Unit 6: Chemical Thermodynamics

Syllabus

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- ❑ Spontaneous process
- ❑ Second law of thermodynamics
- ❑ Entropy and its physical concept
- ❑ Entropy change in phase transformation
- ❑ Entropy and spontaneity
- ❑ Entropy changes and their calculation
- ❑ Gibb's free energy and prediction for the feasibility of reaction
- ❑ Standard free energy change and equilibrium constant
- ❑ Influence of temperature on spontaneous process (Calculation involving in standard free energy change and equilibrium constant)

Some important terms, concepts and formulae

1. Entropy is a measure of randomness or disorderness of a system.
2. Entropy change is related to enthalpy change as:

$$\Delta S = \frac{q_{rev.}}{T}$$

   Where, T = Melting point for solid
   = Boiling point for liquid.
   = Temperature at which a phase change.

3. For a spontaneous process, the total entropy change is always positive. i.e.
   For spontaneous process, $\Delta S = +$ ve.
4. Entropy is a state function.
5. Gibbs free energy is the amount of energy associated with a system that can be manifested into useful work. i.e. $\Delta G = -$ Work done
6. For spontaneous process the value of Gibbs free energy is always negative. i.e.
   If $\Delta G = -$ ve, the process is spontaneous.
   If $\Delta G = 0$, the process is at equilibrium.
   If $\Delta G = +$ ve, the process is at non spontaneous.
7. Gibb's free energy change or simply free energy change, is related to enthalpy change as shown in the Gibb's-Helmholtz equation given below.

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

8. Gibb's free energy is also related with equilibrium constant as:

$$\Delta G = - RT\ell nk$$

   or, $\Delta G = - 2.303 \, RTlog \, k$
   Where, k = equilibrium constant.
   R = Universal gas constant
   T = Absolute temperature

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

Subject Matter

Very Short Questions-Answers

Q.1. *Write the statements of second law of thermodynamics.*

Ans: Second law of thermodynamics can be stated in one of the ways as follows:

   (i) Every spontaneous processes in nature are irreversible.
   (ii) The net entropy of the universe in any natural process always increases and tends to attain a maximum value.
   (iii) In a reversible process, the sum of the entropies of system and surrounding remains constant but in an irreversible process the total entropy of the system and surrounding increases.

   So, we can say that all spontaneous process results in a net increase in entropy of the universe, i.e. the randomness of the universe is increasing.

Q.2. **What is the physical meaning of entropy? Write its unit.**

Ans: In a physical sense, entropy represents the degree of randomness or disorderness of a system. The greater is the degree of disorderness of a system the higher is its entropy and vice-versa. The unit of rate constant of entropy is $JK^{-1}mol^{-1}$.

Q.3. **Define entropy. State the effect of increased temperature on the entropy of a substance.**

Ans: Physically, entropy is defined as a measure of degree of disorderness or randomness of a system. The greater the degree of randomness, greater is entropy of the system.

Mathematically, for a reversible process at constant temperature the change in entropy is equal to heat absorbed or evolved divided by the constant temperature in Kelvin. Thus,

$$\Delta S = \frac{q_{rev}}{T}$$

Its unit is $J\ K^{-1}\ Mole^{-1}$. The value of S is positive if heat is absorbed by the system and it is negative if heat is evolved from the system.

Q.4. **Define standard free energy of formation.**

Ans: It is defined as the free energy change when one mole of a compound is formed from it's constituent elements at 1 atom and 288 k.

Q.5. **How is free energy change of a reaction related to enthalpy change and entropy change?**

Ans: The free energy change is related to enthalpy change and entropy change as follows:

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

Where, ΔG = Free energy change

ΔH = Enthalpy change

ΔS = Entropy change.

Q.6. **The enthalpy change for the transition of liquid water to steam is 40.8 kJ mol^{-1} at 373 K. Calculate $\Delta S°$ for the process.**

Soln: Given; ΔH_{vap} = 48.8 kJ mol^{-1} = 48.8 × 10^3 J mol^{-1}

T_b = 373 K.

