases) is

$$S_B - S_A = 2nR \ln \frac{V_B}{V_A} \qquad \text{..... (26)}$$

Since there is no change of entropy of the reservoir, the entropy change of the universe $= 2nR \ln \frac{V_B}{V_i}$, which is positive.

In general we can say that for any irreversible process the change of entropy is positive. i.e., for all irreversible processes the entropy of the universe increase.

Irreversible part of the second law

The irreversible part of the second law leads to Clausius' inequality or Clausius' inequality is the mathematical statement of the irreversible part of second law.

Clasius inequality theorem states that for any closed irreversible process

$$\oint \frac{đQ}{T} < 0$$

Proof

Consider a heat reservoir (source) at temperature T_1 supplying a small quantity of heat $đQ_1$ to a reversible engine R. The purpose of R is to provide heat for the irreversible engine I. Engine R rejects a small amount of heat $đQ_2$ at temperature T_2 that is supplied to the irreversible engine I. Engine I- does a small amount of work $đW$ during an irreversible cycle, so the combined system of engine R and engine I also performs as an irreversible cycle. The net work of the combined system, according to the first law, equals $\oint đQ_1$. But the net work cannot be positive according to the Kelvin-Planck statement of the second law, since the combined system exchanges heat with a single reservoir. So $\oint đQ_1$ cannot be positive. Moreover if $\oint đQ_1$ equals zero, then at the end of the cycle, engine I and its surroundings have returned to their

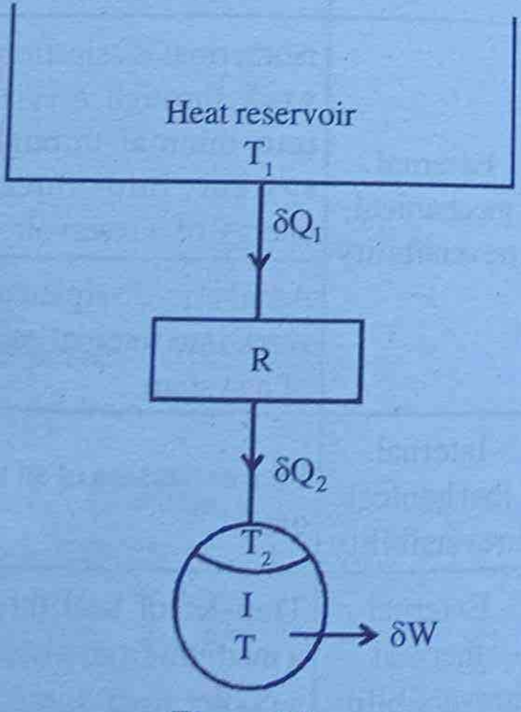


Figure 4.8

original state. This result is contrary to the irreversibility of engine I. So we conclude that

$$\oint đQ_1 < 0 \qquad \text{..... (1)}$$

For the reversible engine R, we have

$$\frac{đQ_1}{T_1} = -\frac{đQ_2}{T_2}$$

Integrating around a closed cycle, we get

$$\oint \frac{đQ_1}{T_1} = -\oint \frac{đQ_2}{T_2}$$

Since T_1 is constant (reservoir temperature)

$$\frac{1}{T_1}\oint_R đQ_1 = -\oint_R \frac{đQ_2}{T_2} \qquad \text{..... (2)}$$

The heat $đQ_2$ rejected from R is absorbed by I, we can write

$$(đQ_2)_R = -(đQ_2)_I$$

When this is substituted in eqn 2 on the right hand side, we get

$$\frac{1}{T_1}\oint_R đQ_1 = \oint_I \frac{đQ_2}{T_2}$$

or

$$T_1\oint_I \frac{đQ_2}{T_2} = \oint_R đQ_1$$

But $\oint_R đQ_1 < 0$ see eqn 1.

$$\therefore \qquad T_1\oint_I \frac{đQ_2}{T_2} < 0$$

Since $T_1 > 0$, we have

$$\oint_I \frac{đQ_2}{T_2} < 0$$

If $đQ$ is the heat absorbed by the irreversible engine at temperature T, we can write

$$\oint_I \frac{đQ}{T} < 0 \qquad \text{..... (3)}$$

This is known as clausius inequality.

Clausius' mathematical statement of second law

For a reversible process, we have

$$\oint_R \frac{đQ}{T} = 0 \qquad \text{..... (4)}$$

For an irreversible process, we have

$$\oint_I \frac{đQ}{T} < 0 \qquad \text{..... (5)}$$

Combining eqns 4 and 5, we get

$$\oint \frac{đQ}{T} \le 0 \qquad \text{..... (6)}$$

Remember that equality sign is for reversible process and inequality sign is for irreversible process. Equation 6 is the *clausius mathematical statement of second law.*

Heat and entropy in irreversible processes

Consider a system under goes an irreversible process (I) from an initial equilibrium state A to final equilibrium state B. The system comes back to initial equilibrium position by a reversible process (R) as shown in figure below.

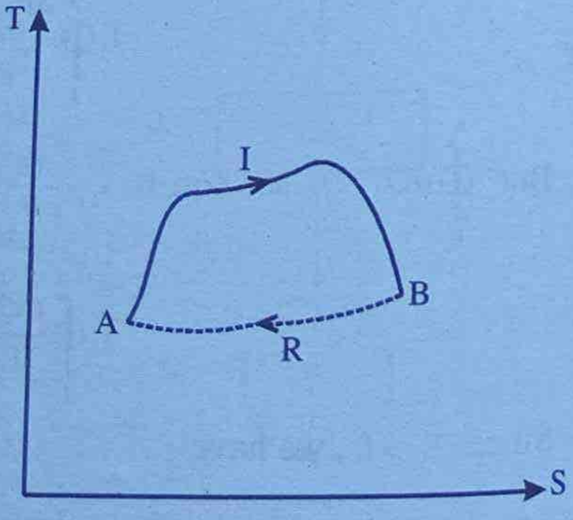


Figure 4.9

The entropy of a closed system is

$$\oint dS = {}_I\!\int_A^B dS + {}_R\!\int_A^B dS \qquad \text{..... (27)}$$

since entropy is a state function

$$\oint dS = 0\,.$$

$$0 = {}_{I}\int_{A}^{B} dS + {}_{R}\int_{A}^{B} dS$$

i.e.

$${}_{-R}\int_{A}^{B} dS = {}_{I}\int_{A}^{B} dS$$

or

$${}_{R}\int_{A}^{B} dS = {}_{I}\int_{A}^{B} dS$$

But from Clausius's inequality theorem we have

$${}_{I}\oint \frac{\text{đ}Q}{T} = {}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T} + {}_{R}\int_{B}^{A} \frac{\text{đ}Q}{T} \propto 0 \qquad \text{..... (28)}$$

From the definition of entropy

$${}_{R}\int_{A}^{B} \frac{\text{đ}Q}{T} = {}_{R}\int_{A}^{B} dS$$

i.e.,

$${}_{I}\oint \frac{\text{đ}Q}{T} = {}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T} + {}_{R}\int_{B}^{A} dS < 0 \qquad \text{..... (29)}$$

i.e.,

$${}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T} + {}_{R}\int_{B}^{A} dS < 0$$

or

$${}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T} - {}_{I}\int_{A}^{B} dS < 0 \qquad \left(\because \quad {}_{R}\int_{B}^{A} dS = {}_{I}\int_{B}^{A} dS\right)$$

or

$${}_{I}\int_{A}^{B} dS - {}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T} > 0$$

$${}_{I}\int_{A}^{B} dS > {}_{I}\int_{A}^{B} \frac{\text{đ}Q}{T}$$

This shows that the change of entropy during irreversible process is greater than the integral of the heat divided by temperature of the reservoir. For infinitesimal changes in state the above inequality can be written as

$$dS_{I} > \left(\frac{\text{đ}Q}{T}\right)_{I}$$

For reversible process, we have

$$dS_R = \left(\frac{\text{đ}Q}{T}\right)_R$$

combining the two we can write

$$dS \geq \frac{\text{đ}Q}{T} \qquad \text{..... (30)}$$

while dealing with entropy we should be careful about whether it is reversible or irreversible.

According to the definition of entropy

$$dS = \frac{\text{đ}Q_R}{T}$$

For a reversible adiabatic process $\text{đ}Q_R = 0$ implies $dS = 0$.

$dS = 0$ means that entropy is constant thus we call this as isentropic.

Suppose we consider an irreversible isentropic process. Obviously $dS = 0$, but

$$\frac{\text{đ}Q}{T} < 0$$

i.e. $\text{đ}Q < 0$ so not adiabatic.

In general isentropy does not mean that it is adiabatic. Only reversible isentropic implies adiabatic. Irreversible isentropic implies not adiabatic.

Principle of increase of entropy

We calculated the change in entropy of universe for several irreversible processes. In all processes it is seen that the entropy of the universe increases. This is known as the entropy principle. Now we want to establish this statement. For this we consider a cyclic process in which a system undergoes an irreversible adiabatic process, a reversible adiabatic process, reversible isothermal process and a reversible adiabatic process and finally comes back to the initial state. These processes are depicted in a work diagram as shown 4.10.

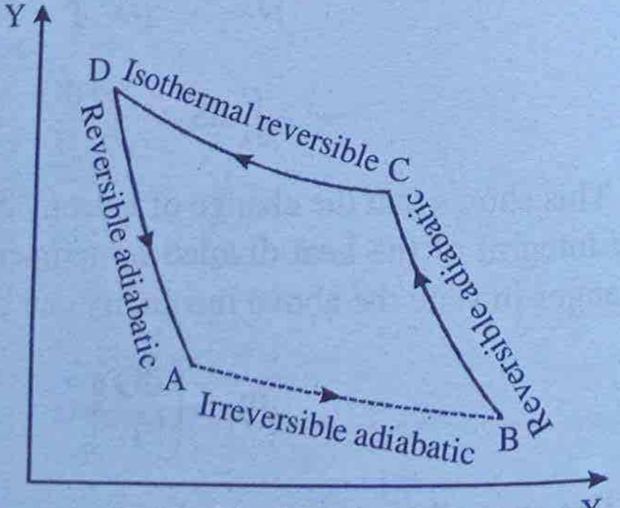


Figure 4.10

Let A be the initial state of the system. Suppose the system undergoes an irreversible adiabatic process to the state B. Then the change in entropy is

$$\Delta S = S_B - S_A \quad \text{..... (31)}$$

The temperature of the system may or may not change.

Now let the system undergo a reversible adiabatic process to the state C in such a way that temperature changes infinitesimally through a sequence of process finally attaining a temperature T' of an arbitrarily chosen reservoir. Since B and C are at the same adiabatic points we can very well write

$$S_B = S_C$$

Thus equation 31, becomes

$$\Delta S = S_C - S_A \quad \text{..... (32)}$$

Now the system is at C in contact with the reservoir at T'. the system at C is allowed to undergo a reversible isothermal process until the system attains an entropy same as in the state A. The system is now at the state D having the same entropy of the system at A.

i.e.
$$S_D = S_A$$

The equation 32 now becomes

$$\Delta S = S_C - S_D \quad \text{..... (33)}$$

Finally the system at D is allowed to undergo a reversible adiabatic process to arrive at the initial state A.

In the entire cyclic process heat transfer occur only during the reversible isothermal process $(C \to D)$. the heat transferred

$$Q_R = T'(S_D - S_C) \quad \text{..... (34)}$$

The net work done in the cycle is

$$W = Q_R$$

According to second law of thermodynamics Q_R cannot be positive that is heat cannot have entered the system, for then we would have a cyclic process where the only effect would be the absorption of heat from a single reservoir and the performance of an equivalent amount of work.

$$\therefore \quad Q_R \leq 0$$

Putting this in equation 34

$$T'(S_D - S_C) \leq 0$$

or

$$T'(S_C - S_D) \geq 0$$

since $T' \geq 0$

$$S_C - S_D \geq 0$$

or

$$\Delta S \geq 0.$$

If we assume that the original irreversible adiabatic process would have occurred without any change in entropy, then it would be to bring the system back to the initial position by means of one reversible adiabatic process. Moreover since the net heat transferred in this cycle is zero, no work would be done. Therefore under these circumstances the system its surroundings would have been restored without producing any changes, which implies that the original process was reversible. Since this is contrary to our assumption that the process was irreversible, the entropy of the system cannot remain unchanged

$$\therefore \qquad \Delta S > 0.$$

Since entropy could not have decreased.

Application of entropy principle

According to the entropy principle for all irreversible processes entropy of the universe increases. When applying this principle to machines such as engines or refrigerator we can gather information regarding the behaviour of the machine.

For example consider a refrigerator operating between temperature T_1 and T_2. Suppose a quantity of heat Q is removed from an object inside the refrigerator by doing W amount of work. Then the body goes from its initial state to final state B.

$$\Delta S \text{ of the body} = S_B - S_A$$

$$\Delta S \text{ of the refrigerant} = 0$$

$$\Delta S \text{ of the reservoir} = \frac{Q + W}{T_1}$$

Since $Q + W$ amount of the heat is rejected to the reservoir.

Applying the entropy principle

$$\Delta S \geq 0, \text{ we get}$$

$$S_B - S_A + \frac{Q+W}{T_1} \geq 0$$

Multiplying T_1 yields.

$$T_1(S_B - S_A) + Q + W \geq 0$$

or

$$W \geq T_1(S_A - S_B) - Q$$

∴

$$(W)_{min} = T_1(S_A - S_B) - Q$$

Knowing T_1, S_A, S_B and Q, the minimum work required to be calculated. It provides us an estimate of the minimum cost of operation of the refrigerator.

