SOLUTION : (A)

We know that work done in a reversible expansion process is always greater than in an irreversible expansion process.

Using First Law of Therodynamics : $q = 0 = \Delta U + (-w)$

Thus, decrease in U will be larger in reversible adiabatic than irreversible adiabatic expansion and since $\Delta U = nC_v \Delta T$, we can conclude that ΔT in reversible adiabatic expansion will be greater than in irreversible adiabatic expansion.

Now, $\Delta H_1 = nC_p$ [redacted]aw of thermodyna

mics 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.

on

A process which proceeds of its own accord without any outside help is termed as a spontaneous process. To understand the concept of spontaneity, we first need to understand the most important factor involved which is Entropy (S) and is explained below :

1. Entropy (S) :

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the system. More is the randomness in the system, more is the entropy of the system.

(i) Entropy is a state function and depends only on initial and final states of the system.

(ii) Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. The distribution of heat also depends on the temperature at which heat is added to the system.

Entropy change of the system for a reversible process is mathematically defined as :

$$dS = \frac{dq_{Rev}}{T} \quad \text{or} \quad \Delta S = \int \frac{dq_{Rev}}{T} = \left(\frac{q_{Rev}}{T}\right) \quad \text{[when the heat is absorbed reversibly at constant T]}$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is released, then ΔS is negative (decrease in entropy). Also, for the same amount of heat absorbed, increase in entropy will be more at lower temperature than at higher temperature.

(iii) If the temperature of a system increases, entropy increases. If the temperature of a system decreases, entropy decreases.

(iv) For a fixed volume system, entropy increases if the number of molecules is increased in the system and vice – versa.

(v) For a system with fixed number of molecules, entropy increases as volume increases and vice – versa.

(vi) Entropy of a system increases with change in the state of a system as : $S(s) \longrightarrow S(\ell) \longrightarrow S(g)$

(vii) Entropy of more complex molecules is larger than those of simpler molecules as in more complex molecules there are more ways of arranging atoms in 3D (i.e. more ramdomness). e.g. $S_{\text{propane}} > S_{\text{ethane.}}$

(viii) Entropy of compounds with similar molecular masses increases (with increase) in their sizes.
e.g. $S_{Ar} < S_{CO_2} < S_{C_3H_8}$

(ix) Entropies of ionic solids becomes larger as the attraction amongst the ions become weaker.
e.g. $S_{NaF} > S_{MgO}$ as in MgO, +2 and –2 charges result in greater attraction.

(x) Harder substances have smaller entropies than softer substances.
e.g. $S_{C(\text{diamond})} < S_{C(\text{graphite})} < S_{Fe} < S_{Al} < S_{Na}$

(xi) All spontaneous processes are irreversible processes or vice - versa.

(xii) When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$. For both reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{Total} is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

2. Criteria for Spontaneity :

First law of thermodynamics is basically the law of conservation of energy. It has no restriction on the way energy can flow. Thus, energy can flow from higher to lower temperature or lower to higher temperature, as per first law of thermodynamics. But, natural processes tend to flow only in one direction (known as direction of spontaneity).

It has been observed that in most of the spontaneous processes/reactions, there is a decrease in energy which seems to be the criteria for spontaneity but it is not the only criteria. Evaporation of water is an endothermic reaction yet it is spontaneous.

There are two criterias which decide the direction of spontaneity:

(a) Decrease in energy **(b)** Increase in entropy

In other words, a chemical reaction or process tends to follow the direction of minimum energy and maximum randomness, i.e. reaction will be more probable to occur if it is exothermic or there is an increase in entropy. A reaction will occur if the value of ΔH is negative and the value of ΔS is positive. But the endothermic reactions in which ΔH is positive, also take place. There are also reactions in which there is decrease in entropy, i.e., ΔS is negative but still they occur. It is, thus, clear that for the spontaneity of a reaction both ΔH and ΔS should be considered simultaneously.

Thus, for processes which do not involve a heat change, increase in entropy is the only criteria. It should be noted that the criterias for the prediction of direction of spontaneity have been derived through mere observations. No process/reaction has been found to violate these.

Illustrating the Concept:

Consider the adiabatic expansion of an ideal gas in vaccum. This system is an isolated system (as no exchange of energy and mass between system and surroundings). So, direction of spontaneity is expansion process because expansion will cause an increase in the entropy of the system.

3. Finding the direction of spontaneity :

For spontaneity, Second Law of Thermodyamics defines the following statements:

(i) In an isolated system, direction of increase in entropy of the system is the direction of spontaneity.

(ii) In a non-isolated system, direction of increase in total entropy i.e. $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings}$, is the direction of spontaneity.