We know, $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T_b}$ where, ΔH_{vap} = Enthalpy of vapourization

$$= \frac{48.8 \times 10^3}{373} \qquad\qquad T_b = \text{Boiling point}$$

$$= 109.38\ J\ mol^{-1}\ K^{-1}.$$

Hence, standard entropy change for the process is 109. 38 J mol^{-1} K^{-1}.

Q.7. **Ksp for AgCl is 1.6 × 10^{-10} at 25°C. Using this value calculate $\Delta G°$ for the process**

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$
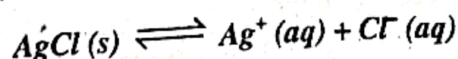
Sol^n: Given,

Temperature (T) = 25°C = 25 + 273 = 298 K

The solubility equilibrium for AgCl is

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$
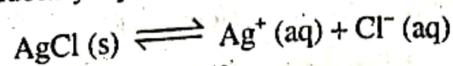
$$Ksp = 1.6 \times 10^{-10}.$$

Since this is a heterogeneous equilibrium, the solubility product is taken as equilibrium constant, i.e. $K_{eq} = 1.6 \times 10^{-10}$

Now, we know,

$$\Delta G^\circ = -2.303 \, RT \log K_{eq}$$

$$= -2.303 \times (8.314 \, J \, K^{-1} \, mol^{-1}) \times 298 \, K \times \log (1.6 \times 10^{-6})$$

$$= -55893.8 \, Jmol^{-1}$$

$$= -55.9 \, kJmol^{-1}$$

∴ The standard free energy change for the reaction is $-55.9 \, kJMol^{-1} \approx -56 \, kJmol^{-1}$. It indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

Short Questions-Answers

Q.8. *State and explain Second Law of thermodynamics.*

Ans: The limitations in the first law of thermodynamics necessiated the formulation of second law of thermodynamics. It can be stated as follows:

In an isolated system, any spontaneous process result in increase in entropy of the system. A more generalized statement for second law of Thermodynamics is "The entropy of the universe always increases in the course of every spontaneous (natural) change", i.e. for spontaneous process

$$\Delta S_{Total} > 0 \text{ (zero)}$$

or, $$\Delta S_{universe} > 0 \text{ (zero)}$$

or, $$\Delta S_{system} + \Delta S_{surrounding} > 0 \text{ (zero)} \quad\text{............. (1)}$$

By combining the statement of First and Second law of Thermodynamics, we can conclude that; "in any natural or spontaneous process the energy of universe remains constant but the entropy of universe always increases."

In equation (1) above we developed entropy criterion for spontaneity which reveals that for a process to be spontaneous the sum of entropy change in system and surrounding should be greater than zero. Again, we know that any spontaneous process after sometimes come under equilibrium where the change in entropy is equal to zero, i.e.

$$\Delta S_{Total} > 0 \text{ (zero)}: \text{process spontaneous}$$

$$\Delta S_{Total} = 0 \text{ (zero)}: \text{process under equilibrium}$$

$$\Delta S_{Total} > 0 \text{ (zero)}: \text{process non-spontaneous}$$

One of the limitations in our developed criterian for spontaneity is the measure of change in entropy of surrounding. We know the surrounding is very vast, so the change in entropy of surroundings are not easy to be determined while dealing with chemical reactions.

In an non-isolated system, when a system absorbs dQ amount of heat an equal amount of heat dQ is lost by the surrounding,

i.e. $$dQ_{system} = -dQ_{surrounding}$$

The −ve sign indicates that heat is lost from surrounding to system.

or, $$\frac{dQ_{system}}{T} = \frac{-dQ_{surrounding}}{T} \quad \text{[dividing both sides by T]}$$

or, $$\Delta S_{system} = -\Delta S_{surrounding} \quad \text{[From definition of entropy]}$$

From the above relationship we can say that entropy change of the system is greater than that of surrounding, i.e.

$$\Delta S_{system} > \Delta S_{surrounding}$$

Now, total entropy of the universe is given as,

$$\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surrounding} > 0 \text{ (zero)} \; [\because \Delta S_{system} > \Delta S_{surrounding}]$$

i.e. $\Delta S_{Total} = + ve$

This proves that for any spontaneous process, the total entropy of the universe is always increased.