Entropy and disorder

We know that all natural processes are irreversible. For all irreversible processes entropy increase. This is because when a system undergoes an irreversible process, the order of the final state is less than the order of the initial state. In other words when the disorder increases entropy increases. That is an increase of entropy of a system can be described as an increase in the disorder of the system. No we will see that how entropy is connected with disorder by taking several examples of irreversible processes.

Examples

1. Consider a solid in its initial state. The particles which are the constituents the solid are infinite order. When the solid is allowed to undergo an irreversible process by supplying heat to it sublimation occurs. During sublimation there is no change in temperature at the same time system absorbs heat (Q). The entropy change can be calculated by $\frac{Q}{T}$, which is positive. We can say that entropy increases. The final state of the solid is obviously vapour. The particles which are the constituents vapour occupy greater volume and particles are in random motion. So the final state is disordered than the initial state.
2. Consider the case of isothermal expansion of an ideal gas. As the gas absorbs heat it expands slowly. At the end of the process the gas occupies a larger volume. The gas molecules are more disordered now. We say that the entropy of the gas has increased because the amount of disorder has increased. At the same time we already proved that during isothermal expansion the entropy increases.

3. Now we consider a ferromagnetic material, its magnetic dipole moments are mostly aligned in one direction i.e., initially ferromagnetic material is in ordered state. When the material is heated to a temperature above Curie temperature phase change occurs and it is an irreversible process. The system now attains another state exhibiting the behaviour of paramagnetic material in which magnetic dipole moments are randomly oriented (disordered). It is due to this behaviour entropy of the system increases.

The above discussions show that entropy of a system and it surroundings will always increase during irreversible processes. i.e., entropy of an irreversible process move always forward. Metamorphically we say entropy is the arrow of time.

Exact differentials

According to first law of thermodynamics

$$đQ = dU + đW$$

or

$$dU = đQ - đW$$

on the L.H.S we have an exact differential. On the R.H.S both are inexact differentials. Then how it is consistent. In mathematics there is a technique of converting inexact differential into exact differential by multiply with an integrating factor. The same technique is followed in thermodynamics. We defined work done as

$$đW = PdV$$

or

$$\frac{đW}{P} = dV$$

Here đW is inexact, by multiply with an integrating factor it becomes an exact differential dV. Or writing

$$đW = PdV$$

it becomes an exact differential. Remember that only for quasistatic infinitesimal process it is valid.

Similarly the inexact differential đQ can be converted into exact differential with the help of definition of entropy, we have

$$dS = \frac{đQ}{T}$$

Here dS is an exact differential as it is a state function. However, đQ is inexact since it depends on path. The definition of temperature enables us to convert inexact differential $đQ$ into an exact differential by multiplying with an integrating factor $\frac{1}{T}$.

$$đQ = TdS$$

or

The first law of thermodynamics can be rewritten as

$$dU = TdS - PdV$$

Now both sides are exact differentials.

Note : While writing the first law of thermodynamics we didn't use sign convention. Even if use sign convention nothing happens to final equation.

IMPORTANT FORMULAE

1. For any reversible cycle: $\oint \frac{đQ_R}{T} = 0$

2. Change in entropy: $S_B - S_A = {}_R\int_A^B \frac{đQ}{T}$

   or $dS = \frac{đQ_R}{T}$

3. Entropy of the ideal gas.

   (i) In terms of T and V

$$\frac{đQ}{T} = C_V \frac{dT}{T} + nR\frac{dV}{V}$$

   or $S = C_V \ln T + nR \ln V + S_0$

   (ii) In terms of T and P

$$\frac{đQ_R}{T} = C_P \frac{dT}{T} - nR\frac{dP}{P}$$

   or $S = C_P \ln T - nR \ln P + S_0$.

   (iii) In terms of P and V

$$\frac{đQ_R}{T} = C_P \frac{dV}{V} + C_V \frac{dP}{P}$$

   or $S = C_P \ln V + C_V \ln P + S_0$.

4. In TS diagram slopes are

(i) $\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$

(ii) $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$

$$\left(\frac{\partial T}{\partial S}\right)_V > \left(\frac{\partial T}{\partial S}\right)_P$$

5. Entropy of reversible processes

   (i) Change in entropy of a Carnot cycle

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

   (ii) Total entropy change of the universe = 0.

6. Entropy and irreversibility.

   (i) The entropy change,

$$S_B - S_A = \int_A^B \frac{đQ}{T}$$

   (This integral cannot be calculated)

   (ii) Entropy change in external mechanical irreversibility process.

   (a) Isothermal dissipation of work through the system into internal energy of the reservoir.

   Entropy change of the system = 0

   Entropy change of the surroundings = $\frac{W}{T}$

   Entropy change of the universe = $\frac{W}{T}$.

   (b) Adiabatic dissipation of work into internal energy of the system.

   Entropy change of the system = $C_P \ln \frac{T_B}{T_A}$

   Entropy change of the surroundings = 0

   Entropy change of the universe = $C_P \ln \frac{T_B}{T_A}$.

(iii) Entropy change in internal mechanical irreversibility process.

(a) Free expansion of ideal gas.

Entropy change of the system = $nR\ln\frac{V_B}{V_A}$

Entropy change of the surroundings = 0

Entropy change of the universe = $nR\ln\frac{V_B}{V_A}$.

(iv) Entropy change in external thermal irreversibility process.

(a) Transfer of heat through a medium from a hotter to a cooler reservoir.

Entropy change of the system = 0

Entropy change of the surroundings = $\frac{Q}{T_B}-\frac{Q}{T_A}$

Entropy change of the universe = $\frac{Q}{T_B}-\frac{Q}{T_A}$.

(v) Entropy change in chemical irreversibility process.

(a) Diffusion of two dissimilar inert ideal gases.

Entropy change of the system = $2nR\ln\frac{V_B}{V_A}$

Entropy change of the surroundings = 0

Entropy change of the universe = $2nR\ln\frac{V_B}{V_A}$.

7. Clausius' theorem: $\oint\frac{đQ}{T}\le 0$

8. Change in entropy of ice at 0°C is converted into steam

$$\Delta S=\frac{mL_{ice}}{T_{ice}}+mC\int_{273}^{373}\frac{dT}{T}+\frac{mL_{steam}}{T_{steam}}$$

$$L_{ice}=336\times10^3\,\mathrm{J\,kg^{-1}}$$

$$L_{steam}=2268\times10^3\,\mathrm{J\,kg^{-1}}$$

C = specific heat of water

$=4200\,\mathrm{J\,kg^{-1}\,K^{-1}}$.

9. When equal amount of water at one at temperature T_1 the other at temperature T_2 are mixed adiabatically and isobarically

$$(\Delta S_3)_I = \int_{T_1}^{T_f} \frac{đQ}{T},\ (\Delta S)_{II} = \int_{T_2}^{T_f} \frac{đQ}{T}$$

where $T_f = \dfrac{T_1 + T_2}{2}$ and $đQ = C_P dT$

$$\Delta S = (\Delta S)_I + (\Delta S)_{II}$$

10. When two different liquids of masses m_1 and m_2, specific heats c_1 and c_2 and temperatures T_1 and T_2 respectively are mixed.

Final temperature

$$T_f = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2}$$

$$(\Delta S)_I = \int_{T_1}^{T_f} \frac{m_1c_1dT}{T},\ (\Delta S)_{II} = \int_{T_2}^{T_f} \frac{m_2c_2dT}{T}$$

Total change in entropy

$$\Delta S = (\Delta S)_I + (\Delta S)_{II}$$

UNIVERSITY MODEL QUESTIONS

Section A

(*Answer questions in about* **two** *or* **three** *sentences*)

Short answer type questions

1. What is work diagram?
2. State Clausius' theorem for a reversible process.
3. Define entropy. What is its unit?
4. Express entropy change of ideal gas in terms of temperature and pressure.
5. Express entropy change of ideal gas in terms of pressure and temperature.
6. Express entropy change of ideal gas in terms of pressure and volume.
7. What enables us to draw TS diagram?
8. What is a TS diagram?
9. What are the advantages of TS diagram over PV diagram?
10. Draw a TS diagram for a Carnot cycle.

11. Show that entropy is a constant for a reversible adiabatic process.
12. Show that $\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$.
13. Show that $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$.
14. Draw isochoric and isobaric curve on a TS diagram.
15. What is meant by entropy change of the universe?
16. Mention four types of irreversibility processes.
17. What is external mechanical irreversibility process?
18. Give two examples of external mechanical irreversibility process.
19. Define internal mechanical irreversible process.
20. Give two examples for internal mechanical irreversibility process.
21. What is meant by chemical irreversibility process?
22. Give two examples of chemical irreversible process.
23. When a system is said to undergo thermal irreversible process?
24. Give two examples of thermal irreversible process.
25. State Clausius' theorem.
26. Write down the Clausius mathematical statement of second law and explain the symbols.
27. In general isentropic does not mean that adiabatic. Justify.
28. Distinguish between isentropic process and adiabatic process.
29. What is meant by entropy principle?
30. What is the relation between entropy and disorder?
31. How will you convert an inexact differential into exact differential?

Section B

(*Answer questions in a* **paragraph** *of about half a page to one page*)

Paragraph / Problem type questions

1. For a reversible process show that heat transferred in an isothermal process can be made equal to that in an adiabatic-isothermal-adiabatic process.
2. Prove Clausius' theorem for a reversible cyclic process.
3. Prove that entropy is a state function.
4. Show that for a Carnot cycle entropy remains constant.
5. Derive an expression for the entropy of ideal gas in terms of temperature and volume.
6. Derive an expression for the entropy of ideal gas in terms of pressure and temperature.

7. Derive an expression for the entropy of ideal gas in terms of pressure and volume.
8. Define entropy. What is its unit?
9. Derive an expression for entropy.
10. Show that during an adiabatic process entropy remains constant.
11. A current of 10A is maintained for 1s in a resistor of 25 Ω while the temperature of resistor is kept constant. What is the entropy change of the universe. [$8.33\,\text{JK}^{-1}$]
12. One kilogram of water at 273K is brought into contact with a heat reservoir at 373 K. When the water has reached 373K, what is the entropy change of the water, of the heat reservoir and of the universe. [$1311\,\text{JK}^{-1}, -1126\,\text{JK}^{-1}, 185\,\text{JK}^{-1}$]
13. A 1μF capacitor is connected to a 100V electrochemical cell at 0°C. Calculate the change in entropy. [$1.83\times10^{-5}\,\text{JK}^{-1}$]
14. Show that an isochoric curve plotted on a T-S diagram have a greater slope than an isobaric curve at the same temperature.
15. Calculate the change in entropy of the universe if a quantity of 100kJ is transferred from a reservoir at 553K to another reservoir at 278K. [$1.449\times10^{3}\,\text{JK}^{-1}$]
16. Show that area of the rectangle of a TS diagram of a Carnot cycle gives the work done.
17. Derive an expression for efficiency from TS diagram of a Carnot engine.
18. Show that for a reversible process the total change in entropy of the universe is zero.
19. How to calculate the entropy change of an irreversible process?
20. Calculate the change in entropy of the universe when a system undergoes external mechanical irreversible process.
21. Calculate the change in entropy of the universe when a system undergoes internal mechanical irreversible process.
22. Calculate the change in entropy of the universe when a system undergoes external thermal irreversibility process.
23. Calculate the change in entropy of the universe when a system undergoes chemical irreversible process.
24. Prove Clausius' inequality theorem.
25. Show that $dS \geq \dfrac{dQ}{T}$
26. Applying the entropy principle to a refrigerator calculate the minimum amount of work required to be done.
27. An increase of entropy of a system can be described as an increase in the disorder of the system. Justify.

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

1. State and prove Clausius theorem for entropy and write down Clausius mathematical statement of second law.
2. Derive the expression for the change in entropy of perfect gas in terms of
   (i) T and V (ii) T and P (iii) P and V.

Hints to problems

8. See example 1
9. See example 2
10. $dS = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right), \frac{V_2}{V_1} = 1$
11. $dS = \frac{\delta Q}{T} = \frac{I^2 Rt}{T} = \frac{10^2 \times 25 \times 1}{300}$
12. Entropy change of water (gain)

$$dS = \int_{273}^{373} \frac{\delta Q}{T} = \int_{273}^{373} ms \frac{dT}{T}$$

$$= 1 \times 10^3 \int_{273}^{373} \frac{dT}{T} = 10^3 \ln\left(\frac{373}{273}\right) \text{cal/K}$$

Entropy change of reservoir (loss)

$$dS = \frac{\delta Q}{T} = ms \frac{dT}{T}$$

$$= 1 \times 10^3 \times \frac{(373 - 273)}{373} = 268.1 \text{ cal/K}$$

Entropy change of the universe

$$= 1311 - 1126 = 185 \text{JK}^{-1}$$

13. $dS = \frac{\delta Q}{T} = \frac{\frac{1}{2} CV^2}{T} = \frac{\frac{1}{2} \times 10^{-6} \times (100)^2}{273}$

14. $\left(\frac{dT}{dS}\right)_V = \frac{T}{C_V}$ see problem 4

$$\left(\frac{dT}{dS}\right)_P = \frac{T}{C_P} \quad \text{see problem 5}$$

$$\therefore \quad \frac{(dT/dS)_V}{(dT/dS)_P} = \frac{C_P}{C_V} = \gamma > 1$$

$$\therefore \quad \left(\frac{dT}{dS}\right)_V > \left(\frac{dT}{dS}\right)_P$$

15. Change in entropy of the reservoir at 553 K,

$$dS = \frac{\delta Q}{T} = \frac{100 \times 10^3}{553} = 1808.3$$

Change entropy of the reservoir at 278 K,

$$dS = \frac{\delta Q}{T} = \frac{100 \times 10^3}{278} = 359.71$$

$$\therefore \quad \text{Net change} = 1808.3 - 359.71$$

$$= 1.449 \times 10^3 \, JK^{-1}$$

16. See book work
17. See book work
18. See book work
19. See book work
20. See book work
21. See book work
22. See book work
23. See book work
24. See book work
25. See book work
26. See book work
27. See book work

UNIT FIVE

THERMODYNAMIC POTENTIALS AND PHASE TRANSITIONS

Introduction

We are familiar with five thermodynamic variables P, V, T, S and U. But according to first law of thermodynamics

$$đQ = dU + PdV$$

From the definition of entropy

$$đQ = TdS$$

$$\therefore \quad TdS = dU + PdV$$

$$\text{or} \quad dU = TdS - PdV \qquad \text{.....} (1)$$

This equation says that the fifth thermodynamic variable U is determined by P, V, T and S. This is the reason why only four thermodynamic variable are defined. Out of the four thermodynamic variables only two variable are required to describe the system completely. Taking two of the four thermodynamic variables P, V, T and S at a time there are six possible pairs. They are (P, V), (P, T), (P, S), (V, T), (V, S), and (T, S). The pairs (P, V) and (T, S) do not occur separately because in the basic equation (1) TdS forms one unit and PdV forms another and they do not occur separately. Thus we are left with four pairs of thermodynamic variables (P, T), (P, S), (V, T) and (V, S). Corresponding to each pair we can associate a function called thermodynamic function or thermodynamic potential. In equation (1) we can very well see that U is a function of (S, V). Similarly we have three more functions. The thermodynamic function associated with (T, V) pair is called Helmholtz function or free energy (A), that associated with the pair (S, P) is called enthalpy (H) and the function associated with the pair (T, P) is called Gibbs function (G).

