

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	Thermodynamics: Part 1
Module Id	kech_10601
Pre-requisites	System, Surrounding, Internal energy, First law of thermodynamics.
Objectives	After going through this module the learners will be able to: <ol style="list-style-type: none">1. Identify various energy conversions and different type of thermodynamic systems.2. Define state functions.3. Calculate internal energy in various systems.4. State first law of thermodynamics in mathematical terms.5. Explain pV-diagrams for various thermodynamic processes and calculate work done from these diagrams.
Keywords	Isochoric process, free expansion of gas, pV -diagram

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1. Introduction

What happens when a fuel is burnt, a cell is used in torch, water is used to run a turbine, a wind mill is used to pump water. Obviously there is transformation of one form of energy into another. The study of all these transformations of energies is called as thermodynamics. The laws of thermodynamics deals with energy changes of large macromolecules rather than microscopic systems. These laws are applicable only in the state of equilibrium.

There are so many things happening around us. Some of these are physical in nature, some are chemical. Whatever may be the change is, it can be studied broadly from two main viewpoints.

- a. Exchange of matter.
- b. Exchange of energy.

2. Thermodynamic terms

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

2.1 The System and the Surroundings

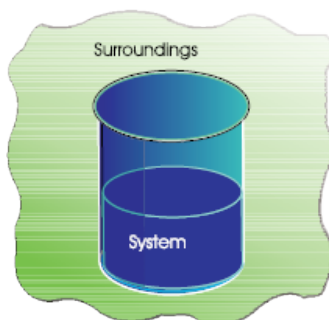


Fig. 1 System and the surroundings

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe.

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 1).

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

2.2 Types of the System

We, further classify the systems according to the movements of matter and energy in or out of the system.

I. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 2 (a)]. The presence of reactants in an open beaker is an example of an open system*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

II. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.

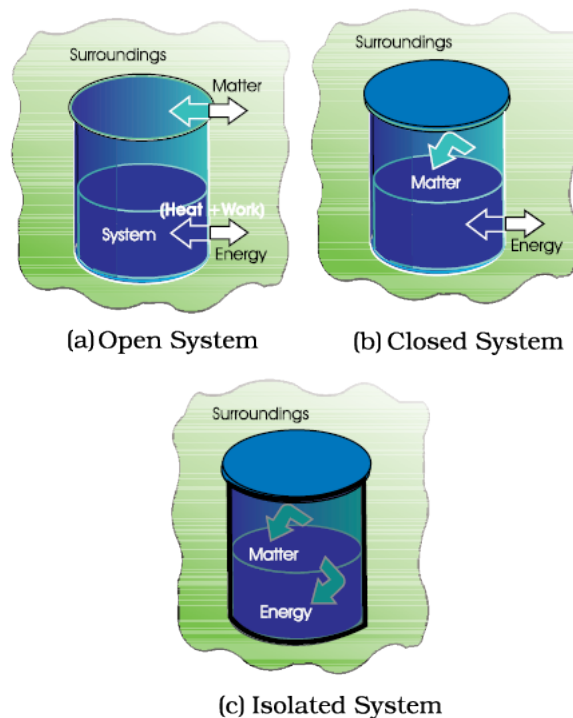


Fig. 2 Open, closed and isolated systems.

III. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

3. The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by state functions or state variables.

The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p , V , T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the

properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once this minimum number of macroscopic properties is fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

4. The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

(a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as adiabatic. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 3).

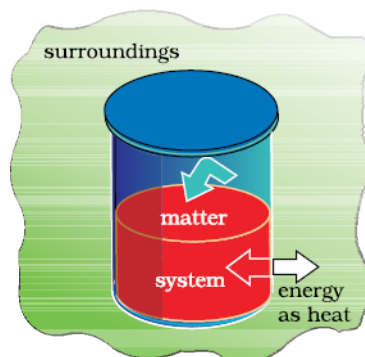


Fig. 3 An adiabatic system which does not permit the transfer of heat through its boundary.

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as T_A . Let the internal energy

of the system in state A be called U_A . We can change the state of the system in two different ways.

One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as T_B . It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be U_B and the change in internal energy, $\Delta U = U_B - U_A$.

Second way: We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$.

In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system.

So, it seems appropriate to define a quantity, the internal energy U , whose value is characteristic of the state of a system, whereby the adiabatic work, w_{ad} required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, ΔU i.e.,

$$\Delta U = U_2 - U_1 = w_{ad}$$

Therefore, internal energy, U , of the system is a state function.

