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.

By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that w_{ad} is positive when work is done **on** the system and the internal energy of system increases. Similarly, if the work is done **by** the system, w_{ad} will be negative because internal energy of the system decreases.

Can you name some other familiar state functions? 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°C–25°C = +10°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 (the same initial and final states as before in section 6.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 6.4).
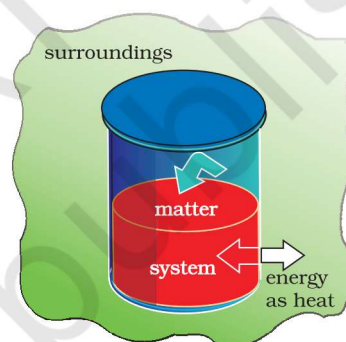

Fig. 6.4 *A system which allows heat transfer through its boundary.*

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.

By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system..

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* *Earlier negative sign was assigned when the work is done on the system and positive sign when the work is done by the system. This is still followed in physics books, although IUPAC has recommended the use of new sign convention.*

(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:

$$\Delta U = q + w \qquad (6.1)$$

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 6.1 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.

Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system.

Problem 6.1

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.

6.2 APPLICATIONS

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. Let us see how!

6.2.1 Work

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
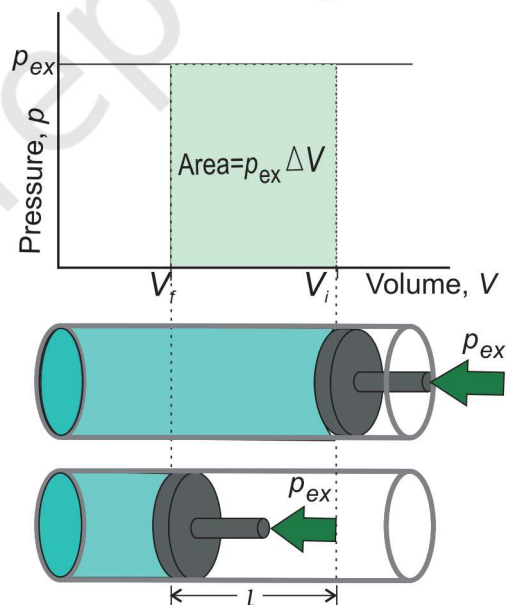

Fig. 6.5(a) *Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.*

be achieved in a single step and the final volume be V_f. During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A [Fig. 6.5(a)].

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

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

Therefore, force on the piston = p_{ex} . A

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

w = force × distance = p_{ex} . A .l

$= p_{ex} . (-\Delta V) = - p_{ex} \Delta V = - p_{ex} (V_f - V_i)$ (6.2)

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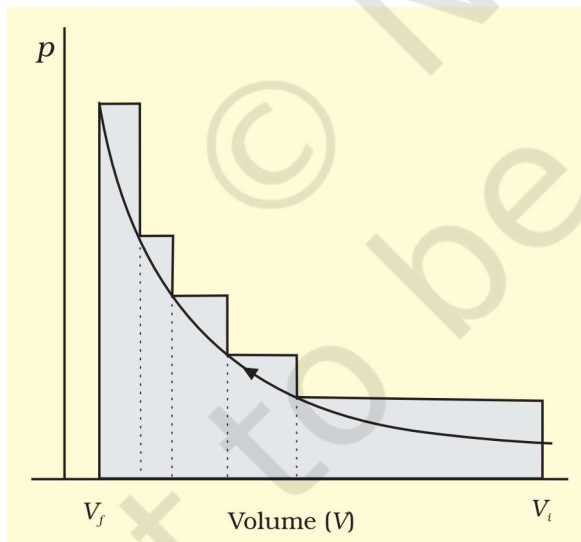
If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} p_{ex} dV \qquad (6.3)$$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression [Fig. 6.5(c)]. 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, $p_{ex} = (p_{in} \pm dp)$. 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
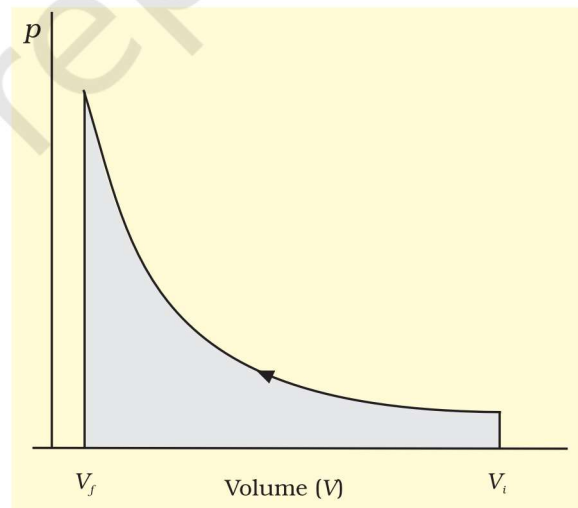