Look at the functions carefully

(S, V),	(T, V),	(T, P),	(P, S)
I	II	III	IV

Going from set I to set II only one variable is changed

Going from set II to set III only one variable is changed

Similarly going from III to IV again one variable is changed. This enables us go from I to II, II to III and III to IV by a mathematic technique called Legendre transformation.

Characteristic functions

Legendre transformation

If the state of the system is described by a function f of two variables (x, y)

i.e.,
$$f = f(x, y)$$

Taking differential on both sides

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy \qquad \text{..... (2)}$$

Let $\frac{\partial f}{\partial x} = u$ and $\frac{\partial f}{\partial y} = v$

$$\therefore \qquad df = u\,dx + v\,dy \qquad \text{..... (3)}$$

Now we want to change the variables (x, y) to (u, y). We get a new function g(u, y) which can be expressed in terms of the differentials du and dy. Let g be a function of new variables u and y defined by the equation

$$g = f - ux \qquad \text{..... (4)}$$

Taking differential on both sides, we get

$$dg = df - udx - xdu$$

Putting the value of df, yields

$$dg = udx + vdy - udx - xdu$$

or
$$dg = -xdu + vdy \qquad \text{..... (5)}$$

which is exactly the desired form. From equation 5 we get

$$x = -\left(\frac{\partial g}{\partial u}\right)_y \quad v = \left(\frac{\partial g}{\partial y}\right)_x$$

Enthalpy (H)

We have

$$dU = -PdV + TdS$$

$$U = U(V, S)$$

we want to generate a function called enthalpy (H) which depends on (P, S) we make use of equation 4

$$H = U - -PV = U + PV$$

i.e.

$$H = U + PV \qquad \ldots\ldots (6)$$

Since U, P and V are state function enthalpy is also a state function.

From equation 6, we get

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP \qquad \ldots\ldots (7)$$

Thus H is obviously a function of (S, P)

Helmholtz function A

A is a function of (T, V) and U is function of (S, V). So we can go over from U to A by Legendre transformation using equation 4, we get

$$A = U - TS \qquad \ldots\ldots (8)$$

Taking the differential

$$dA = dU - TdS - SdT$$

Substituting for dU, we get

$$dA = TdS - PdV - TdS - SdT$$

or

$$dA = -PdV - SdT \qquad \ldots\ldots (9)$$

Thus A is obviously a function of (T, V).

Gibbs function G

G is a function of (P, T) and A is a function (V, T). This shows that we can go over from A to G by Legendre transformation. Using equation (4) we can define G.

$$G = A - -PV$$

$$G = A + PV \qquad \ldots\ldots (10)$$

Taking differentials on both sides, we get

$$dG = -PdV - SdT + PdV + VdP$$

$$dG = VdP - SdT \qquad \ldots\ldots (11)$$

Thus G is obviously a function of P and T.

Altogether we obtained four differential equations that are formulations of first law of thermodynamics we collect all together

$$dU = -PdV + TdS \quad : \quad U(V,S)$$

$$dH = VdP + TdS \quad : \quad H(P, S)$$

$$dA = -PdV - SdT \quad : \quad A(V, T)$$

$$dG = VdP - SdT \quad : \quad G(P, T)$$

The main advantage of this formulation is that for example when a system undergoes changes in V and S then it is convenient to use differential equation for U. If P and T are convenient variables for describing a system we go for G. Similarly others.

The functions $U(V, S), H(P, S), A(V,T)$ and (G, P) are called thermodynamic potential functions. This is because they have the property that if functions are expressed in terms of appropriate thermodynamic variables, then all the thermodynamic properties of a system can be calculated by differentiation only.

Examples

(i) U is a function of V and S

i.e., $$U = U(V, S)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$$

we already have

$$dU = -PdV + TdS$$

comparing the two equations, we get

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \text{ and } \left(\frac{\partial U}{\partial S}\right)_V = T$$

(ii) H is a function of P and S

$$H = H(P, S)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_S dP + \left(\frac{\partial H}{\partial S}\right)_P dS$$

we have $$dH = VdP + TdS$$

on comparing we get

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{and} \quad \left(\frac{\partial H}{\partial S}\right)_P = T$$

see also examples 2 and 3.

Example 1

Show that the Legendre transformation of $S(U, V)$ that produces the characteristic function $J\left(\frac{1}{T}, V\right)$ known as Massien function is given by the transform

$$J = -\frac{U}{T} + S = -\frac{A}{T}$$

and

$$dJ = \frac{U}{T^2}dT + \frac{P}{T}dV$$

Solution

$$S = S(U, V)$$

$$J = S - \frac{U}{T} \qquad \text{..... (1)}$$

or

$$J = S - \frac{(A+TS)}{T} \qquad A = U - TS$$

$$\because \quad A = U - TS$$

$$\therefore \quad J = -\frac{A}{T}$$

Taking differential on both sides of eq (1), we get

$$dJ = dS + \frac{U}{T^2}dT - \frac{1}{T}dU$$

Substituting for $dU = TdS - PdV$, we get

$$dJ = dS + \frac{U}{T^2}dT - \frac{TdS}{T} + \frac{PdV}{T}$$

or

$$dJ = \frac{U}{T^2}dT + \frac{PdV}{T}$$

Example 2

Show that $\left(\frac{\partial A}{\partial V}\right)_T = -P$ and $\left(\frac{\partial A}{\partial T}\right)_V = -S$

Solution

We know that $A = A(V, T)$. Taking differentials on both sides, yields

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

we have the relation

$$dA = -PdV - SdT$$

on comparing we get

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S.$$

Example 3

Show that $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$

Solution

We know that $G = G(P, T)$

Taking differentials on both sides, we get

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

We have the relation

$$dG = VdP - SdT$$

on comparing we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Example 4

Derive the relation $U = A - T\left(\frac{\partial A}{\partial T}\right)_V$

$$= -T^2 \left(\frac{\partial (A/T)}{\partial T} \right)_V$$

Solution

We have $$U = A + TS \qquad \text{..... (1)}$$

Using $$\left(\frac{\partial A}{\partial T} \right)_s = -S$$

$$U = A - T\left(\frac{\partial A}{\partial T} \right)_V$$

$$\left[\frac{\partial}{\partial T}\left(\frac{A}{T} \right) \right]_V = -A \cdot \frac{1}{T^2} + \frac{1}{T}\left(\frac{\partial A}{\partial T} \right)_V$$

or $$T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T} \right) \right]_V = -A + T\left(\frac{\partial A}{\partial T} \right)_V$$

or $$-T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T} \right) \right]_V = A - T\left(\frac{\partial A}{\partial T} \right)_V = A + TS = U.$$

Example 5

Show that $$C_V = -T\left(\frac{\partial^2 A}{\partial T^2} \right)$$

Solution

We have $U = A + TS$

Differentiate with respect to T, keeping V constant

$$\left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial A}{\partial T} \right)_V + T\left(\frac{\partial S}{\partial T} \right)_V + S$$

or $$\left(\frac{\partial U}{\partial T} \right)_V = -S + T\left(\frac{\partial S}{\partial T} \right)_V + S$$

Use
$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$$\therefore \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

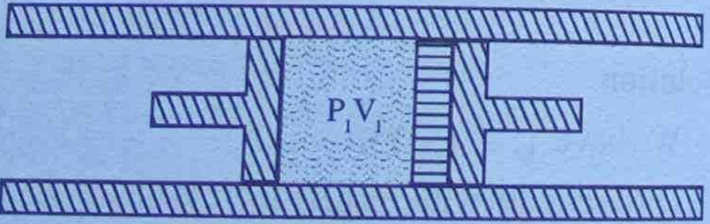
Using
$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

$$\therefore \quad C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V$$

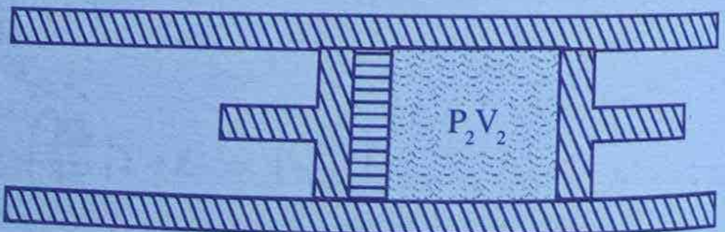
Enthalpy-Joule-Thomson expansion or Throttling process

The throttling process is also known as a porus plug process or a Joule - Thomson expansion. To understand this process consider a cylinder thermally insulated and provided with two adiabatic pistons on opposite sides of a porus wall which is also adiabatic (see figure below). The porus wall allows the gas (system) to flow from one side to another while changing pressure. Between the left hand side piston and the porus wall there is a gas at pressure P_1 and volume V_1. Since the right hand piston against the wall prevents any gas from seeping through the porus plug, the initial state of the gas is an equilibrium state contained between the two pistons. Now imagine that both pistons move simultaneously at different speeds to the right such that a constant higher pressure P_1 is maintained on the left hand side of the porus wall and a constant lower pressure P_2 is maintained on the right hand side. After all the gas flowed through the porus plug, the final equilibrium state of the system is reached (see figure 5.1). This is called a throttling process or a Joule-Thomson expansion.

This throttling process is an irreversible process due to friction between the gas and the walls of the pores in the plug. In otherwords, the gas passes through dissipative non-equilibrium states



(a) Initial state



(b) Final state

Figure 5.1

on its way from initial equilibrium state to the final equilibrium state. These intermediate non-equilibrium states cannot be described by thermodynamic coordinates, but an interesting conclusion can be drawn about the initial and final equilibrium states, which are described by the thermodynamic coordinates.

From the first law we have

$$dU = \text{đ}Q + \text{đ}W$$

or

$$U_2 - U_1 = Q - \int PdV \qquad \because \quad \text{đ}W = PdV$$

Since the throttling process occurs in an adiabatic enclosure $Q = 0$, we get

$$U_2 - U_1 = -\int PdV \qquad \text{.....(12)}$$

The right hand side is the work done on the system.

$$-\int PdV = -\int_{V_1}^{0} P_1 dV - \int_{0}^{V_2} P_2 dV$$

$$-\int PdV = +P_1V_1 - P_2V_2$$

Now equation 12 becomes

$$U_2 - U_1 = +P_1V_1 - P_2V_2$$

or

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1 \qquad \text{.....(13)}$$

Note: It is not correct to say that enthalpy remains constant during a throttling process since it is an irreversible process and passing through non-equilibrium states and we cannot predict what is happening in the intermediate states.

Other properties of enthalpy

1. We have

$$dH = TdS + VdP \qquad \text{.....(14)}$$

or

$$dH = \text{đ}Q + VdP$$

Dividing throughout by dT, we get

$$\frac{dH}{dT} = \frac{\text{đ}Q}{dT} + \frac{VdP}{dT}$$

At constant pressure

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{đQ}{dT}\right)_P$$

By definition $$\left(\frac{đQ}{dT}\right)_P = C_P$$

i.e., $$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad \text{..... (15)}$$

Equation 14 shows that the function enthalpy H is related to an experimental quantity the specific heat capacity at constant pressure. This equation provides a means of calculating the enthalpy from C_P.

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

or $$H_2 - H_1 = \int_1^2 C_P dT \qquad \text{..... (16)}$$

For an ideal gas C_P is a constant, thus

$$H_2 - H_1 = C_P(T_2 - T_1)$$

2. For an isobaric process, equation 14 becomes

$$dH = TdS$$

or $$dH = đQ$$

i.e., $$H_2 - H_1 = Q_P \qquad \text{..... (17)}$$

This shows that the change in enthalpy during an isobaric process is equal to the heat that is transferred between the system and the surroundings.

3. For an adiabatic process, equation 14 becomes

$$dH = VdP \qquad \text{integrating}$$

$$H_2 - H_1 = \int_1^2 VdP \qquad \text{..... (18)}$$

R.H.S is the area under the curve of PV diagram projected to the pressure axis.

In an $x-y$ graph we can have two areas under the curve one is $-\int ydx$ and the other one is $\int xdy$. $-\int ydx$ is the area under the curve projected on to x-axis and $\int xdy$ is the area of the curve projected onto the y-axis as shown in figure below.