$\Rightarrow$ For a reaction/process to be spontaneous: $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings} > 0$

To focus on the system for thermodynamic analysis, $\Delta S_{Surroundings}$ is defined and eliminated as :

(a) For a reaction :

$$\Delta S_{Surroundings} = \frac{q_{Surroundings}}{T} = \frac{-q_{System}}{T}$$

$$\Delta S_{Surroundings} = \frac{-\Delta H_{System}}{T}$$ [Chemical reactions occur at constant T and P]

$$\Rightarrow \quad \Delta S_{Total} = \Delta S_{System} - \frac{\Delta H_{System}}{T} \quad \Rightarrow \quad -T\Delta S_{Total} = \Delta H_{System} - T\Delta S_{System}$$

(b) For a process :

$$\Delta S_{Surroundings} = \frac{q_{Surroundings}}{T} = \frac{-q_{System}}{T}$$

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings}$$ [In a short while, we will learn to calculate ΔS_{System}]

Also, a new thermodynamic function, Gibbs energy 'G' is introduced to check the spontaneity of the reaction directly and is defined as :

$$G = H - TS$$

$$\Rightarrow \quad \Delta G = \Delta H - \Delta(TS) \quad \text{or} \quad dG = dH - TdS - SdT$$

Thus, for a reaction taking place at a certain temperature, we can also define spontaineity of a reaction in terms of change in Gibbs energy as : $\Delta G_{System} = -T\,\Delta S_{Total} = \Delta H_{System} - T\Delta S_{System}$

(i) If $\Delta S_{Total} > 0 \Rightarrow \Delta G_{System} < 0$ [Spontaneous]

(ii) If $\Delta S_{Total} < 0 \Rightarrow \Delta G_{System} > 0$ [Non- spontaneous]

(iii) If $\Delta S_{Total} = 0 \Rightarrow \Delta G_{System} = 0$ [At Equilibrium]

The free energy of a reaction is the chemical analogue of 'potential energy' of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free enrgy, i.e., ΔG is negative.

For any system in which a reaction/process taking place, $\Delta G = 0$ denotes the attainment of equilibrium. In other words, a reaction/process proceeds till its entropy has become maximum i.e. no furthur change in entropy is possible. A very famous example is the mixing of two ideal gases which happens till the new system has become homogenous (because in that state only it will have maximum entropy).

Calculation of Gibbs energy is very important in finding out the direction of spontaineity and is widely, mostly and mainly used in chemical reactions. We will discuss more on this in the upcoming portions of this chapter.

Case (i) : $\left.\begin{matrix}\Delta S_{\text{System}} > 0 \\ \Delta S_{\text{Surroundings}} > 0\end{matrix}\right\} \Rightarrow \Delta S_{\text{Total}} > 0$

Case (ii) : $\left.\begin{matrix}\Delta S_{\text{System}} < 0 \\ \Delta S_{\text{Surroundigs}} > 0\end{matrix}\right\} \Rightarrow \Delta S_{\text{Total}} > 0 \text{ or } < 0$

Case (iii) : $\left.\begin{matrix}\Delta S_{\text{System}} > 0 \\ \Delta S_{\text{Surroundigs}} < 0\end{matrix}\right\} \Rightarrow \Delta S_{\text{Total}} > 0 \text{ or } < 0$

Case (iv) : $\left.\begin{matrix}\Delta S_{\text{System}} < 0 \\ \Delta S_{\text{Surroundigs}} < 0\end{matrix}\right\} \Rightarrow \Delta S_{\text{Total}} < 0$

Clearly, Case (i) is always spontaneous since change in total entropy is always positive i.e. total entropy is increasing. Case (ii) and (iii) may or may not be spontaneous. Case (iv) is always non-spontaneous since change in total entropy is always negative i.e. total entropy is decreasing.

4. Calculating entropy change in phase change :

When a substance changes phase (e.g., solid to liquid), there is a change in entropy associated with it (even though temperature is constant at phase change).

(a) Melting : $\Delta S_{\text{melting}} = \dfrac{\Delta H_{\text{melting}}}{T_{\text{melting}}}$ = Entropy change due to melting (takes place at constant temperature)

e.g. Entropy change for 1 kg ice at its melting point :

$$\Rightarrow \quad \Delta S_{\text{melting}} = \frac{\left(\dfrac{1000}{18}\right) \times 6 \times 1000}{273} = 1220.8 \text{ J/K}$$

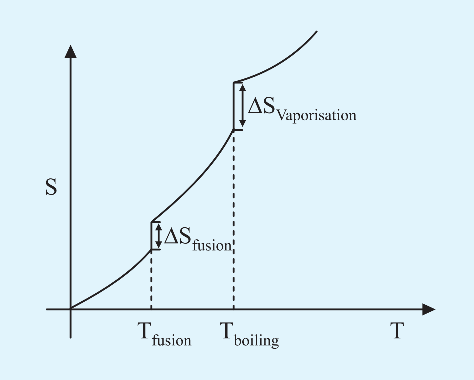
[Enthalpy of fusion of water = 6 kJ/mole]

(b) Vaporisation : $\Delta S_{\text{vaporisation}} = \dfrac{\Delta H_{\text{vaporisation}}}{T_{\text{boiling}}}$

e.g. Entropy change for 1 kg water at its boiling point :

$$\Delta S_{\text{vaporisation}} = \frac{\left(\dfrac{1000}{18}\right) \times 44 \times 1000}{373} = 6552.8 \text{ J/K}$$

[Enthalpy of vaporisation of water = 44 kJ/mole]



***Note* :** According to Trouton's rule $\Delta S_{\text{vap.}}$ of most of the liquids is 88 ± 5 J/mol K at normal boiling point.