The positive sign expresses that w_{ad} is positive when work is done on the system. Similarly, if the work is done by the system, w_{ad} will be negative.

Some of other familiar state functions are V , p , and T . For example, if we bring a change in temperature of the system from 25°C to 35°C , the change in temperature is $35^\circ\text{C} - 25^\circ\text{C} = +10^\circ\text{C}$, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both,

(b) Heat

We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q . Let us consider bringing about the same change in temperature by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).

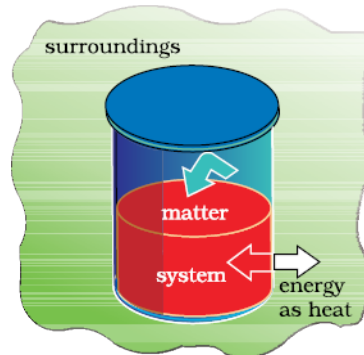


Fig. 4 A system which allows heat transfer through its boundary.

We take water at temperature, T_A in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, T_B . The heat absorbed by the system (water), q can be measured in terms of temperature difference, $T_B - T_A$. In this case change in internal energy, $\Delta U = q$, when no work is done at constant volume.

The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

(c) The general case

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + w \quad (1)$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $q + w = \Delta U$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.

The equation (1) i.e., $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics, which states that

“The energy of an isolated system is constant”.

It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

Example 1 :

Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Solution

(i) $\Delta U = w_{ad}$, wall is adiabatic

(ii) $\Delta U = -q$, thermally conducting walls

(iii) $\Delta U = q - w$, closed system.

5. Work

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy.

First of all, let us concentrate on the nature of work a system can do. We will consider only mechanical work i.e., pressure-volume work. For understanding pressure-volume work, let us

consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p . If external pressure is p_{ex} which is greater than p , piston is moved inward till the pressure inside becomes equal to p_{ex} . Let this change be achieved in a single step and the final volume be V_f . During this compression, suppose piston moves a distance, l and its cross-sectional area of the piston is A [Fig.5].

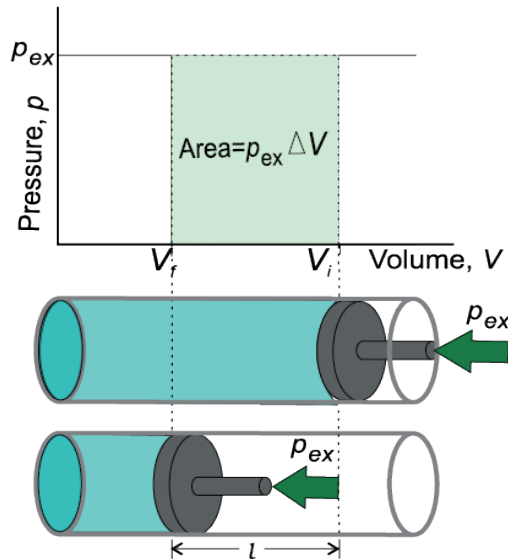


Fig. 5 Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.

then, volume change = $l \times A = \Delta V = (V_f - V_i)$

We also know, $\text{pressure} = \frac{\text{force}}{\text{area}}$

Therefore, force on the piston = $p_{ex} \cdot A$

If w is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l$$

$$= p_{ex} \cdot (-\Delta V) = -p_{ex} \Delta V = -p_{ex} (V_f - V_i) \quad (1)$$

The negative sign of this expression is required to obtain conventional sign for w , which will be positive. It indicates that in case of compression work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$ [Fig. 6]

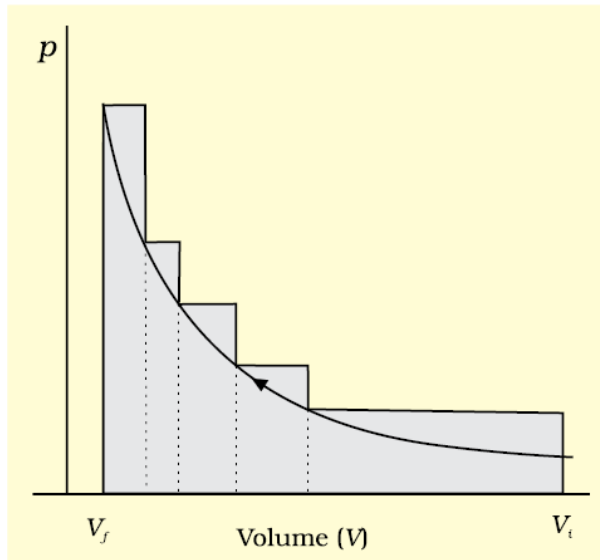


Fig. 6 pV -plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f . Work done on the gas is represented by the shaded area.