Similarly in PV diagram the area under the curve which give work done are of two type 1) $-\int PdV$ 2) $\int VdP$. See figure below.

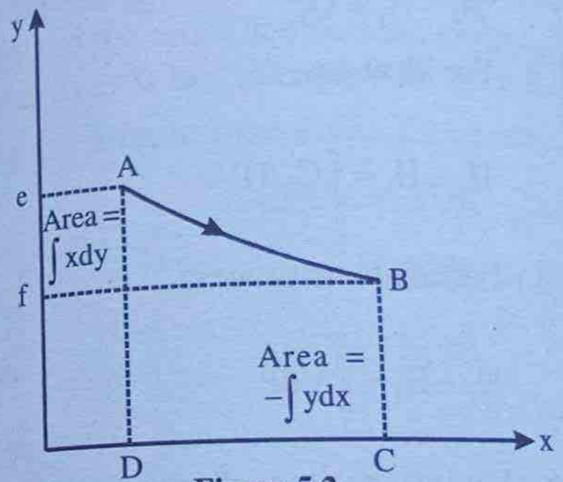


Figure 5.2

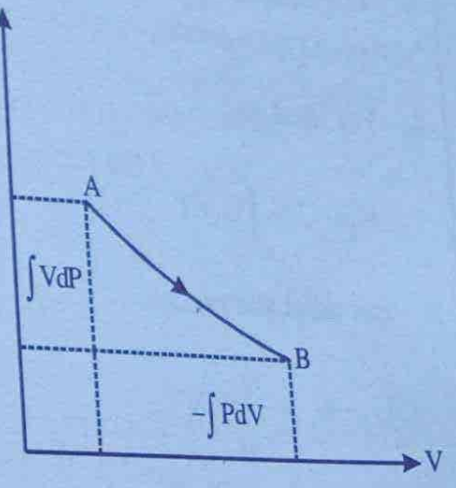


Figure 5.3

Note: $-\int PdV$ is the adiabatic work and $\int VdP$ is the flow work.

4. For a reversible isobaric-adiabatic process equation 14 becomes

$$dH = 0$$

or

$$H = \text{constant}$$

Thus enthalpy is defined as that something which remains constant during a reversible isobaric-adiabatic process.

Comparison of properties of U and H of a hydrostatic system

Internal energy U(V, S)	**Enthalpy H (P, S)**
1. For free expansion (irreversible) $H_f = H_i$	1. Throttling process (irreversible) $H_f = H_i$
2. $dU = \text{đ}Q - PdV$ $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	2. $dH = \text{đ}Q + VdP$ $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
3. For isochoric process $U_f - U_i = Q_V$	3. For isobaric process $H_f - H_i = Q_P$
4. For ideal gas $U_f - U_i = \int_i^f C_V dT$	4. For ideal gas $H_f - H_i = \int_i^f C_P dT$
5. For adiabatic process $U_f - U_i = -\int_i^f PdV$	5. For adiabatic process $H_f - H_i = \int_i^f VdP$
6. For infinitesimal change $dU = TdS - PdV$ $\left(\frac{\partial U}{\partial S}\right)_V = T$ $\left(\frac{\partial U}{\partial V}\right)_S = -P$	6. For infinitesimal change $dH = TdS + VdP$ $\left(\frac{\partial H}{\partial S}\right)_P = T$ $\left(\frac{\partial H}{\partial P}\right)_S = V$

Helmholtz and Gibbs functions

Helmholtz function and its properties

1. The Helmholtz function A(T, V) was defined as

$$A = U - TS \qquad \text{..... (19)}$$

For any infinitesimal reversible process

$$dA = -PdV - SdT \quad \text{.....(20)}$$

The pressure and entropy can be calculated from partial differential equations.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S$$

2. For a reversible isothermal process $dT = 0$

$$dA = -PdV$$

∴

$$A_f - A_i = -\int_i^f PdV$$

or .....(21)

It means that an increase in Helmholtz function during an isothermal process is equal to the work done on the system. For this reason Helmholtz function is referred to as free energy of the system at constant temperature.

For any infinitesimal isothermal process equation (19) becomes

$$(\Delta A)_T = (\Delta U)_T - T(\Delta S)_T$$

or

$$(\Delta A)_T = (\Delta U)_T - (\Delta Q)_T$$

i.e.

$$(\Delta A)_T = (\Delta W)_T$$

This means that the decrease of the Helmholtz energy $(\Delta A)_T$ of the system equals the maximum amount of isothermal work $(\Delta W)_T$ that is performed by the system. The internal energy of the system also decreases. But this is not equal to $(\Delta W)_T$ since

$$(\Delta U)_T - (\Delta Q)_T = (\Delta W)_T$$

as

$$(\Delta Q)_T \gtrless 0$$

∴

$$(\Delta W)_T \gtrless (\Delta U)_T$$

3. For a reversible isothermal-isochoric process, equation 20 gives

$$dA = 0$$

or

$$A = \text{constant}$$

i.e. Helmholtz function of a system remains constant during reversible isothermal-isochoric process.

4. When a system is in equilibrium it tries to minimise its internal energy and tries to maximise its entropy. Thus $A = U - TS$, the Helmholtz function is always minimum for a system in equilibrium.

Properties of Gibbs function

1. The Gibbs function $G(T, P)$ was defined to be

$$G = A + PV$$

or $$G = U - TS + PV \qquad (\because \quad A = U - TS)$$

or $$G = H - TS \qquad (\because \quad H = U + PV)$$

For any infinitesimal reversible process we have

$$dG = VdP - SdT \qquad \text{.....} (22)$$

The entropy and volume can be calculated by the partial differential equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

2. If the process is reversible isothermal and isobaric $dT = 0$ and $dP = 0$, equation (22) gives

$$dG = 0$$

$$\therefore \qquad G = \text{constant}$$

i.e., during a reversible isothermal and isobaric process Gibbs function remains constant. For example first order change of phase. The processes like sublimation, fusion and vapourisation takes place at constant temperature and pressure. Hence during such processes the Gibbs function of the system remains constant.

Maxwell's thermodynamical relations

Maxwell established four relations between the four thermodynamic quantities P, V, T and S. There are several methods to derive these relations. We adopt here the method based on the four thermodynamic potentials U, H, F and G. By using the condition for an exact differential we can derive Maxwells relations. This is possible since dU, dH, dF and dG are exact differentials. You may think that how do we say that they are exact differentials. Suppose we go from a point A to point B and come back to A in a P–V diagram where all the points are uniquely fixed. The net changes in the values of P, V, T, S and U are all zero.

i.e. $\oint dP = 0, \oint dV = 0, \oint dT = 0, \oint dS = 0$ and $\oint dU = 0$.

Therefore dP, dV, dT, dS and dU are exact differentials.

The differentials of any quantity which depends on P, V, T, S, U etc. (e.g. TS, PV, U + TS, U + PV etc.) will also be a perfect differential. It follows that dU, dF, dH and dG are all exact differentials.

Condition for exact differential

If a relation exists among x, y and z, then we suppose that z is a function of x and y.

i.e. $z = z(x, y)$

Taking the differentials on both sides we get

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Put $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

then $dz = Mdx + Ndy$

where z, M and N are functions of x and y. Partially differentiating M with respect to y and N with respect to x, we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

and

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

since the second derivatives of the right hand terms are equal, it follows that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \text{.....(23)}$$

This is the condition for exact differential

Maxwell's relations

(i) From first law we have

$$dU = TdS - PdV$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $M = T, N = -P, x = S, y = V$ and $z = U$

But $$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

or $$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad -P = \left(\frac{\partial U}{\partial V}\right)_S$$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

We get $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad ..... (24)$$

This is the first Maxwell's relation.

(ii) From the enthalpy change, we have

$$dH = TdS + VdP$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $z = H, M = T, x = S, N = V$ and $y = P$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

We get $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad ..... (25)$$

This is the second Maxwell's relation

(iii) From the Helmholtz function change, we have

$$dF = -SdT - PdV$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get $z = F, M = -S, x = T, N = -P$ and $y = V$.

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

We get $$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad ..... (26)$$

This is the third Maxwell's relation.

(iv) From the Gibbs function change, we have

$$dG = -SdT + VdP$$

This is in the form

$$dz = Mdx + Ndy$$

Comparing we get

$$z = G, M = -S, x = T, N = V \text{ and } y = P$$

Using the condition for exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

or $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ..... (27)$$

This is the fourth Maxwell's relation.

Equations 24, 25, 26 and 27 are called Maxwell's thermodynamic relations.

A device to remember four characteristic functions and their relations

To deal with characteristic functions U, A, H and G it is necessary to remember their functional dependence, all of its partial derivatives leading to thermodynamic variables and Maxwell's relations. It is not possible to memorise all these 16 (4 + 8 + 4) relations. For this we devised a mnemonic diagram called VAT - VUS diagram. VAT - VUS diagram is a square labelled the corners with V, A, T and V, U, S as shown.

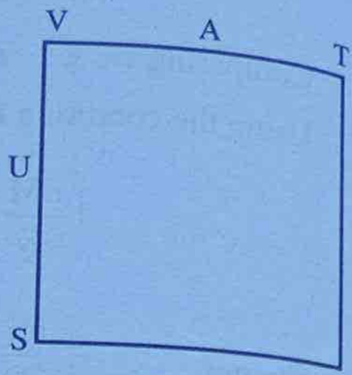


Figure 5.4

The fourth unlabelled corner of the square is labelled with the remaining fourth thermodynamic variable P. Thermodynamic functions are marked on the sides of the square. We have to fill two more thermodynamic functions G and H. Fill it with alphabetic order starting from A. After A, G comes first and then H. Fill it accordingly. Finally draw arrow marks from S and P to its conjugate variables T and V respectively. Now VAT-VUS diagram becomes figure 5.5.

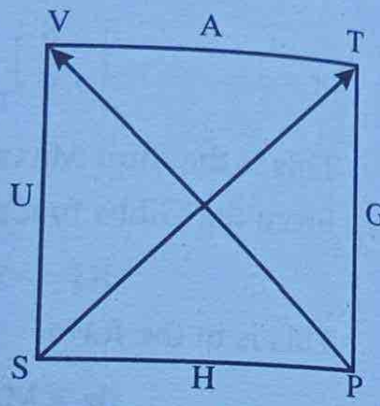


Figure 5.5

This diagram containing all 16 relations that we require.

For example A is in between V and T. This implies that A is a function of V and T. Similarly U is a function of V and S, G is a function of T and P and H is a function of S and P once functional dependence is known, the differential of the thermodynamic function is always equal to the sum of the terms that include the differential of the thermodynamic coordinates. The coefficient of the differential in each term is found by connecting the arrow from the thermodynamic coordinate of the differential to its conjugate coordinate.

Example 1

$$A = A(V, T)$$

$$dA = (\ )dV + (\ )dT$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

In both cases connection goes against the arrow mark.

Example 2

$$U = U(V, S)$$

$$dU = (\ )dV + (\ )dS$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\therefore \qquad dU = -PdV + TdS$$

Example 3

$$G = G(T, P)$$

$$dG = (\ )dT + (\ )dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

Thus $$dG = -SdT + VdP$$

Example 4

$$H = H(S, P)$$

$$dH = (\ )dS + (\ )dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\therefore \qquad dH = TdS + VdP$$

Finally we can write down all four Maxwell's relations from the VAT-VUS diagram by applying the condition for exact differential

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

It is better you to construct your own gimmick by closely observing Maxwell's relations and the diagram.

TdS equations

The entropy of a pure substance can be considered as a function of two variables such as T and V. Thus

i.e.
$$S = S(T, V)$$

$$\therefore \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying throughout by T, we get

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

But
$$T\left(\frac{\partial S}{\partial T}\right)_V = C_V$$

From Maxwells relations, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \quad TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

This is called first TdS equation.

Second TdS equation

The entropy of a pure substance can be considered as a function of two variables T and P.

i.e.
$$S = S(T, P)$$

$$\therefore \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

or
$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

But $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$ and from Maxwells relations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

∴ We get $$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

This is called the second TdS equation.

Variation of intrinsic energy with volume

When a system undergoes an intinitesimal reversible process between two equilibrium state, the change in intrinsic energy is given by

$$dU = dQ - PdV$$

or $$dU = TdS - PdV.$$

Substituting for TdS from first TdS equation, we get

$$dU = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV - PdV$$

But from $U = U(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Comparing this equation with the above equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

This is the energy equation of state. From this the change in energy (dU) can be calculated.

Case I Perfect gas

Consider one mole of perfect gas, we have

$$PV = RT$$

∴ $$P = \frac{RT}{V}$$

or $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

From the energy equation, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\therefore \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\cdot\frac{R}{V} - P$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \qquad \left(\because \frac{RT}{V} = P\right)$$

It means that there is no change in the intrinsic inergy of a perfect gas during an isothermal change in volume. (see also example 1).

Case II Real gas

For one mole of gas, we have

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

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$\therefore \qquad P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

From the energy equation, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{TR}{V - b} - P = \frac{a}{V^2}$$

We also have

$$dU = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV - PdV = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dP$$

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = C_V dT + \frac{a}{V^2} dV$$

Integrating we get

$$U = \int C_V dT - \frac{a}{V} + \text{constant}$$

This shows that the intrinsic energy of an actual gas increases with isothermal increase in volume.

Applications of TdS equations

1. Suppose a system undergoes a reversible isothermal change of pressure. Here our aim is to calculate the amount of heat transferred, the work done and the change in internal energy of the system.

   For this consider the second TdS equation.

Thus $$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

For isothermal process $dT = 0$

Thus $$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP$$

or $$đQ = -T\left(\frac{\partial V}{\partial T}\right)_P dP$$

From the definition of volume expansivity

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

or $$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

$\therefore$ $$đQ = -T\beta V dP$$

Integrating, we get

$$Q = -T\int_{P_i}^{P_f} \beta V dP$$

Where P_i is the initial pressure and P_f is the final pressure.