Fig. 6.5 (b) *pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

Fig. 6.5 (c) *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.*

other than reversible processes are known as irreversible processes.

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 6.3 as follows:

$$\mathrm{w}_{rev} = -\int_{V_i}^{V_f} p_{ex} dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\, dV$$

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

$$\mathrm{w}_{rev} = -\int_{V_i}^{V_f} p_{in} dV \qquad (6.4)$$

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),

$$\mathrm{w}_{rev} = -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.303\, nRT \log \frac{V_f}{V_i} \qquad (6.5)$$

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 6.2 and 6.3).

Now, we can write equation 6.1 in number of ways depending on the type of processes.

Let us substitute $\mathrm{w} = -p_{ex}\Delta V$ (eq. 6.2) in equation 6.1, and we get

$$\Delta U = q - p_{ex}\Delta V$$

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.

Isothermal and free expansion of an ideal gas

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

Equation 6.1, $\Delta U = q + \mathrm{w}$ can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change

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

2. For isothermal reversible change

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

    $= 2.303\, nRT \log \dfrac{V_f}{V_i}$

3. For adiabatic change, $q = 0$,

    $\Delta U = \mathrm{w}_{ad}$

Problem 6.2

Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C 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 $q = -\mathrm{w} = p_{ex}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

Problem 6.3

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

Solution

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

Problem 6.4

Consider the expansion given in problem 6.2, for 1 mol of an ideal gas conducted reversibly.

Solution

We have $q = -\mathrm{w} = 2.303\, nRT \log \dfrac{V_f}{V_s}$

$= 2.303 \times 1 \times 0.8206 \times 298 \times \log \dfrac{10}{2}$

= 2.303 x 0.8206 x 298 x log 5

= 2.303 x 0.8206 x 298 x 0.6990

= 393.66 L atm

6.2.2 Enthalpy, *H*

(a) A Useful New State Function

We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_v$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation (6.1) as $\Delta U = q_p - p\Delta V$ at constant pressure, where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$U_2 - U_1 = q_p - p(V_2 - V_1)$

On rearranging, we get

$q_p = (U_2 + pV_2) - (U_1 + pV_1)$ 　　(6.6)

Now we can define another thermodynamic function, the enthalpy *H* [Greek word *enthalpien*, to warm or heat content] as :

$H = U + pV$ 　　(6.7)

so, equation (6.6) becomes

$q_p = H_2 - H_1 = \Delta H$

Although *q* is a path dependent function, *H* is a state function because it depends on *U*, *p* and *V*, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path.

For finite changes at constant pressure, we can write equation 6.7 as

$\Delta H = \Delta U + \Delta pV$

Since *p* is constant, we can write

$\Delta H = \Delta U + p\Delta V$ 　　(6.8)

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure.

ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

At constant volume ($\Delta V = 0$), $\Delta U = q_v$, therefore equation 6.8 becomes

$\Delta H = \Delta U = q_v$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$pV_A = n_A RT$

and 　　　$pV_B = n_B RT$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or 　$p(V_B - V_A) = (n_B - n_A)RT$

or 　$p\Delta V = \Delta n_g RT$ 　　(6.9)

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation 6.9 in equation 6.8, we get

$\Delta H = \Delta U + \Delta n_g RT$ 　　(6.10)

The equation 6.10 is useful for calculating ΔH from ΔU and *vice versa*.

Problem 6.5

If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol^{-1}. Calculate the internal energy change, when