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV . In such a case we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} p_{ex} dV \quad (2)$$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression [Fig. 6]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} - dp)$. In general case we can write, $p_{ex} = (p_{in} + dp)$. Such processes are called reversible processes.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as irreversible processes.

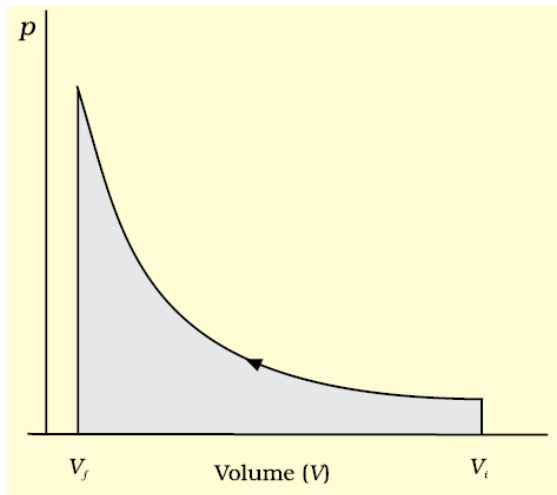


Fig. 7 pV -plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f . Work done on the gas is represented by the shaded area.

In chemistry, we face problems that can be solved if we relate the work term to the internal pressure of the system. We can relate work to internal pressure of the system under reversible conditions by writing equation (3) as follows:

$$w_{rev} = - \int_{V_i}^{V_f} p_{ex} dV = - \int_{V_i}^{V_f} (p_{in} \pm dp) dV$$

Since $dp \times dV$ is very small we can write

$$w_{rev} = - \int_{V_i}^{V_f} p_{in} dV \tag{3}$$

Now, the pressure of the gas (p_{in} which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$\begin{aligned} w_{rev} &= - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \\ &= -2.303 nRT \log \frac{V_f}{V_i} \end{aligned}$$

3. Free expansion: Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation (2) and (3)).

Now, we can write equation $\Delta U = q + w$ in number of ways depending on the type of processes.

Let us substitute $w = -p_{\text{ex}}\Delta V$ (eq. 2) in equation $\Delta U = q + w$, and we get $\Delta U = q - p_{\text{ex}}\Delta V$

If a process is carried out at constant volume ($\Delta V = 0$), then $\Delta U = q_V$ the subscript V in q_V denotes that heat is supplied at constant volume.

4. *Isothermal and free expansion of an ideal gas*

For isothermal ($T = \text{constant}$) expansion of an ideal gas into vacuum; $w = 0$ since $p_{\text{ex}} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$

Equation (1) $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

$$q = -w = p_{\text{ex}}(V_f - V_i)$$

2. For isothermal reversible change

$$q = -w = nRT \ln \frac{V_f}{V_i}$$

$$= 2.303 nRT \log \frac{V_f}{V_i}$$

3. For adiabatic change, $q = 0$, $\Delta U = w_{\text{ad}}$

Example 2 :

Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion?

Solution

We have $q = -w = p_{\text{ex}}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

Example 3 :

Consider the same expansion, but this time against a constant external pressure of 1 atm.

Solution

We have $q = -w = p_{\text{ex}}(8) = 8 \text{ litre-atm}$

Example 4 :

Consider the same expansion, to a final volume of 10 litres conducted reversibly.

Solution

We have $q = -w = 2.303 \times 10 \log \frac{10}{2}$
 $= 16.1 \text{ litre-atm}$

7. Conclusions:

There are three types of system in thermodynamics:

Open systems in which both heat and matter can be exchanged

Closed systems in which only heat can be exchanged

Isolated systems in which neither heat nor matter can be exchanged

First law of thermodynamics states “*The energy of an isolated system is constant*”.

Chemical reactions involve the generation of gases capable of doing mechanical work i.e., pressure volume work or the generation of heat. $\Delta U = q + w$. ΔU , change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system.

We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $nq = C\Delta T$. Work can be measured by $w = -p_{\text{ex}}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{\text{ex}} = p$ for infinitesimal changes in the volume making $w_{\text{rev}} = -pdV$. In this condition, we can use gas equation, $pV = nRT$.

At constant volume, $w = 0$, then $\Delta U = q_v$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function enthalpy. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.