In the case of solids and liquids β and V are almost constants.

This $$Q = -TV\beta\int_{P_i}^{P_f} dP$$

$$Q = -TV\beta(P_f - P_i)$$

(see example 6 and 7)

This is the expression for heat transferred in a reversible isothermal pressure change.

Now we calculate the work done.

Work done, $$W = -\int PdV$$

At constant temperature, dV can be written as

$$dV = -\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\therefore \quad W = -\int P\left(\frac{\partial V}{\partial P}\right)_T dP$$

From the definition of isothermal compressibility

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

or $$\left(\frac{\partial V}{\partial P}\right)_T = -kV$$

$$W = \int_{P_i}^{P_f} kVPdP$$

since K and V are almost constants take it outside the integral, then integrate we get

$$W = \frac{kV}{2}\left(P_f^2 - P_i^2\right)$$

This is the expression for work done. (See example10(b))

From Q and W, we can very well calculate the internal energy U, by using first law of thermodynamics.

i.e. $\Delta W = Q + W$ (See example 10)

2. Suppose a system undergoes a reversible adiabatic change of pressure

From second TdS equation, we have

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

For adiabatic process $dS = 0$

$$0 = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

or $$dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP$$

From $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

or $$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

$\therefore$ $$dT = \frac{T}{C_P} V\beta dP$$

Integrating we get

$$\Delta T = \int_{P_i}^{P_f} \frac{T}{C_P} V\beta dP$$

Suppose pressure increases, obviously β is positive. Since T, V, β and C_p are constants.

$$\Delta T = \frac{TV\beta}{C_P}(P_f - P_i) \qquad \text{..... (1)}$$

This is the expression for the change in temperature when a system undergoes a reverse adiabatic change of pressure. This can be applied to all solids and liquids. (See example 10)

Example 6

One mole of van der waals gas undergoes a reversible isothermal expansion from volume V_1 to V_2. Calculate the amount of heat transferred.

Solution

From first TdS equation we have

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

From van der waals equation, we have

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Hence $TdS = C_V dT + \frac{TR}{V-b} dV$

For isothermal expansion $dT = 0$

$$TdS = \frac{TR}{V-b} dV$$

or

$$đQ = \frac{TR}{V-b} dV \text{ integrating}$$

$$Q = TR\ln(V-b)\Big|_{V_1}^{V_2}$$

So

$$Q = RT\ln\left(\frac{V_2 - b}{V_1 - b}\right)$$

Example 7

If the pressure on 15 cm^3 of mercury at $20°C$ is increased reversibly and isothermally from 0 to 1000 atm; calculate the heat transferred. $\beta = 1.81 \times 10^{-4} K^{-1}$, $1 \text{atm} = 1.01 \times 10^5 \text{Pa}$

Solution

From the second TdS equation, we have

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

For isothermal process $dT = 0$

$$\therefore \qquad \text{đ}Q = -T\left(\frac{\partial V}{\partial T}\right)_P dP$$

Integrating we get

$$Q = -T\int_0^{1000}\left(\frac{\partial V}{\partial T}\right)_P dP$$

But $\qquad \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \beta \quad \text{or} \quad \left(\frac{\partial V}{\partial T}\right)_P = \beta V$

$$\therefore \qquad Q = -T\int_0^{1000} \beta V\, dP$$

For solid β and V are almost constants.

$$Q \simeq -T\beta V \times (1000 \text{ atm})$$

$$Q \simeq -293 \times 1.81 \times 10^{-4} \times 1.5 \times 10^{-5} \times 1000 \times 1.01 \times 10^5$$

$$Q \simeq -80.34 \text{ J}$$

Note: TdS equations are very useful to calculate the heat transferred, the change in temperature and change in pressure.

Example 8

Derive the third TdS equation

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

Solution

Assume that entropy is a function of P and V.

i.e. $$S = S(P, V)$$

∴ $$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

or $$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV$$

$$\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P$$

∴ $$TdS = T\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

But $T\left(\frac{\partial S}{\partial T}\right)_V = C_V$ and $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

∴ $$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

Example 9

Show that first TdS equation may be written as

$$TdS = C_V dT + \frac{\beta}{k} T dV$$

Solution

From first TdS equation we have

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{..... (1)}$$

Using $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\therefore \qquad \frac{\beta}{k} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Put this in equation (1) yields

$$TdS = C_V dT + T\frac{\beta}{k}dV.$$

Example 10

The pressure on 500 g of copper is increased reversibly and isothermally from 0 to 5000 atm at $298K(\rho = 8.96\times10^3 \, kg\, m^{-3})$, volume expansivity $\beta = 49.5\times10^{-6} K^{-1}$, isothermal compressibility $k = 6.18\times10^{-12} Pa^{-1}$ and specific heat $C_p = 385J\, kg^{-1}\, K$ to be constant.

a) How much heat is transferred during the compression?

b) How much work is done during compression?

c) Determine the change of internal energy.

Solution

$m = 0.5$ kg, $T = 298\, K$, $\beta = 49.5\times10^{-6} K^{-1}$ $k = 6.18\times10^{-12} Pa^{-1}$

$C_P = 385J\, kg\, K^{-1}$.

a) Heat transferred $Q \simeq TV\beta P_f$ (see example 7)

$$Q \simeq -298\times\frac{0.5}{8.96\times10^3}\times49.5\times10^{-6}\times5000\times1.01\times10^5$$

$$Q \simeq -298\times5.58\times10^{-5}\times49.5\times10^{-6}\times5\times1.01\times10^8$$

$$Q \simeq -298\times5.58\times4.95\times5\times1.01\times10^{-2}$$

$$Q = -415.67 \text{ J}$$

b) Work done, $W = \frac{1}{2}kV\left(P_f^2 - P_i^2\right)$

$$W = \frac{6.18\times10^{-12}}{2}\times\frac{0.5}{8.96\times10^3}(5000\times1.01\times10^5)^2$$

$$W = 43.97 \text{ J}$$

c)

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

$$\Delta U = -415.67 + 43.97$$

$$\Delta U = -371.7 \text{ J}$$

Example 11

From the Maxwells equation show that for a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Solution

We have $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

or $\frac{1}{T}\left(\frac{\partial Q}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

or $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

But $\delta Q = dU + PdV$

$\therefore$ $\frac{dU + PdV}{dV} = T\left(\frac{\partial P}{\partial T}\right)_V$

$$\frac{dU}{dV} + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

or $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

For a perfect gas $PV = RT$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{PV}{V} - P$$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Example 12

Using Maxwells relation show that $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$. Deduce $C_P - C_V = R$ for a perfect gas.

Solution

We have $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying throughout by T, we get

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

By definitiion $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

and $T\left(\frac{\partial S}{\partial T}\right)_V = C_V$

$$C_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

∴

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

or

From Maxwells relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

∴

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

For a perfect gas $PV = RT$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

and

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

∴

$$C_P - C_V = T\frac{R}{V}\frac{R}{P} = \frac{TR^2}{RT}$$

∴

$$C_P - C_V = R$$

Example 13

Prove that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ for an ideal gas as well as for a Vander waal's gas. What does it mean.

Solution

We have $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ (see example 3)

For an ideal gas $PV = RT$

or

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

∴

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

and

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

∴

This means that at a given temperature C_V is independent of volume

For a vander waals gas

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

∴

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

This means that at a given temperature C_V is independent of volume.

Example 14

Show that the differential of the thermodynamic potential U may be written as $dU = (C_P - PV\beta)dT + V(kP - \beta T)dP$

Solution

We have $$dU = TdS - PdV \qquad \text{..... (1)}$$

of $$V = V(P, T)$$

then $$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$S = S(P, T)$$

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

Put this in eqn (1), we get

$$dU = \left[T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P.$$

By definition

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

$$\therefore \quad dU = (C_P - P\beta V)dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

By definition $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\therefore \quad \left(\frac{\partial V}{\partial P}\right)_T = -kV$$

From Maxwell's relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\beta V$$

$$\therefore \quad dU = (C_P - P\beta V)dT + (kP - \beta T)VdP.$$

Example 15

Derive the relation $\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V\beta T}$

Solution

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting C_P and β on the R.H.S. of the given equation, we get

$$\text{R.H.S} = \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{V\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_\beta T} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\text{R.H.S} = \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_S \qquad \text{(By Maxwell's relation)}$$

$$= \text{L.H.S.}$$

PV diagram for a pure substance

To draw a PV diagram for a pure substance we need a set of values of P and V. To obtain this we conduct a simple experiment. Here we take pure water as the pure substance since the triple point water is the bases of the thermodynamic temperature scale.

The experimental arrangement consists of a graduated cylinder 2 litres in volume closed at one end and the other end is provided with a piston. The pressure inside the cylinder is measured by a manometer and the temperature inside is controlled by ovens and refrigerators. Initially the cylinder is evacuated.

To begin the experiment 1 gram of water at 94°C introduced into the cylinder. It is due to vacuum inside, water will evaporate completely. Now the cylinder is filled with unsaturated vapour. This unsaturated vapour state of the system is represented by the point A on the system. The pressure of vapour is read from the manometer this will be obviously less than the atmospheric pressure.

Slowly compress the piston isothermally, volume of vapour decreases and pressure increases until the system reaches a state of saturated vapour. This state is represented by the point B on the PV diagram.

If the compression is continued condensation occurs to form water droplets. During compression pressure remains constant as long as the temperature is constant and volume decreases. The region BC represents the change of the system from vapour state to liquid state i.e. liquefaction. In this region vapour and liquid are in equilibrium. This is represented by the straight line BC on the PV diagram. **The**

constant pressure at which isothermal isobaric condensation occurs is called the vapour pressure. The line CB represents the isothermal isobaric evaporation of water vapour. Here the volume increases. The line BC or CB are called vapourisation line. At any point between B and C water and vapour coexist in equilibrium. At the point C, the system is only liquid water or saturated liquid.

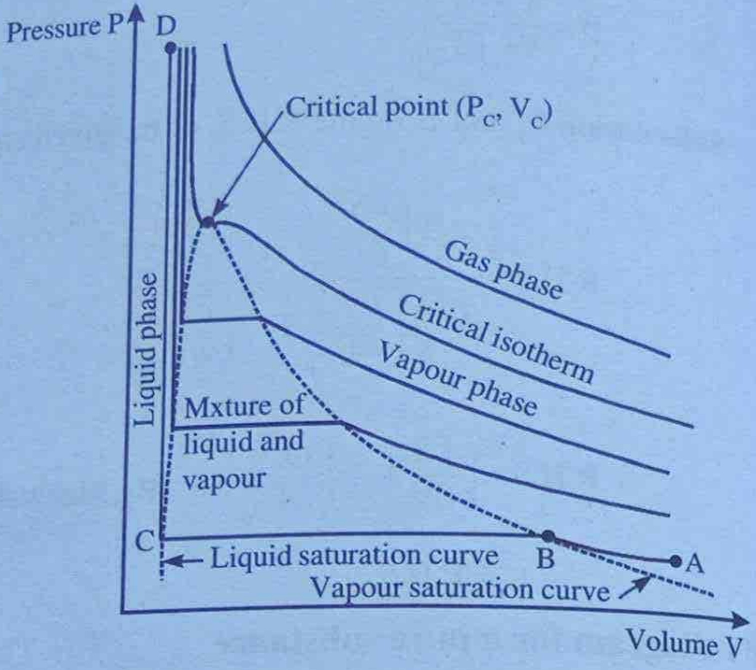


Figure 5.6: Isotherms of pure substance water

Suppose we want to compress liquid water slightly a very large increase of pressure is required. It is represented by the vertical line CD on the PV diagram.

It may be noted that any point on the line AB is in the vapour state, any point on the line BC, there is equilibrium between vapour and liquid phases. The curve ABCD is a typical isotherm with discontinuities at B and C.

A graph is plotted between P and V at various temperatures called isotherms.

If we increase the temperature and drawing isotherms, it can be seen that the vapourisation line (horizontal line) becomes shorter. As the temperature rises ultimately the vapourisation line vanishes. **The temperature at which the vapourisation line vanishes is called critical temperature (T_C)**. The corresponding volume and pressure are called critical volume (V_C) and critical pressure (P_C) respectively. It is seen that the critical point (point corresponding to P_C and V_C on the isotherm) is a point of inflection on the PV diagram. The isotherm at the critical temperature is called the critical isotherm. (see the PV diagram).

Results of the experiment

1. For every substance, there is a critical temperature characteristic of the substance.
2. Above the critical point the isotherms are continuous curves which lose their inflection points and take the form of rectangular hyperbolas.
3. Above the critical point there is no longer any distinction between a liquid and a vapour. That is meniscus between the liquid and vapour disappears.

4. At critical temperature the densities of the vapour and liquid are the same.

If the densities of both liquid and vapour of water are measured as functions of temperature and a graph is plotted between temperature and density we get a graph as shown in figure 5.7. From the graph we can evaluate the critical temperature, where density of liquid is equal to density of water. The graph also gives critical density. At temperatures below the critical point the liquid and vapour densities vary only slightly and are significantly different from each other.