(c) Allotropic Transition : $\Delta S_{\text{Transition}} = \dfrac{\Delta H_{\text{Transition}}}{T_{\text{Transition}}}$

e.g. Transition of 1 mole of Sulphur from Rhombic to Monoclinic :

$$\Delta S_{\text{transition}} = \frac{402}{368\ 5} = 1.09 \text{ JK}^{-1}\text{ mol}^{-1}$$

[Enthalpy of transition from rhombic to monoclinic Sulphur = 402 J mole^{-1} and $T_{\text{transition}}$ = 368.5 K]

Entropy of a substance :

First of all, we need to know an important law helpful in finding the entropy of a substance i.e. Third Law of Thermodynamics. As per Third Law of Thermodynamics (also knows as Nernst heat theorem) :

(a) All substance have same heat capacities at 0 K.

(b) Heat capacity of every substance is zero at 0 K.

(c) Entropy of a perfectly crystalline substance is zero at 0 K.

This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy.

Entropy change of a reaction :

To calculate ΔS_{system} for a reaction at say T (K), simply balance the reaction and use the following formula:

$$\Delta S_{\text{System}} = \Delta_r S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}} \quad \text{and} \quad \Delta S_{\text{Surroundings}} = \frac{q_{\text{Surr.}}}{T_{\text{Surr.}}} = \frac{-q_{\text{Sys.}}}{T_{\text{Surr.}}} = \frac{-\Delta H_{\text{Sys.}}}{T_{\text{Surr.}}}$$

as chemical reactions occur at constant T and P.

At standard conditions : $\Delta_r S^{\ominus} = \sum S_P^{\ominus} - \sum S_R^{\ominus}$

Note : Every reactant/product will have a non-zero Entropy for T above 0 K.

Variation of Spontaneity of a reaction with temperature :

We can have an idea of the spontaneity of reaction with temperature using :

$$\Delta G = \underbrace{\Delta H}_{\text{Enthalpy Factor}} - \underbrace{T\Delta S}_{\text{Entropy Factor}}$$

In general, $|\Delta H| >> |T\Delta S|$. Clearly, Entropy factor increases as T increase and decreases as T decreases.

For an exothermic reaction proceeding with a decrease in entropy, ΔG is in general, negative i.e. spontaneous reaction.

For an endothermic reaction proceeding with an increases in entropy, ΔG is in general, positive i.e. non-spontaneous reaction.

Thus, in general, exothermic reaction are spontaneous at room temperature and may tend to become non-spontanceous (if $\Delta S_{\text{system}} < 0$) at higher temperatures. In general, endothermic reactions are non-spontaneous at room temperature and may tend to become spontaneous (if $\Delta S > 0$) at higher temperatures.

Thus, we need to calculate : $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$ for the reaction/process and if it comes out to be > 0 then that direction will be spontaneous.

Note :
- The decrease in Gibbs energy is a measure of the maximum useful work that can be obtained from a system. The Gibbs energy is the *maximum* amount of non-expansion work that can be extracted from a system and this maximum can be attained only in a completely reversible process.
- We can have a rough idea of temperature about which there is a spontaneity change for a reaction and is given by :

$$T_{\text{Switch}} = \frac{\Delta H^{\ominus}_{\text{System}}}{\Delta S^{\ominus}_{\text{System}}}$$

Here, we have assumed that $\Delta H^{\ominus}_{\text{System}}$ and $\Delta S^{\ominus}_{\text{System}}$ doesn't vary with temperature just to get an idea of T_{Switch}

$\Delta_r H^0$	$\Delta_r S^0$	$\Delta_r G^0$	Description
–	+	– (at low T)	Reaction spontaneous at all temperature
–	–	– (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 temperature

Illustration - 4 *Assuming $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ to be independent of temperature, at what temperature will the reaction given below becomes spontaneous?*

$$\begin{array}{lccccc} & N_2(g) & + & O_2(g) & \longrightarrow & 2NO(g) \quad ; \quad \Delta_r H^\ominus = 180.8\ kJ\ mol^{-1}. \\ S^\ominus / JK^{-1}mol^{-1} & 191.4 & & 204.9 & & 210.5 \end{array}$$

SOLUTION :

First calculate $\Delta_r S^\ominus$ for the given reaction as follows :

$$\Delta_r S^\ominus = \sum S_P^\ominus - \sum S_R^\ominus = 2S^\ominus_{NO} - S^\ominus_{N_2} - S^\ominus_{O_2} = 2 \times 210.5 - 191.4 - 204.9 = 24.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Using: $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = 180.8 - 298 \times 24.7 \times 10^{-3} = 173.4\ \mathrm{kJ\ mol^{-1}}$

Clearly, the given endothermic reaction is non–spontaneous at room temperature. So, we need to increase the temperature to make the reaction spontaneous.

$$\Rightarrow \qquad \Delta_r G^\ominus = 180.8 - (T \times 24.7 \times 10^{-3})\ \mathrm{kJ\ mol^{-1}}$$

For spontaneity, put $\Delta_r G^\ominus = 0$ to get :

$$T_{Switch} = \frac{\Delta_r H^\ominus_{Sysstem}}{\Delta_r S^\ominus_{System}} \qquad \Rightarrow \qquad T_{switch} = \frac{180.8 \times 10^3}{24.7} \approx 7320\ \mathrm{K}$$

The reaction becomes spontaneous above a temperature of 7320K.

