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,

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

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

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

Solution

One decides the spontaneity of a reaction by considering

$\Delta S_{total} \left(\Delta S_{sys} + \Delta S_{surr} \right)$. 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

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

$= - \dfrac{\left(-1648 \times 10^3 \, J \, mol^{-1} \right)}{298 \, K}$

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

Thus, total entropy change for this reaction

$\Delta_r S_{total} = 5530 \, JK^{-1}mol^{-1} +$

$\qquad\qquad \left(-549.4 \, JK^{-1}mol^{-1} \right)$

= 4980.6 JK^{-1} 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

$G = H - TS$ \hspace{2cm} (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

$\Delta G = \Delta H - T\Delta S$ \hspace{1.5cm} (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 $T\Delta S = (K) (J/K) = J$.

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

We know,

$\Delta S_{total} = \quad \Delta S_{sys} + \Delta S_{surr}$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T} \right)$$

Rearranging the above equation:

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

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > O$$

$$\Rightarrow -\left(\Delta H_{sys} - T\Delta S_{sys} \right) > 0$$

Using equation 6.21, the above equation can be written as

$-\Delta G > O$

$\Delta G = \Delta H - T\Delta S < 0$ \hfill (6.22)

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous.

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.4 summarises the effect of temperature on spontaneity of reactions.

(d) *Entropy and Second Law of Thermodynamics*

We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

(e) *Absolute Entropy and Third Law of Thermodynamics*

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. **The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.** This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that

it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing $\dfrac{q_{rev}}{T}$ increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

6.7 GIBBS ENERGY CHANGE AND EQUILIBRIUM

We have seen how a knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium
$A + B \rightleftharpoons C + D$; is
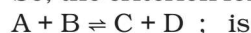
$\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

or $\quad \Delta_r G^\ominus = - RT \ln K$

or $\quad \Delta_r G^\ominus = - 2.303\, RT \log K \qquad (6.23)$

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = - RT \ln K \qquad (6.24)$$

For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G^\ominus$ also depends upon $\Delta_r S^\ominus$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected,

Table 6.4 Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
–	+	–	Reaction spontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

* *The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

depending upon whether $\Delta_r S^{\ominus}$ is positive or negative.

Using equation (6.24),

(i) It is possible to obtain an estimate of $\Delta G^{\ominus}$ from the measurement of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, and then calculate K at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of $\Delta G^{\ominus}$ at any other temperature can be calculated.

Using equation (6.24),

Problem 6.12

Calculate $\Delta_r G^{\ominus}$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. if K_p for this conversion is 2.47×10^{-29}.
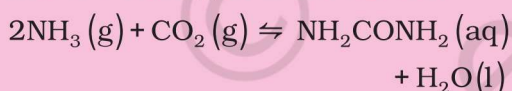
Solution

We know $\Delta_r G^{\ominus} = -2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$

Therefore, $\Delta_r G^{\ominus} =$
$-2.303\ (8.314\ J\ K^{-1}\ mol^{-1})$
$\qquad\qquad \times (298\ K)\ (\log 2.47 \times 10^{-29})$

$= 163000\ J\ mol^{-1}$

$= 163\ kJ\ mol^{-1}$.

Problem 6.13

Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

Standard Gibbs energy change, $\Delta_r G^{\ominus}$ at the given temperature is $-13.6\ kJ\ mol^{-1}$.

Solution

We know, $\log K = \dfrac{-\Delta_r G^{\ominus}}{2.303\ RT}$

$$= \frac{\left(-13.6 \times 10^3\ J\ mol^{-1}\right)}{2.303\left(8.314\ JK^{-1}\ mol^{-1}\right)(298\,K)}$$

$= 2.38$

Hence $K = $ antilog $2.38 = 2.4 \times 10^2$.

Problem 6.14

At 60°C, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1 - 0.5}{1 + 0.5} : x_{NO_2} = \frac{2 \times 0.5}{1 + 0.5}$$

$$p_{N_2O_4} = \frac{0.5}{1.5} \times 1\ atm,\ p_{NO_2} = \frac{1}{1.5} \times 1\ atm.$$

The equilibrium constant K_p is given by

$$K_p = \frac{\left(p_{NO_2}\right)^2}{p_{N_2O_4}} = \frac{1.5}{(1.5)^2\ (0.5)}$$

$= 1.33\ atm.$

Since

$\Delta_r G^{\ominus} = -RT \ln K_p$

$\Delta_r G^{\ominus} = (-8.314\ JK^{-1}\ mol^{-1}) \times (333\ K)$
$\qquad\qquad \times (2.303) \times (0.1239)$

$= -763.8\ kJ\ mol^{-1}$

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + w$. 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 $q = C\Delta T$. Work can be measured by w $= -p_{ex}\Delta V$, in case of expansion of gases. Under reversible process, we can put $p_{ex} = p$ for infinitesimal changes in the volume making $w_{rev} = - p\, dV$. 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, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f \left(a_i \Delta_f H_{\text{products}}\right) - \sum_i \left(b_i \Delta_f H_{\text{reactions}}\right)$$

and in gaseous state by

$\Delta_r H^{\ominus} = \Sigma$ *bond enthalpies of the reactants* $– \Sigma$ *bond enthalpies of the products*

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S, **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation

$\Delta S = \dfrac{q_{\text{rev}}}{T}$ for a reversible process. $\dfrac{q_{\text{rev}}}{T}$ is independent of path.

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G, which is related to entropy and enthalpy changes of the system by the equation:

$\Delta_r G = \Delta_r H - T \Delta_r S$

For a spontaneous change, $\Delta G_{\text{sys}} < 0$ and at equilibrium, $\Delta G_{\text{sys}} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$\Delta_r G^{\ominus} = - RT \ln K$.

K can be calculated from this equation, if we know $\Delta_r G^{\ominus}$ which can be found from $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.