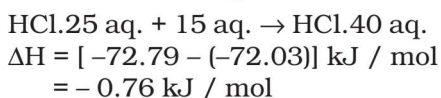


If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain–



This value (–0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

6.6 SPONTANEITY

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes? What determines the direction of a spontaneous change? In this section, we shall establish some criterion for these processes whether these will take place or not.

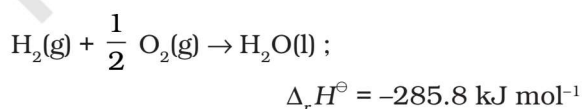
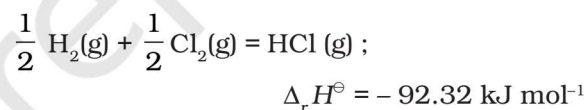
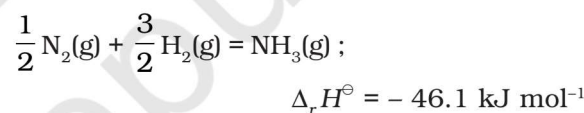
Let us first understand what do we mean by spontaneous reaction or change? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place

between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

A spontaneous process is an irreversible process and may only be reversed by some external agency.

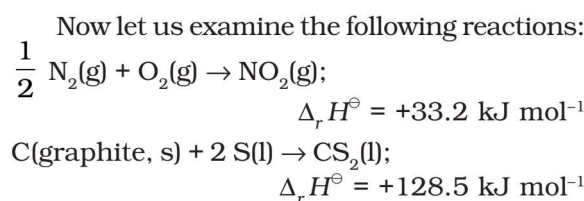
(a) Is Decrease in Enthalpy a Criterion for Spontaneity ?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:



The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.10(a).

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far!



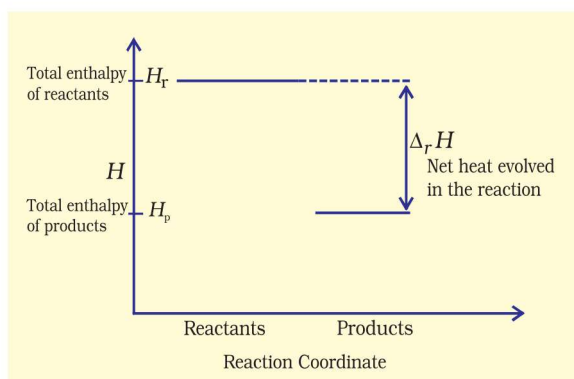


Fig. 6.10 (a) Enthalpy diagram for exothermic reactions

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.10(b).

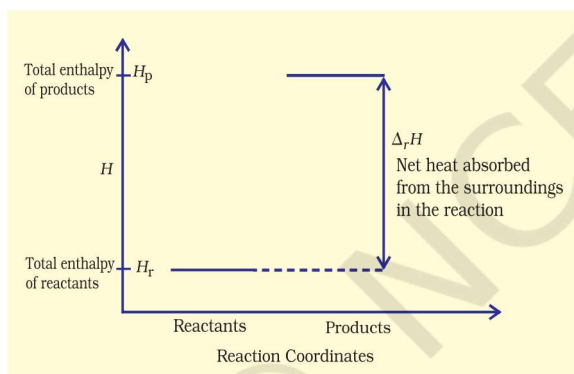


Fig. 6.10 (b) Enthalpy diagram for endothermic reactions

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and Spontaneity

Then, what drives the spontaneous process in a given direction? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 6.11.

The two gases, say, gas A and gas B are represented by black dots and white dots

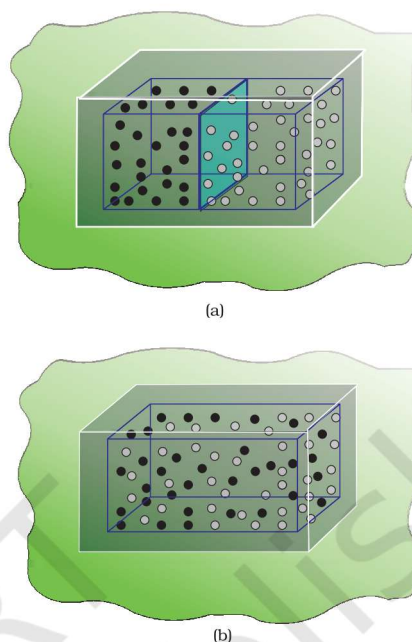


Fig. 6.11 Diffusion of two gases

respectively and separated by a movable partition [Fig. 6.11 (a)]. When the partition is withdrawn [Fig.6.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !

At this point, we introduce another thermodynamic function, **entropy** denoted as S . The above mentioned disorder is the manifestation of entropy. To form a mental

picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (q) has randomising influence** on the system. Can we then equate ΔS with q ? Wait! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average chaotic motion of particles in the system.** Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \quad (6.18)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \quad (6.19)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Problem 6.10

Predict in which of the following, entropy increases/decreases :

- (i) A liquid crystallizes into a solid.
- (ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
- (iii) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- (iv) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$

Solution

- (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
- (ii) At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115 K, these

begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

- (iii) Reactant, NaHCO_3 is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.
- (iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Problem 6.11

For oxidation of iron,



entropy change is $-549.4 \text{ JK}^{-1}\text{mol}^{-1}$ at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^\ominus$ for this reaction is $-1648 \times 10^3 \text{ J mol}^{-1}$)

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total} (\Delta S_{sys} + \Delta S_{surr})$. For calculating ΔS_{surr} , we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^\ominus}{T} \text{ (at constant pressure)}$$

$$= -\frac{(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}}$$

$$= 5530 \text{ JK}^{-1}\text{mol}^{-1}$$

Thus, total entropy change for this reaction

$$\Delta_r S_{total} = 5530 \text{ JK}^{-1}\text{mol}^{-1} + (-549.4 \text{ JK}^{-1}\text{mol}^{-1})$$

$$= 4980.6 \text{ JK}^{-1}\text{mol}^{-1}$$

This shows that the above reaction is spontaneous.

(c) Gibbs Energy and Spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as

$$G = H - TS \quad (6.20)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \quad (6.21)$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS , a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S = (\text{K})(\text{J/K}) = \text{J}$.

Now let us consider how ΔG is related to reaction spontaneity.