Illustration - 5 *Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs :*

$$S\ (rhombic) \longrightarrow S\ (monoclinic)$$

If $\Delta_r H = 276.144\ J$ at 298 K and 1 atm and $\Delta_r G = 75.312\ J$

(a) *Calculate $\Delta_r S$ at 298 K*

(b) *Assume that $\Delta_r H$ and $\Delta_r S$ do not vary significantly with temperature, calculate T_{eq}, the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.*

SOLUTION :

(a) Since $\Delta_r G = \Delta_r H - T\Delta_r S$

$$\Rightarrow \quad \Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144 - 75.312}{298} = 0.674\ \mathrm{J\ K^{-1}}$$

(b) Under equilibrium condition $\Delta_r G = 0$

$$\Rightarrow \quad \Delta_r H - T_{eq}\,\Delta_r S = 0 \qquad \Rightarrow \qquad T_{eq} = \frac{\Delta_r H}{\Delta_r S} = \frac{276.144}{0.674} = 409.7\ \text{K}$$

Free energy change of a reaction :

$\Delta_r G$ for a reaction can be calculated using following two methods :

(i) Using : $\Delta_r G = \Delta_r H - T\Delta_r S$

(ii) Using : $\Delta_r G = \sum G_{\text{Poducts}} - \sum G_{\text{Reactants}}$

Take note of the followings while calculating Gibbs energy change for a reaction :

(a) Chemical reaction in which a compound in its standard state is formed from its elements in their standard states, the Gibbs energy change is the Standard Gibbs energy of formation, $\Delta_f G^{\ominus}$.

(b) $\Delta_f G^{\ominus} = 0$ for an element in its standard state.

(c) $\Delta_f G^{\ominus} = \sum G^{\ominus}_{\text{products}} - \sum G^{\ominus}_{\text{reactants}} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$

(d) $\Delta_r G$ is an extensive property.

(e) $\Delta_r G$ changes sign when a process is reversed. [It can be treated in a similar manner as with $\Delta_r H$]

Illustration - 6 *Compute the Gibbs energy change of the reaction at 27°C for the combustion of methane.*

	$CH_4(g)\ +$	$2O_2(g)\ \longrightarrow$	$CO_2(g)\ +$	$2H_2O(\ell)$
$\Delta_f H^{\ominus}$ (in kJ mol^{-1})	-74.8	—	-393.5	-285.8
$S^{\ominus}_m$ (in J K^{-1} mol^{-1})	186	205	214	70

SOLUTION :

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}_{(CO_2)} + 2\Delta_f H^{\ominus}_{(H_2O)} - \Delta_f H^{\ominus}_{(CH_4)} = -393.5 + 2\times(-285.8) - (-74.8) = -890\ \text{kJ mol}^{-1}$$

$$\Delta_r S^{\ominus} = S^{\ominus}_{(CO_2)} + 2S^{\ominus}_{(H_2O)} - S^{\ominus}_{(CH_4)} - 2S^{\ominus}_{(O_2)} = 214 + 2\times 70 - 186 - 2\times 205 = -242\ \text{J/K/mol}$$

$$\Delta_r G = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = -890 - 300\times(-242\times 10^{-3}) = -890 + 72.6 = -817.4\ \text{kJ mol}^{-1}$$

Illustration - 7 *Show that the reaction $CO(g) + (1/2)O_2(g) \longrightarrow CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is -0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and -137.2 kJ mol^{-1}, respectively.*

SOLUTION :

For the given reaction, we have : $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r S^{\ominus} = -0.094\ \text{kJ K}^{-1}\ \text{mol}^{-1}$

The free-energy change of the reaction is :

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}_{CO_2} - \Delta_f G^{\ominus}_{CO} - \frac{1}{2}\Delta_f G^{\ominus}_{O_2}$$

$$= (-394.4 + 137.2)\ \text{kJ mol}^{-1} = -257.2\ \text{kJ mol}^{-1} \qquad [\because \Delta_f G^{\ominus}_{O_2} = 0]$$

Since $\Delta_r G^\ominus$ is negative, the reaction is spontaneous. The enthalpy change of the reaction is:

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus = [-257.2 + (300)(-0.094)]\ \text{kJ mol}^{-1} = -285.4\ \text{kJ mol}^{-1}$$

Since $\Delta_r H^\ominus$ is negative, the reaction is exothermic.