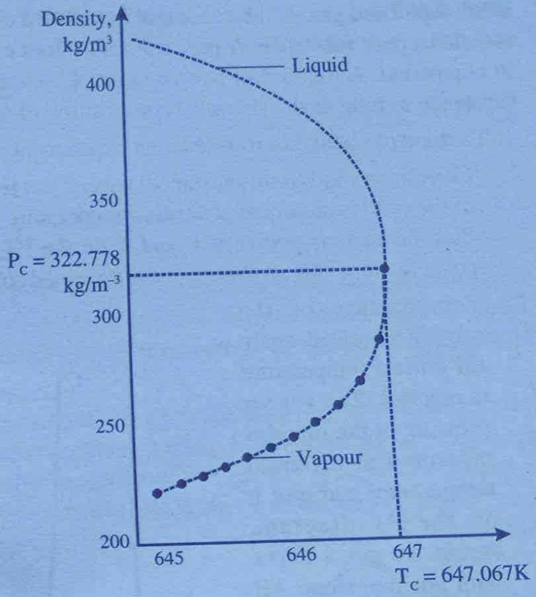


Figure 5.7: Density curves of liquid and vapour

For H_2O the critical temperature is 647.067K and critical pressure is 22.046MPa and critical volume for 1kg is 0.00309 m^3 and the critical density is 322.778 kgm^{-3}.

If the pure substance is a solid we have a solid phase and a solid-vapour phase. It occurs in the low-temperature region than the liquid-vapour phase. This is not shown in our graph. In the solid-vapour of the PV diagram, the isotherms have the same general character as the vapourisation lines in the liquid-vapour region. This horizontal line represents the isobaric transition from solid to vapour or sublimation. There is one such line that separates the solid-vapour region below from the liquid-vapour region above. The line is associated with the co-existence of all the three phases together called the triple point. Its value for water is 273.16K.

When a liquid or solid is in equilibrium with vapour at a given temperature, the vapour exerts a pressure that depends only on the temperature. In general, the higher the temperature the greater the vapour pressure. As the temperature of a liquid is lowered at triple point the liquid starts to solidify. At lower temperatures only solid and vapour are present. The vapour pressure of most solids is very small.

PT diagram for a pure substance: phase diagram

A graph showing the variation of pressure with temperature is called PT diagram. A PT diagram is the most common way to show the phases of a pure substance hence called as phase diagram. At its simplest a phase can be just another term for solid, liquid and gas. A substance that has a fixed chemical composition throughout is called a pure substance. A pure substance does not have to be of a single element or compound. A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

To draw phase diagram conduct an experiment in the following way.

1. Consider a solid (pure substance) at very low temperature. The vapour pressure of the solid is measured at various temperatures until the triple point is reached. Plot the various points of P and T on the PT diagram. We get a curve with positive slope OA as shown in figure called sublimation curve.
2. Temperature of the sample is raised again till critical temperature is reached. The vapour pressure of the liquid is measured at different temperature and plot it on the PT diagram. Again we get a curve with positive slope AB as shown in figure 5.8 called vapourisation curve.

   The graph so obtained is called a phase diagram.

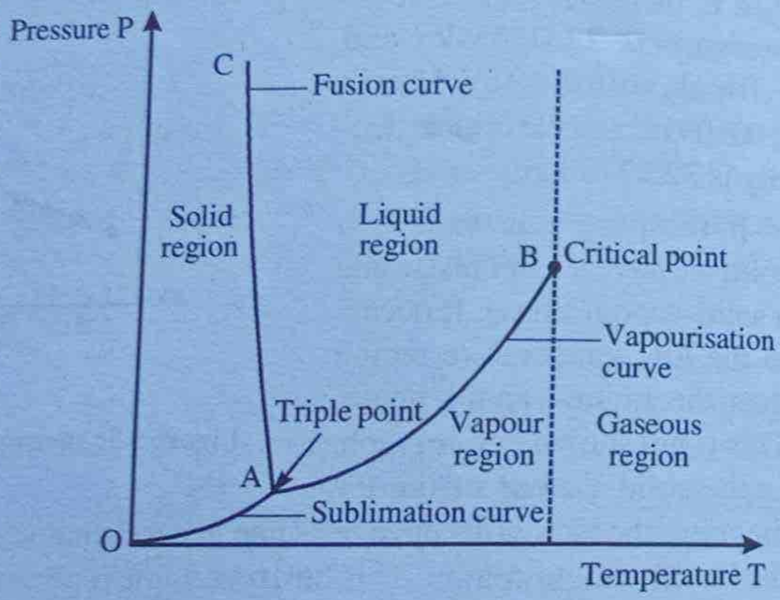


Figure 5.8

3. If a substance at its triple point is compressed until there is no vapour left and the pressure on the resulting mixture of solid and liquid is increased, the temperature must change for equilibrium to exist between the solid and the liquid. Measure the pressures and temperatures of the solid coexisting with the liquid. Plot it on the same PT diagram. We get a curve with positive or negative AC as shown in slope figure above is called fusion curve. This is the picture of complete phase diagram of a pure substance.

It may be noted that (i) the sublimation curve represents the coexistence of solid and vapour is bounded by absolute zero and the triple point (ii) The vapourisation curve on which vapour and liquid lie is bounded by the triple point and the critical point and (iii) solid and liquid lies on the fusion curve starts at the triple point and is unbounded.

In the case of water the sublimation curve is called the frost line, the vapourisation curve is called the steam line and the fusion line is called the ice line.

Distinction between PT and PV diagrams

1. In a PT diagram no two phase regions are shown but in a PV diagram two phase regions are shown. In PT diagram two phases collapse into one of the three curves.
2. The PT diagram gives the triple point where the sublimation, vapourisation and fusion curve meets. PV diagrams gives triple phase state line not triple point.

The essential feature of triple point is that **three phases, solid, liquid and vapour coexist in equilibrium. However a triple point is defined as the state in which two different solid phases coexist with a liquid or three different solid phases coexist.**

PT diagram enables us to distinguish between gas and vapour. Away from the curves there are only single phase equilibrium state. Above the critical temperature we can see a single phase equilibrium state called gas. So gas can be defined as follows. **A substance with no free surface and with a volume determined by that of the container when the temperature is above the critical temperature is called gas.**

Below the critical temperature gas in equilibrium with liquid is called vapour. The properties of vapour and gas are the same except that a vapour can be liquid by an isothermal increase of pressure due to compression but a gas cannot be liquefied no matter how high the pressure. There is an exemption, helium gas can be solidified under high pressure.

First order phase transitions: Calusius Clapeyron equation

Changes of phase

Almost all substances can exist in different forms such as solid, liquid and vapour. Each one is said to be a phase. When solid changes to liquid or liquid changes to vapour it is called as the phase change. Here we will see during changes of phase what happens to the thermodynamical variables P, T, V, S, U and G.

Let us consider the equilibrium between the liquid phases and its vapour phases of the same substance enclosed in a cylinder. The temperature and pressure are equal in both the phases. As each of these phases is in equilibrium, the temperature and pressure must remain constant throughout the phase and hence the thermodynamical coordinates. V, S, U and G will be equal to the product of the specific value and mass of the substance in that phase.

Suppose m_1 and m_2 are the masses in the liquid and vapour phases and g_1 and g_2 are the specific values of the Gibbs potential in the two phases. Then for the whole system.

$$G = m_1 g_1 + m_2 g_2$$

If a small quantity of liquid changes into vapour, differentiating the above equation we get

$$\delta G = \delta m_1 g_1 + \delta m_2 g_2 \qquad \text{....... (i)}$$

Since the phase change occur at constant temperature and pressure, the process is isothermal and isobaric.

$$\therefore \qquad \delta G = 0$$

$\therefore$ Equation (i) becomes

$$0 = \delta m_1 g_1 + \delta m_2 g_2$$

But $\qquad \delta m_1 = -\delta m_2$

$$\therefore \qquad g_1 = g_2$$

This shows that the thermodynamical Gibbs Potential per unit mass (g) will be equal in the two phases. This is valid for solid to liquid, liquid to vapour and vice versa.

First order phase transition

The changes of phase which takes place at constant temperature and pressure and in which heat is either absorbed or evolved are called first order phase transitions. In first order phase transitions, the entropy and density (or volume) change. The Gibbs function G remains constant in both phases, while it derivatives with respect to temperature and pressure is discontinuous at transition point.

Transformation of ice into water, water into vapour are examples of first order phase transition:

Now we will see whether a change in pressure will produce any effect on temperature on transition from one phase into the other. The answer will be given by Clausius - Clapeyron equation.

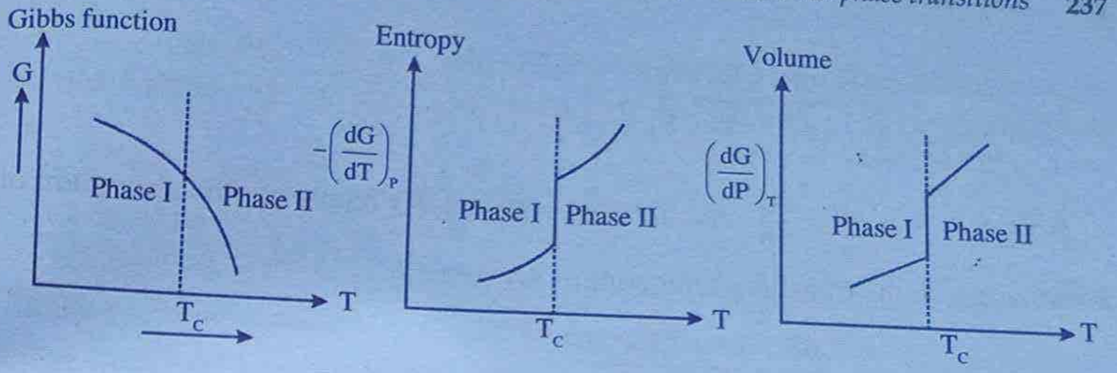


Figure 5.9: First order phase transition

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal, isobaric change, we know that, the Gibb's potential of both phases are the same

i.e., $G_1 = G_2$

This is at pressure P and temperature T.

Let the temperature of the system be increased from T to T + dT and pressure be increased from P to P + dP, then Gibbs potential goes from $G_1 + dG_1$ to $G_2 + dG_2$. So we must have

$$G_1 + dG_1 = G_2 + dG_2$$

or $$dG_1 = dG_2 \qquad (\because \quad G_1 = G_2)$$

We have $$G = U - TS + PV$$

Taking the differential on both sides we get

$$dG = dU - TdS - SdT + PdV + VdP$$

Using $$dU = TdS - PdV$$

or $$dG = -SdT + VdP$$

$\therefore$ $$dG_1 = -S_1dT + V_1dP$$

$$dG_2 = -S_2dT + V_2dP$$

Since $dG_1 = dG_2$, we have

$$-S_1dT + V_1dP = -S_2dT + V_2dP$$

$$(S_2 - S_1)dT = (V_2 - V_1)dP$$

or
$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}$$

Now $S_2 - S_1 = dS = \frac{dQ}{T}$ and T being constant dQ represents the absorption of latent heat L at the transition temperature, we get

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

This is our Clausius - Clapeyron latent heat equation.

It is also very interesting to note the changes of specific heat capacity at constant pressure C_p, coefficient of cubical expansion β, and compressibility k during a first order phase change. All these parameters go to infinity. This is because transition occurs at constant T and P. When P is constant, $dT = 0$ or when T is constant, $dP = 0$

$$\therefore \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_P \to \infty$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \to \infty$$

$$B = -\left(\frac{\partial P}{\partial V / V}\right)_T \to 0$$

$$k = \frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \to \infty$$

compressibility k is the reciprocal of bulk modulus B.

The Clausius -Clapeyron equation for 1 mole of substance becomes

$$\frac{dP}{dT} = \frac{s_2 - s_1}{(v_2 - v_1)}$$

where s_1 and s_2 are initial and final the molar entropies and v_2 and v_1 are final and initial molar volumes respectively.

Remember that $\quad s_2 - s_1 = \frac{h_2 - h_1}{T}$

where s_1 and s_2 are initial and final molar entropies and h_1, h_2 are initial and final molar enthalpies.

Thus $$\frac{dP}{dT} = \frac{h_2 - h_1}{T(v_2 - v_1)}$$

This is another form of Clausius-Clapeyron equation.

Clausius-Clapeyron equation and phase diagrams

The Clausius-Clayperon equation plays an important role in the analysis of phase diagrams. In a phase diagram we found the sublimation curve, vapourisation curve and fusion curve. A point on each curve represents the coexistence of two phases except at the triple point and the critical point. Each point on the curve gives the thermodynamic coordinates P and T. But Clausius-Clayperon equation is not concerned with coordinates rather it deals with the slope of the curve $\left(\frac{dP}{dT}\right)$.

Here we analyse the phase diagram for water in the light of Clausius-Clayperon equation.

Consider a sample of ice at temperature T (which is less than its melting point) opened to atmospheric pressure P. The system is in its solid state and is represented by a point 'a' on the phase diagram shown in figure below.

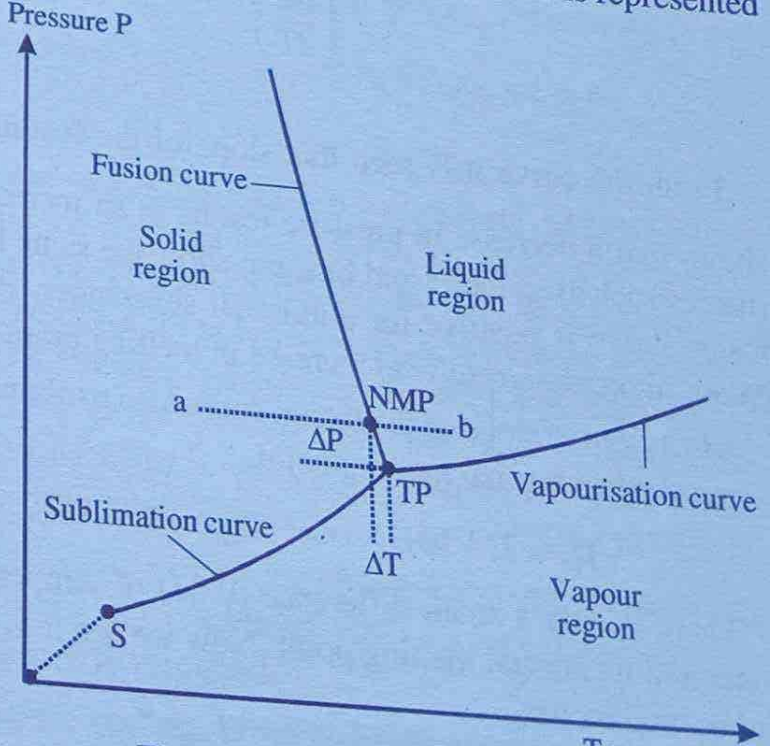


Figure 5.10: Phase diagram for water

Suppose heat is given to the system, its temperature increases so also its enthalpy. During this the state of the system moves horizontally until it reaches the fusion curve. Absorption of heat melts ice produce water. After reaching the fusion curve the system again absorbs heat without any change of temperature. The corresponding temperature is called normal melting point represented by a point NMP on the fusion curve. When ice melts completely the temperature of the system rises again. This is represented by a horizontal line (pressure constant) move along to the point b. The point b is in the liquid region. Supplying heat again the line moves towards the vapourisation curve.