Gibbs energy and Equilibrium Constant:

We can relate $\Delta_r G$ for a reaction under any set of conditions to its value for standard conditions, that is, to $\Delta_r G^\ominus$ by:

$$\Delta_r G = \Delta_r G^\ominus + 2.303\ RT \log_{10} Q \quad \text{where Q is reaction quotient.}$$

If a system is at equilibrium, $\Delta_r G^\ominus = 0$. Thus from the above equation :

$$\Delta_r G^\ominus = -2.303\ RT \log_{10} K_{eq} \qquad \text{where } K_{eq} \text{ is thermodynamic equilibrium constant.}$$

Magnitude of $\Delta_r G^\ominus$ determines the value of $K_{eq.}$ Consider three cases:

(i) $K_{eq} >> 1$: Reaction proceeds mainly in forward direction and is almost complete ($X_{\text{Products}} \approx 1; X_{\text{Reactants}} \approx 0$)

(ii) $K_{eq} << 1$: Reaction does not "wish" to proceed in forward direction ($X_{\text{Produts}} \approx 0; X_{\text{Reactants}} \approx 1$)

(iii) $K_{eq} \approx 1$: Both products and reactants exists in appreciable amounts, at equilibrium.

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

1. Prediction of the spontaneity of the chemical reaction.

2. 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.

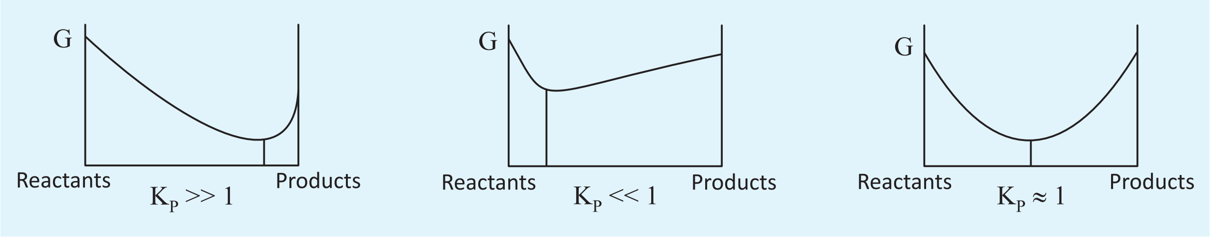
'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction. the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a synamic 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 chnage to configuration of lower free energy.

So, the criterion for equilibrium

$$A + B \rightleftharpoons C + D \quad \text{is}$$

$$\Delta_r G = 0$$

Variation of Gibbs Energy and Equilibrium Constant :



Note :
- Equilibrium is the point of minimum in the above diagrams.
- If we move away from the point of minimum, there will be an increase in Gibbs energy which is non-spontaneous.

Equilibrium constant vs. Temperature:

For a reaction : $\Delta_r G = \Delta_r H - T\Delta_r S$

At standard conditions : $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

When the reaction reaches equilibrium at temperature T, we have : $\Delta_r G^\ominus = -RT \ln K_{eq}$

Thus, we have at tempertaure T_1 : $-RT_1 \ln (K_{eq.})_1 = \Delta_r H^\ominus - T_1\,\Delta_r S^\ominus$

and at tempertaure T_2 : $-RT_2 \ln (K_{eq.})_2 = \Delta_r H^\ominus - T_2\,\Delta_r S^\ominus$

Solve to get : $\ln \dfrac{(K_{eq.})_2}{(K_{eq.})_1} = \dfrac{\Delta_r H^\ominus}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Illustration - 8 *A certain gas in expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If the initial temperature of gas is 300 K and heat capacity for the process is 50 J/°C, the enthalpy change during the process is : (Use : 1L atm ≈ 100 J)*

(A) 15 *kJ* *(B)* 15.7 *kJ* *(C)* 14.3 *kJ* *(D)* 14.7 *kJ*

SOLUTION : (B)

Use : $\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$

Calculate ΔU as follows :

(i) Use : $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \Rightarrow \dfrac{10 \times 1}{300} = \dfrac{5 \times 4}{T_2} \Rightarrow T_2 = 600\,\text{K}$

(ii) $q = C\Delta T = 50 \times (600 - 300) = 15\,\text{kJ}$ **(iii)** $-w = P_{Ext}\Delta V = 1\,(4 - 1) = 3\,\text{L atm} \equiv 0.3\,\text{kJ}$

(iv) $q = \Delta U + (-w) \Rightarrow 15 = \Delta U + 0.3 \Rightarrow \Delta U = 14.7\,\text{kJ}$

$\Rightarrow \Delta H = 14.7 + (5 \times 4 - 10 \times 1) \times 100 \times 10^{-3} = 15.7\,\text{kJ}$

Illustration - 9 *For the reaction :* $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Calculate $\Delta_r G$ of the system in a mixture of 5 mol of N_2O_4 (g) and 5 mol of $NO_2(g)$ at 298 K at a total pressure of 20 atm. Use the following data in kJ mol^{-1} : $\Delta_f G^\ominus (NO_2, g) = 50$; $\Delta_f G^\ominus (N_2O_4, g) = 100$

SOLUTION :

We need to calculate $\Delta_r G$.. Use : $\Delta_r G = \Delta_r G^\ominus + RT\,\ell n\,Q$

So, first calculate $\Delta_r G°$ using : $\Delta_r G^\ominus = \sum G^\ominus_{Products} - \sum G^\ominus_{Reactants} = \sum\left(\Delta_f G^\ominus\right)_{Products} - \sum\left(\Delta_f G^\ominus\right)_{Reactants}$

[∵ At standard conditions : $G^\ominus_{compound} = \Delta_f G^\ominus_{compound}$]

$= 2 \times \Delta_f G^\ominus (NO_2, g) - \Delta_f G^\ominus (N_2O_4, g) = 2 \times 50 - 100 = 0$

and $\Delta_r G = \Delta_r G^\ominus + RT\,\ell n Q = 0 + 8.314 \times 298\,\ell n \left(\dfrac{10^2}{10}\right) = 5.70\,\text{kJ mol}^{-1}$ $\left[\because Q = \dfrac{p^2_{NO_2}}{p_{N_2O_4}} = \dfrac{\left(\frac{5}{10} \times 20\right)^2}{\left(\frac{5}{10} \times 20\right)}\right]$

Note : $\Delta_f G^\ominus$ of an element in its standard state is zero.

Illustration - 10 *Calculate $\Delta_r G$ at 298 K for the following reaction if the reaction mixture consists of 1 atm of N_2, 3 atm of H_2 and 1 atm of NH_3.* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta_r G^{\ominus} = -33.32\,kJ$

SOLUTION :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta_r G^{\ominus} = -33.2 \text{ kJ mol}^{-1}$$

$$\text{Using : } \Delta_r G = \Delta_r G^{\ominus} + RT\,\ell nQ$$

$$\text{where} \quad Q = \frac{p^2_{NH_3}}{p_{N_2}\,p^3_{H_2}} = \frac{1^2}{1 \times 3^3} = \frac{1}{27}\ ; T = 298\text{ K}\ ; R = 8.314 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Rightarrow \quad \Delta_r G = -33.2 + (8.314 \times 10^{-3}) \times 298 \times 2.303 \log_{10}\frac{1}{27} = -33.2 - 8.16 = -41.36 \text{ kJmol}^{-1}$$

Illustration - 11 *The temperature dependence of equilibrium constant of a reaction is given by :* $\ln K_{eq} = 4.8 - \dfrac{2059}{T}$

Find $\Delta_r G^{\ominus}, \Delta_r H^{\ominus}, \Delta_r S^{\ominus}$.

SOLUTION :

$$\text{Compare} \quad \ln K_{eq} = 4.8 - \frac{2059}{T} \quad \text{with} \quad \ln K_{eq} = \frac{\Delta_r S^{\ominus}}{R} - \frac{\Delta_r H^{\ominus}}{RT}$$

$$\text{We have : } \frac{\Delta_r S^{\ominus}}{R} = 4.8 \quad \Rightarrow \quad \Delta_r S^{\ominus} = 4.8 \times 8.314 \text{ J/K} = 39.9 \text{ J/K}$$

$$\frac{\Delta_r H^{\ominus}}{R} = 2059 \quad \Rightarrow \quad \Delta_r H^{\ominus} = 2059 \times 8.314 \text{ J/K} = 17.12 \text{ kJ/K}$$

$$\text{and} \quad \Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = 17.12 - 298 \times 39.9 \times 10^{-3} = 5.31 \text{ kJ/K}$$

Illustration - 12 *K_a for acetic acid at 27°C is 2.0×10^{-5} and at 77° C, K_a is 2.5×10^{-5}. What are $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the ionization of acetic acid ?*

SOLUTION :

$$\text{Using : } \ell n\frac{(K_{eq})_2}{(K_{eq})_1} = \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \quad \ell n\left(\frac{2.5 \times 10^{-5}}{2.0 \times 10^{-5}}\right) = \frac{\Delta_r H^{\ominus}}{8.314} \times \left(\frac{1}{300} - \frac{1}{350}\right) \quad \Rightarrow \quad \Delta_r H^{\ominus} = 3.89 \text{ kJ mol}^{-1}$$

$$\text{Also,} \quad \Delta_r G^{\ominus} = -RT\,\ell n\,K_{eq}$$

$$\Rightarrow \quad \Delta_r G^{\ominus} = -8.314 \times 298 \times \ell n\,(2.0 \times 10^{-5}) = 26.81 \text{ kJ mole}^{-1} \qquad \left[\text{Taking } (K_{eq})_{25°C} \approx (K_{eq})_{27°C}\right]$$

$$\text{Using : } \Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

$$\Rightarrow \quad 26.81 = 3.89 - (298 \times 10^{-3}) \times \Delta_r S^{\ominus} \quad \Rightarrow \quad \Delta_r S^{\ominus} = 76.9 \text{ J mole}^{-1}\text{ K}^{-1}$$

IN-CHAPTER EXERCISE

1. *A gas expands by* 0.5 *litre against a constant pressure of one atmosphere. Calculate the work done.*

2. *Calculate the work done when* 1.0 *mole of water of* 373 *K vaporizes against an atmospheric pressure of* 1.0 *atmosphere. Assume ideal gas behaviour.*