Now we change the scenario. Suppose our system is at NMP, where ice coexists with water and air at standard atmospheric pressure. If the sample is placed in a chamber and the air pressure of the system is lowered. It is due to small decrease in pressure (say ΔP), the system is no longer on the fusion curve. The result is that the temperature of the system will change by ΔT to return to the fusion curve.

From the graph we get

$$\frac{\Delta P}{\Delta T} = \tan\theta$$

where $\tan\theta$ is the slope of the fusion curve $\frac{dP}{dT}$ approximately.

i.e.

$$\frac{\Delta P}{\Delta T} = \frac{dP}{dT}$$

or

$$\Delta T = \frac{\Delta P}{\left(\frac{dP}{dT}\right)}$$

From the curve it is seen that slope of the fusion curve $\frac{dP}{dT}$ is negative. This shows that a decrease in pressure results in an increase in the melting point. Substances such as graphite and bismuth show the same behaviour. In general slope of fusion curve is positive for almost all substances. Positive slope implies that increase in pressure results in increase in melting point and vice versa.

The negative slope of the fusion curve also explains why the triple point of water is greater than normal melting point.

$$T_{TP} = 273.16\,K \quad \text{and} \quad T_{NMP} = 273.15\,K.$$

There is only a small difference (0.01) of temperature between triple point of water and its normal melting point. Now we are in a position to define triple point and normal melting.

Definitions of TP and NMP point of water using phase diagram

Triple point: It is the temperature at which ice and water are in equilibrium with water vapour with a vapour pressure of 612 Pa.

Normal melting point: It is the temperature at which ice and water are in equilibrium with air at a standard atmospheric pressure.

Now we will see how to arrive at difference in value of temperature between T_{TP} and T_{NMP} using Clausius-Clapeyron equation.

We have
$$\Delta T = \frac{\Delta P}{\left(\frac{dP}{dT}\right)}$$

Substituting for $\frac{dP}{dT}$ from Clausius-Clapeyron equation, we get

$$\Delta T = \frac{T(v_2 - v_1)}{(h_2 - h_1)} \Delta P$$

The subscript 1 refers to the solid phase and 2 refers to the liquid phase. Putting the values for all parameters

$T = 273\,K$, $v_1 = 19.65 \times 10^{-6}\,m^3/mol$, $v_2 = 18.02 \times 10^{-6}\,m^3/mol$,

$h_2 - h_1 = 6.01 \times 10^3\,J\,mol^{-1}$ and $\Delta P = 1.01 \times 10^5\,Pa$, we get

$\Delta T = -0.0073\,K.$

That is, the increase of pressure depresses the temperature from the triple point of ice by 0.0073 K. The lowering of temperature from the triple point of ice to the normal melting point is also affected by the air that is dissolved in a mixture of ice and water. The effect of the dissolved air is to lower the temperature at which ice melts by 0.0023 K with respect to melting temperature of pure water. Therefore, the two effects combine to lower the temperature of the triple point by 0.0096 K or approximately 0.01 K. The triple point is arbitrarily assigned an exact value of 273.16 K, the result is that the normal melting point is approximately 273.15 K.

The above discussion can be used to explain the phenomenon of regelation. **Regelation is defined as the phenomenon in which ice melts under high pressure and freezes again when this pressure is removed.**

This is the principle behind ice skating. When a person stands on a skating platform, it is due to the pressure exerted by the person the melting point of ice under the skating blade decreases and ice melts. This provides a slippery (water) surface to move the skate.

Unlike fusion curves the slope of sublimation and vapourisation curves of all substances is always positive, because the molar volume of vapour is always larger than the molar volume of liquid. This increase in volume suggests that the vapour has more disorder than its solid or liquid that change in entropy $s_2 - s_1$ is positive.

We have
$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

$s_2 - s_1$ is positive and $v_2 - v_1$ is positive implies that $\frac{dP}{dT}$ is positive. This means that when pressure increases the boiling point also increases and vice versa.

Example 16

Calculate the melting point of ice under a pressure of 2 atmospheres. It is given that the melting point of ice under one atmospheric pressure is 273.16 K. Latent heat of fusion of ice is 79.6 cal/g and at the melting point specific volume of ice is 1.0908 cc and that of water is 1.0001 cc. One atm $= 1.013 \times 10^6$ dynes cm^{-2}.

Solution

$$L = 79.6 \times 4.185 \text{ergs}\, g^{-1}$$

$$T = 273.16 \text{K}$$

$$V_2 = 1.0001 \text{cc}$$

$$V_1 = 1.0908 \text{cc}$$

$$dP = 2 - 1 = 1 \text{ atm} = 1.013 \times 10^6$$

Using
$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$\therefore \quad dT = \frac{dPT(V_2 - V_1)}{L}$$

$$= \frac{1.013 \times 10^6 \times 273.16 \times (1.0001 - 1.0908)}{79.6 \times 4.185 \times 10^7}$$

$$= -0.007533 \text{ K}$$

$\therefore$ The new melting point is $273.16-0.007533=272.41\,\mathrm{K}$

Example 17

Calculate the boiling point of water under a pressure of two atmospheres. It is given that the boiling point of water under a pressure of one atmosphere is 373.2K. Latent heat of vapourisation is 539 cal/g. Specific volume of water is 1cc and specific volume of steam is 1674 cc.

Solution

$$dP = 2-1 = 1\,\mathrm{atm} = 1.013\times10^{6}\ \mathrm{dynes\ cm^{-2}}$$

$$V_2 = 1674\,\mathrm{cc}$$

$$V_1 = 1\,\mathrm{cc}$$

$$L = 539\times4.185\times10^{7}\,\mathrm{erg/g}$$

$$T = 373.2\,\mathrm{K}$$

Using
$$\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}$$

or
$$dT=\frac{dP\cdot T\cdot(V_2-V_1)}{L}$$

$$=\frac{1.013\times10^{6}\times373.2\times(1674-1)}{539\times4.185\times10^{7}}$$

$$dT = 28.04\,\mathrm{K}.$$

$\therefore$ Boiling point $=373.2+28.04=401.24\,\mathrm{K}$

Example 18

Calculate under what pressure ice freezes at 272 K if the change in specific volume when 1 kg of water freezes is $91\times10^{-6}\,\mathrm{m^3}$. Latent heat of ice $3.36\times10^{5}\ \mathrm{Jkg^{-1}}$

Solution

$$dT = 273-272 = 1\,\mathrm{K}$$

$$V_2 - V_1 = 91\times10^{-6}\,\mathrm{m^3}$$

$$T = 273$$

$$L = 3.36 \times 10^5 \text{J kg}^{-1}$$

Using $$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$\therefore \quad dP = \frac{LdT}{T(V_2 - V_1)} = \frac{3.36 \times 10^5 \times 1}{273 \times 91 \times 10^{-6}}$$

$$= 13.525 \times 10^6 \text{Nm}^{-2}$$

or $$dP \doteq \frac{13.525 \times 10^6}{1.013 \times 10^5} = 133.5 \text{atm}$$

Example 19

Calculate the change in temperature of boiling water when the pressure is increased by 2.712 cm of Hg. The normal boiling point of water at atmospheric pressure is $100°C$. Latent heat of steam is 537cal g^{-1} and specific volume of steam 1674 cc.

Solution

$$dP = 2.712 \text{ cm of Hg}$$

$$= 2.712 \times 13.6 \times 980 \text{ dynes cm}^{-2}$$

$$T = 100 + 273 = 373$$

$$V_1 = 1 \text{cc}, \quad V_2 = 1674 \text{cc}, L = 537 \times 4.2 \times 10^7 \text{ergs}$$

Using $$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \cdot T \cdot (V_2 - V_1)}{L}$$

$$dT = \frac{2.712 \times 13.6 \times 980 \times 373 \times (1674 - 1)}{537 \times 4.2 \times 10^7}$$

$$dT = 1K \cdot$$

Example 20

The latent heat of fusion of ice I is 3.34 × 105 J kg^{-1} at 0°C and atmospheric pressure. If the change in specific volume on melting is –9.05 × 10–5 $m^3 kg^{-1}$, then calculate the change of melting temperature due to change of pressure.

Solution

$L = 3.34 \times 10^5\,\mathrm{J\,kg^{-1}},\ T = 273\,\mathrm{K},\ v_2 - v_1 = -9.05 \times 10^{-5}\,\mathrm{m^3 kg^{-1}}$

Using $$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

or $$dT = \frac{T(v_2 - v_1)}{L}\,dP$$

$$dT = \frac{-273 \times 9.05 \times 10^{-5}}{3.34 \times 10^5}\,dP$$

$$dT = 7.39 \times 10^{-8}\,dP$$

If $dP = 1\,\mathrm{atm}$

$\therefore$ change melting temperature $= 7.39 \times 10^{-8}\,\mathrm{K\,Pa^{-1}}$

IMPORTANT FORMULAE

1. Legendre transformation:

   If f is a function of (x, y), then $g(u, y)$ is

   $$g(u, y) = f - ux$$

   where $$u = \frac{\partial f}{\partial x}$$

2. Enthalpy (H):

   $$H = H(V, S)$$

   $$H = U + PV$$

   $$dH = TdS + VdP$$

   $$\left(\frac{\partial H}{\partial S}\right)_P = T,\quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

3. Helmholtz function (A):

   $$A = A(S, V)$$

   $$A = U - TS$$

$$dA = -PdV - SdT$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P, \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

4. Gibb's function (G):

$$G = G(P, T)$$

$$G = A + PV$$

or
$$G = U - TS + PV$$

or
$$G = H - TS$$

$$dG = VdP - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

5. Internal energy function (U):

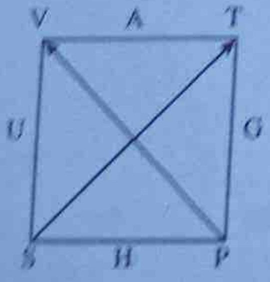
$$U = U(V, S)$$

$$dU = -PdV + TdS$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P, \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

6. $C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \; ; \; C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P .$

7. VAT - VUS diagram:



8. Condition for exact differential:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y .$$

9. Maxwell's relations:

(i) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(ii) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(iii) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(iv) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

10. (i) First TdS equation: S(T, V)

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

(ii) Second TdS equation: S(T, P)

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

(iii) third TdS equation: $S = S(P, V)$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV.$$

11. For a perfect gas: $\left(\frac{\partial U}{\partial T}\right)_V = 0$

12. For a real gas: $U = \int C_V dT - \frac{a}{V} + \text{constant}$

13. Volume expansivity: $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

14. Isothermal compressibility: $k = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$.

15. When a system undergoes a reversible isothermal change of pressure

(i) Heat transferred $Q = -TV\beta(P_f - P_i)$

(ii) Work done $$W = \frac{kV}{2}\left(P_f^2 - P_i^2\right)$$

(iii) Change in internal energy
$$\Delta U = Q + W.$$

16. When a system undergoes a reversible adiabatic change of pressure

change in temperature $$\Delta T = \frac{TV\beta}{C_P}(P_f - P_i).$$

17. For a first order phase change
    (i) Pressure and temperature are constant
    (ii) Gibb's free energy is continuous
    $$G_1 = G_2$$
    (iii) The entropy and density (volume) change.

18. Clausius' Clapeyron equation:

(i) $$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

(ii) $$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

(iii) $$\frac{dP}{dT} = \frac{h_2 - h_1}{T(v_2 - v_1)}$$

UNIVERSITY MODEL QUESTIONS

Section A

(*Answer questions in about* **two** *or* **three** *sentences*)

Short answer type questions

1. What it Legendre transformation?
2. What are thermodynamic functions?
3. What are thermodynamic potentials?
4. Define internal energy of a system. What are its properties?
5. What is Helmholtz free energy? Give two of its properties.
6. What is enthalpy? Give two of its properties.
7. What is Gibbs function? Give two of its properties.
8. How will you construct enthalpy H from internal energy U?

9. What is the significance of thermodynamic potential?
10. What is throttling process?
11. What is the connection between throttling process and enthalpy?
12. Why do we say that dU, dF, dH and dG are exact differentials?
13. Write down the four Maxwells relationships.
14. Write down the Clapeyron latent heat equation, and explain the symbols.
15. Explain the effect of change of pressure on the melting point.
16. Explain the effect of change of pressure on the boiling point.
17. Write down TdS equations and explain the symbols.
18. What is phase change?
19. Define a first order phase change. Give two examples.
20. How will you characterise a first order phase change?
21. Draw the graphical variation of Gibb's potential, entropy and volume with respect to temperature during a first order phase change.
22. What is the effect of change in pressure on temperature during first order phase transition?
23. What is meant by a pure substance?
24. What is a phase diagram?
25. Draw a PV diagram for a pure substance.
26. Draw phase diagram for pure water.
27. Distinguish between gas and vapour.
28. Draw the density curve of liquid and vapour.
29. Distinguish between PT and PV diagrams.
30. Define the following:

    (i) sublimation curve (ii) vapourisation curve and (iii) fusion curve.
31. What is triple point?
32. Distinguish between triple point and normal melting point of ice.
33. What is regelation?
34. What is the relation between Clausius-Clapeyron equation and phase diagram?
35. During first order phase what happens to the parameters C_p, β and K.