3. *A gas contained in a cylinder fitted with a frictionless piston expands against a constant pressure* 1 *atmosphere from a volume of* 4 *litre to a volume of* 14 *litre. In doing so, it absorbs* 800 *J thermal energy from surroundings. Determine* ΔU *for the process.*

4. *Zinc reacts with dilute hydrochloric acid to give hydrogen at* 17°C. *The enthalpy of the reaction is* $-12.55\ kJ\ mol^{-1}$ *of zinc and entropy change equals* $5.0\ JK^{-1}\ mol^{-1}$ *for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.*

5. $\Delta_r H$ *and* $\Delta_r S$ *for the system* $H_2O(\ell) \rightleftharpoons H_2O(g)$ *at* 1 *atmospheric pressure are* $40.64\ kJ\ mol^{-1}$ *and* $108.8\ JK^{1}\ mol^{-1}$ *respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free energy for this transformation above this temperature.*

Choose the correct alternative. Only one choice is correct. However, question marks '*' may have more than one correct option.

6. *With thermodynamics, one cannot determine*

(A) *the speed of a reaction* **(B)** *the direction of a reaction*
(C) *the extent of a reaction* **(D)** *the temperature at which a reaction will be spontaneous*

7. *The reaction* $2X(g) + Y(g) \longrightarrow 2Z(g)$ *is slightly exothermic. What can you say about whether or not it is spontaneous?*

(A) *The reaction is spontaneous at any temperature.*
(B) *The reaction is not spontaneous at any temperature.*
(C) *The reaction is spontaneous at high temperature but not at low temperature.*
(D) *The reaction is spontaneous at low temperature but not at high temperature.*

***8.** *When an ideal gas expands into a vacuum, which of the following is true?*

(A) *Its entropy stays the same* **(B)** *Its temperature stays the same*
(C) *Its internal energy decreases* **(D)** *Its pressure increases*

***9.** *At what temperature will following process would not be spontaneous?*

$$A(g) \longrightarrow A(\ell) \qquad \Delta_r H = -20\ kJ \text{ and } \Delta_r S = -50\ J/K$$

(A) $> 200\ K$ **(B)** $> 300\ K$ **(C)** $> 350\ K$ **(D)** $> 400\ K$

10. *For a reaction* $\Delta_r G^{\ominus}$ *is* 50.0 *kJ at* 250 *K and* 30.0 *kJ at* 350 *K. Calculate* $\Delta_r S^{\ominus}$ *for the reaction. Assume* $\Delta_r H^{\ominus}$ *and* $\Delta_r S^{\ominus}$ *are constant.*

(A) 200 *J/K* **(B)** 400 *J/K* **(C)** 100 *J/K* **(D)** 80 *J/K*

11. *In a system where* $\Delta U = -52.0\ kJ$, *a piston expanded against a* P_{ext} *of* 1.5 *atm given a change in volume of* 30.0 *L. What was the change in heat of this system ?*

(A) –36 *kJ* **(B)** –13 *kJ* **(C)** –47.5 *kJ* **(D)** 24 *kJ*

12. *For the process* $H_2O(\ell)$ (1bar, 373 *K*) $\rightleftharpoons$ $H_2O(g)$ (1 *bar*, 373 *K*), *the correct set of thermodynamic parameters is :*

(A) $\Delta G = 0, \Delta S = +ve$ **(B)** $\Delta G = 0, \Delta S = -ve$
(C) $\Delta G = +ve, \Delta S = 0$ **(D)** $\Delta G = -ve, \Delta S = +ve$

***13.** *In which of the following processes, entropy of the system is increasing?*

(A) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ **(B)** $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(C) $COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$ **(D)** $H_2O(\ell) + C(s) \longrightarrow H_2(g) + CO(g)$

14. *For a chemical reaction, ΔG will always be negative if :*

(A) ΔH *and* $T\Delta S$ *both are positive* **(B)** ΔH *and* $T\Delta S$ *both are negative*

(C) ΔH *is negative and* $T\Delta S$ *is positive* **(D)** ΔH *is positive and* $T\Delta S$ *is negative*

15. *The entropy change for the following reversible process :*

$1\ mole\ Sn(\alpha, 13°C) \rightleftharpoons 1\ mole\ Sn(\beta, 13°\ C)$ $\Delta_r H = 2090\ J\ mol^{-1}$

(A) $-7.2\ JK^{-1}\ mol^{-1}$ **(B)** $3.8\ JK^{-1}\ mol^{-1}$ **(C)** $7.2\ JK^{-1}\ mol^{-1}$ **(D)** $-3.8\ JK^{-1}\ mol^{-1}$

16. *Calculate standard entropy change in the reaction :* $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(\ell)$

Given : $S_m^{\ominus}(Fe_2O_3, s) = 87.3,\ S_m^{\ominus}(Fe,\ s) = 27.3,\ S_m^{\ominus}(H_2, g) = 130.7,\ S_m^{\ominus}(H_2O, \ell) = 69.9 JK^{-1} mol^{-1}$

(A) $-212.5\ kJ\ mol^{-1}$ **(B)** $-215.1\ kJ\ mol^{-1}$ **(C)** $-120.1\ kJ\ mol^{-1}$ **(D)** *None of these*

***17.** *For which process(s) will $\Delta_r H^{\ominus}$ and $\Delta_r G^{\ominus}$ be expected to be most similar :*

(A) $2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$ **(B)** $2Na(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2(g)$

(C) $2NO_2(g) \longrightarrow N_2O_4(g)$ **(D)** $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

18. $MCO_3(s) \rightleftharpoons MO(s) + CO_2(g)$

The equilibrium pressure of CO_2 at 127°C and 147° C are 0.14 bar and 0.35 bar respectively. The enthalpy of the reaction is :

(A) 64.0 *kJ/mol* **(B)** 35.8 *kJ/mol* **(C)** 31.1 *kJ/mol* **(D)** 79.8 *kJ/mol*

19. *The direct conversion of A to B is difficult, hence it is carried out by the following shown path :*

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

$\Delta S(A \longrightarrow C) = 50$; $\Delta S(C \longrightarrow D) = 30$; $\Delta S(B \longrightarrow D) = 20$

The entropy change for the process $A \longrightarrow B$ is :

(A) 100 **(B)** –60 **(C)** –100 **(D)** +60

20. *The value of $\log_{10} K_{eq}$ for reaction $A \rightleftharpoons B$ is :*

(*Given :* $\Delta_r H^{\ominus} = -54.07 kJ\ mol^{-1}$, $\Delta_r S^{\ominus} = 10\ JK^{-1}\ mol^{-1}$ *and* $R = 8.314\ JK^{-1} mol^{-1}$; $-\Delta_r G^{\ominus} = RT \ln K_{eq}$)

(A) 5 **(B)** 10 **(C)** 95 **(D)** 100

21. *For the reaction* $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$ *at* 298*K*,

If $\Delta H = +177\ kJ$ *and* $\Delta S = +285\ JK^{-1}$, ΔG *will be……..and reaction is :*

(A) – 92.07 *kJ* ; *Spontaneous* **(B)** 92.07 *kJ*; *non spontaneous*

(C) 92.07 *kJ* ; *at equilibrium* **(D)** *Anything can't be said*

22. *If a reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, while total energy of reactant is less than that of the product then :*

(A) ΔH *is –ve,* ΔS *is +ve* **(B)** ΔH *and* ΔS *both are +ve*

(C) ΔH *and* ΔS *both are –ve* **(D)** ΔH *is +ve,* ΔS *is –ve*

23. *For the auto-ionization of water at* $25°C, H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$ equilibrium constant is 10^{-14} .

For this reaction :

(A) $\Delta H < 0$ **(B)** $\Delta S > 0$ **(C)** $\Delta G° = 0$ **(D)** *None of these*

24. *A certain homogenous gas-phase reaction is exothermic and proceeds with decrease in the number of moles of gas. Which of the following statements concerning this reaction is true?*

(A) *This reaction is spontaneous at lower temperatures but non-spontaneous at higher temperatures*
(B) *This reaction is non-spontaneous over all possible temperatures*
(C) *This reaction is spontaneous over all possible temperatures*
(D) *There is a temperature at which this reaction can be at equilibrium where all species are present at standard concentrations*

25. *Consider the following reaction* $C_6H_6 + 7.5O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$ *the signs of* ΔH, ΔS *and* ΔG *for the above reaction will be :*

(A) $+, -, +$ **(B)** $-, +, -$ **(C)** $-, +, +$ **(D)** $+, +, -$

26. *The occurrence of a reaction is impossible if :*

(A) ΔH *is +ve;* ΔS *is also +ve* **(B)** ΔH *is –ve;* ΔS *is also –ve*
(C) ΔH *is –ve;* ΔS *is –ve* **(D)** ΔH *is +ve;* ΔS *is –ve*

27. *For isothermal expansion in case of an ideal gas:*

(A) $\Delta G = \Delta S$ **(B)** $\Delta G = \Delta H$ **(C)** $\Delta G = -T.\Delta S$ **(D)** *None of these*

28. *Consider the* ΔG_f^0 *and* ΔH_f^0 *(kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas?*

(A) $ZnO\ (\Delta G^\circ = -318.4,\ \Delta H^\circ = -348.3)$ **(B)** $Cu_2O\ (\Delta G^\circ = -146.0,\ \Delta H^\circ = -168.8)$
(C) $HgO\ (\Delta G^\circ = -58.5,\ \Delta H^\circ = -90.8)$ **(D)** $PbO\ (\Delta G^\circ = -187.9,\ \Delta H^\circ = -2173.3)$

ANSWERS TO IN-CHAPTER EXERCISE

1. −50.65 J **2.** −3.10 kJ **3.** −213 J **4.** −14 kJ/mol **5.** 373.5 K ; Negative **6.** A
7. D **8.** B **9.** D **10.** A **11.** C **12.** A **13.** CD
14. C **15.** C **16.** B **17.** A **18.** A **19.** D **20.** B
21. B **22.** B **23.** B **24.** A **25.** B **26.** D **27.** C
28. C