Section B

(*Answer questions in a* **paragraph** *of about half a page to one page*)

Paragraph / Problem type questions

1. Starting from internal energy U, derive the remaining thermodynamic functions using Legendre transformation.

2. Distinguish between $-\int PdV$ and $\int VdP$.
3. Derive the condition for exact differential.
4. Derive any two Maxwell's relations.
5. Derive the first TdS equation.
6. Derive the second TdS equation.
7. Derive the third TdS equation.
8. Derive the relation $\left(\frac{\partial U}{\partial S}\right)_V = T$
9. Derive the relation $\left(\frac{\partial H}{\partial S}\right)_P = T$
10. Derive the relation $\left(\frac{\partial U}{\partial V}\right)_S = -P$
11. Derive the relation $\left(\frac{\partial H}{\partial P}\right)_S = V$
12. Derive the relation $\left(\frac{\partial H}{\partial T}\right)_P = C_P$.
13. Using Maxwell's equation show that for a Vander waal's gas $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$
14. Using Maxwell's relation show that $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$
15. Prove that $\left(\frac{\partial C_P}{\partial P}\right)_T = 0$ for all gases.
16. Water boils at a temperature of 101°C at a pressure of 787 mm of Hg. One gram of water occupies $1601 cm^3$ on evaporation. Calculate the latent heat of vapourisation. [511.33 cal/g]
17. Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres
    Density of ice = $0.917\ gcm^{-3}$ and latent heat of ice = $336\ Jg^{-1}$. [–0.7326 K]
18. Lead is melted at 600K at one atmospheric pressure. Its density decreases from 11.01 to

$10.65\,\mathrm{gcm^{-3}}$. The latent heat of fusion is $24.5\,\mathrm{Jg^{-1}}$. What is the melting point at a pressure of 100 atmospheres. [600.754 K]

19. The ratio of densities of ice and water at $0^{\circ}\mathrm{C}$ is $\frac{10}{11}$. Calculate the decrease in the melting point of ice. $L = 80\,\mathrm{calg^{-1}}$ and change in specific volume $0.1\,\mathrm{cc\,g^{-1}}$. The increase in pressure is one atmosphere. $[8.2\times10^{-3}\,\mathrm{K}]$

20. Calculate the change in melting point of naphthalene for 2 atmosphere rise in pressure. Melting point of naphthalene is $80^{\circ}\mathrm{C}$. $L = 4563\,\mathrm{cal/mol}$. Increase in volume on fusion $18.7\,\mathrm{cm^3 mol^{-1}}$. [0.06976 K]

21. Show that for an ideal gas $A = \int C_V dT - T\int \frac{C_V}{T} dT - nRTV - \text{constant } T + \text{constant}$

22. Derive the relation $H = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P$.

23. Derive the ration $C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$.

24. Show that the Legendre transformation $J\left(\frac{1}{T}, V\right)$ that produces the thermodynamical potential $Y\left(\frac{1}{P}, \frac{P}{T}\right)$ known as the Planck function and defined by the transformation

$$Y = -\frac{H}{T} + S = -\frac{G}{T}$$

and
$$dY = \frac{H}{T^2}dT - \frac{V}{T}dP$$

where
$$J = -\frac{U}{T} + S$$

25. From the fact that $\frac{dV}{V}$ is an exact differential, derive the relation

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial k}{\partial T}\right)_P.$$

26. Show that the second TdS equation may be written as

$$TdS = C_P dT - V\beta T dP.$$

27. The pressure on 0.2 kg of water is increased reversibly and isothermally from atmospheric pressure to 3×10^8 Pa at 20°C. $\beta = 206.80 \times 10^{-6} K^{-1}$, $k = 4.589 \times 10^{-10} Pa^{-1}$
    a) How much heat is transferred
    b) How much is the work done
    c) Calculate the change in internal energy.

28. Derive the relation $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$.

29. A gas obeys the equation $P(v-b) = RT$ where b is constant and c_v is constant show that $P(v-b)^\gamma =$ constant for an adiabatic process.

30. When lead is melted at atmospheric pressure, the melting point is 600 K, the density decreases from 11.01 to 10.65 gcm^{-3} and latent heat of fusion is 24.5 $J\,g^{-1}$. What is the melting point at the pressure of 1.01×10^7 Pa ? [600.76 K]

Section C

(Answer questions in about **two** *pages)*

Long answer type questions (Essays)

1. Derive Maxwells four thermodynamical relations. Use one of them to obtain Clausius - Clapeyron's latent heat equation.
2. Deduce thermodynamic potentials and derive Maxwells relations.
3. Discuss the first order phase transition in detail.
4. Discuss the second order phase transition in detail.
5. Discuss the phase diagram for pure water in detail.

Hints to problems

1 to 12 - All book works

13. See example 1

We have $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ ..... (1)

For Vander waal's gas $\left(P+\frac{a}{V^2}\right)(V-b)=RT$

Find $\left(\frac{\partial P}{\partial T}\right)_V$ and substitute in eq (1).

14. Start with $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ then proceed as in example 3

Remember that $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

15. See example 13.

16. $\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}$

$dP = 787-760 = 27$ mm of Hg

$dT = 1K,\ V_2-V_1 = 1601-1 = 1600,\ T = 373K$

17. $\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}$

$dP = 100-1 = 99\,\text{atm} = 99\times 76\times 13.6\times 980$

$L = 336\times 10^7\,\text{ergs}\,g^{-1} \qquad T = 273K$

$V_2-V_1 = 1-\frac{1}{0.917} = -0.091\,\text{cm}^3$ Find dT.

18. $\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}$ $\qquad dP = 100-1 = 99$

$= 99\times 76\times 13.6\times 980$

$L = 24.5\,J/g = 24.5\times 10^7\,\text{ergs}\,g^{-1} \quad V_1 = \frac{1}{11.01}\text{cm}^3, \quad V_2 = \frac{1}{10.65}\text{cm}^3$ Find dT.

19. $dP = 1.01\times 10^5\,\text{Nm}^{-2} \qquad L = 80\times 4.2\times 10^3\,\text{J kg}^{-1}$

$T = 273K \qquad V_2-V_1 = -0.1\,\text{cm}^3 g^{-1} = -0.1\times 10^{-3}\,\text{m}^3\text{kg}^{-1}$ Find dT

20. $dP = 2\,\text{atm} = 2\times 1.013\times 10^6\,\text{dynes}\,\text{cm}^{-2}$

$T = 80+273 \qquad L = 4563\times 4.2\times 10^7\,\text{ergs}\,\text{mol}^{-1}$

$V_2 - V_1 = 18.7\,\text{cm}^3$ Find dT.

21. We have $dA = -SdT - PdV$ ..... (1)

For ideal gas $PV = nRT$

$$\therefore \quad dA = -SdT - \frac{nRT}{V}dV \quad \text{..... (2)}$$

Use $S = \int \frac{dQ}{T}$

Then integrate eqn (2) to get the result.

22. We have $G = H - TS$

or $H = G + TS$ ..... (1)

But $dG = VdP - SdT$

$$\therefore \quad \left(\frac{\partial G}{\partial T}\right)_P = -S.$$ Put this in eq (1)

$$\therefore \quad H = G - \left(\frac{\partial G}{\partial T}\right)_P$$

The above relation can be written as

$$H = T^2\left[G - \frac{T\left(\frac{\partial G}{\partial T}\right)_P}{T^2}\right]$$

but $$\frac{T\left(\frac{\partial G}{\partial T}\right)_P - G}{T^2} = \frac{\partial}{\partial T}(G/T)$$

$$\therefore \quad H = -T^2\frac{\partial}{\partial T}(G/T)$$

23. We have $H = G + TS$

Differentiate with respect to T, keeping P constant

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial G}{\partial T}\right)_P + T\left(\frac{\partial S}{\partial T}\right)_P + S$$

$$C_P = \left(\frac{\partial G}{\partial T}\right)_P + T\left(\frac{\partial S}{\partial T}\right)_P + S$$

or

Use $$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and we get } = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P.$$

24. $f(x, y) \rightarrow g(u, y)\ g = f - ux$

Here $J\left(\frac{1}{T}, V\right) \rightarrow Y\left(\frac{1}{T}, \frac{P}{T}\right)$

we get $Y = J\left(\frac{1}{T}, V\right) - \frac{PV}{T}$

$$Y = -\frac{U}{T} + S - \frac{PV}{T}$$

$$Y = -\frac{U + TS}{T} - \frac{PV}{T} \qquad \text{..... (2)}$$

Use $H = U - TS$ $\quad Y = -\frac{H}{T} + S$

Taking the differential of eq (2), we get

$$dY = \frac{H}{T^2}dT - \frac{V}{T}dP.$$

25. Since $\frac{dV}{V}$ is an exact differential we can write

$$\left(\frac{\partial^2 V}{\partial T \partial P}\right)_P = \left(\frac{\partial^2 V}{\partial P \partial T}\right)_T$$

Using $$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The above eqn becomes

$$\left[\frac{\partial}{\partial T}(-kV)\right]_P = \left[\frac{\partial}{\partial P}(\beta V)\right]_T$$

Perform differentiation

$$-k\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial k}{\partial T}\right)_P = \beta\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial \beta}{\partial P}\right)_T$$

Deside by V

$$-\frac{k}{V}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial k}{\partial T}\right)_P = \frac{\beta}{V}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial P}\right)_T$$

or

$$-\frac{k}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{\beta}{V}\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial k}{\partial T}\right)_P + \left(\frac{\partial \beta}{\partial P}\right)_T$$

Substituting for

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

and

$$\left(\frac{\partial V}{\partial P}\right)_T = -kV$$

$$-\frac{k}{V}\cdot\beta V - \frac{\beta}{V} - kV = \left(\frac{\partial k}{\partial T}\right)_P + \left(\frac{\partial \beta}{\partial P}\right)_T$$

$$0 = \left(\frac{\partial k}{\partial T}\right)_P + \left(\frac{\partial \beta}{\partial P}\right)_T$$

or

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial k}{\partial T}\right)_P$$

26. From second TdS equation, we have

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP.$$

Using

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$\therefore$

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

$\therefore$

$$TdS = C_p dT - T\beta V\, dP.$$

27. a) Heat transferred $Q = -T\beta V(P_f - P_i)$

$$T = 20 + 273 = 293\,\text{K} \qquad V = \frac{m}{\rho} = \frac{0.2}{10^3}$$

$$\beta = 206.80 \times 10^{-6}\,\text{K}^{-1},$$

$$P_f - P_i = (3\times10^8 - 1\times10^5) = 2999\times10^5$$

Substituting $Q = -3634.3\,\text{J}$

b) Work done

$$= \frac{kV}{2}\left(P_f^2 - P_i^2\right)$$

$$= \frac{4.589}{2}\times10^{-10}\times0.2\times10^{-3}\left[(3\times10^8)^2 - (10^5)^2\right]$$

$$= 4130.1\,\text{J}$$

c) Change in internal energy

$$\Delta U = Q + W = 495.8\,\text{J}$$

28. From Maxwell's relations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

Differentiate with respect to temperature

$$\left(\frac{\partial^2 S}{\partial T\partial P}\right)_T = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad \text{..... (2)}$$

But $C_P = T\left(\dfrac{\partial S}{\partial T}\right)_P$, we get

$$\left(\frac{\partial C_P}{\partial P}\right)_T = T\left(\frac{\partial^2 S}{\partial T\partial P}\right)_T \qquad \text{..... (4)}$$

From eqs 2 and 4 we get the result.

29. We have

$$đQ = dU + PdV$$

$$TdS = C_V dT + PdV$$

For adiabatic process $dS = 0$ and put $p = \dfrac{RT}{v - b}$

$$0 = C_V dT + \frac{RT}{v - b} dV$$

Using $$C_P - C_V = nR$$

$$c_p - c_v = R$$

$$c_v \frac{dT}{T} + (c_p - c_v) \frac{T}{v - b} dv = 0$$

Divide by T $$c_v \frac{dT}{T} + (c_p - c_v) \frac{dv}{v - b}$$

Integrate $$c_v \ln T + (c_p - c_v) \ln(v - b) = \text{constant}$$

Divide by c_v $$\ln T + (\gamma - 1) \ln(v - b) = \text{constant}$$

$$\ln T - \ln(v - b) + \gamma \ln(v - b) = \text{constant}$$

$$\ln \frac{T}{v - b} + \ln(v - b)^{\gamma} = \text{constant}$$

$$\ln \frac{P}{R} + \ln(v - b)^{\gamma} = \text{constant}$$

$$\ln \frac{P(v - b)^{\gamma}}{R} = \text{constant}$$

or $$P(v - b)^{\gamma} = \text{constant}$$

30. Use $$\frac{dP}{dT} = \frac{l}{T(v_1 - v_2)}$$

$$dT = \frac{T(v_1 - v_2)}{l} dP.$$

$$T = 600\,\text{K}, \; v_1 - v_2 = \frac{1}{\rho_1} - \frac{1}{\rho_2}, \; l = 24.5\,\text{J g}^{-1} \; dP = 1.01 \times 10^7 - 1.01 \times 10^5,$$

we get 600.75 K.