Q.9. *Define Gibb's Free energy. How is the feasibility of exothermic and endothermic reactions predicted in the light of Free energy change and entropy change.*

Ans: Gibb's Free energy or standard free energy change of a reaction is defined as the amount of energy available to do useful work when the reactants in their standard state is converted into products in their standard state. The term standard state means that the temperature is 25°C and the reactants and products have their unit concentration. Mathematically it is given as:

$$\Delta G° = \Delta H° - T\Delta S°$$

Where, $\Delta G°$ = Standard free energy change

$\Delta H°$ = Standard Enthalpy change

$\Delta S°$ = Standard Entropy change

The criteria of spontaneity, non-spontaneity and equilibrium of exothermic and endothermic reactions can be predicted in terms of free energy and entropy change.

From Gibb's Helmhotz equation,

$$\Delta G = \Delta H - T\Delta S \text{ ------ (I)} \quad \text{where,} \quad \Delta G = \text{free energy change}$$
$$\Delta H = \text{Enthalpy change}$$
$$\Delta S = \text{Entropy change}$$

a) **For exothermic rxn,**

Enthalpy change (ΔH) is always Negative

i) If ΔS is +ve ie if $T\Delta S$ is +ve

Then, $\Delta G = (-) - (+ve) = -ve$ value and hence the process is spontaneous at all temperature.

ii) If ΔS is -ve ie if $T\Delta S$ is -ve

Then, $\Delta G = (-) - (-) = (-)(+) =$ Either -ve or +ve value

At high temperature,

$\Delta G = +ve$ value [$\because$ at higher temperature the $T\Delta S$ value exceeds the ΔH value]

At low temperature,

$\Delta G = -ve$ value

Therefore, at higher temp, the process is non-spontaneous and at lower temperature the process is spontaneous.

Hence, the exothermic rxn is favoured at low temperature.

b) **For Endothermic Reaction:**

For endothermic reaction, $\Delta H = +ve$

Here,

i) if $T\Delta S = -ve$ [ie if $\Delta S = -ve$]

$\Delta G = (+ve) - (-)$

$= (+)(+) = +ve$

$\therefore \Delta G = +ve$, the process is non - spontaneous.

ii) If $T\Delta S = +ve$ [$\because \Delta S \rightarrow +ve$]

Then,

$$\Delta G = (+ve) - (+ve)$$
$$= (+ve) \; (-ve)$$
$$\therefore \quad \Delta G = \text{may be } +ve \text{ or } -ve$$

At higher temp $T\Delta S > \Delta H$

then $\Delta G = -ve$ $\qquad [\because \Delta G = \Delta H - T\Delta S]$

hence, the process is spontaneous at higher temperature.

At lower temperature,

$T\Delta S < \Delta H$

Then, $\Delta G = +ve$ value, & hence the process is non-spontaneous

Therefore, endothermic reactions are favoured at low temp.

These can be summarised as follows:

Reaction	ΔH	$T\Delta S$	ΔG	Nature of reaction
Exothermic	–	+	–	Spontaneous
		–	– (at low temp)	Spontaneous
			+ve (at high temp)	Non-spontaneous
Endothermic	+	–	+	Non-spontaneous
		+	+ (at low temp)	Non-spontaneous
			– (at high temp)	spontaneous

At quilibrium

$$\Delta G = 0$$

We have, $\Delta G = \Delta H - T\Delta S$

$$0 = \Delta H - T\Delta S$$
$$\Delta H = T\Delta S$$

Q.10. *What do you mean by a spontaneous process? Explain your answer with suitable examples.*

Ans: Spontaneous process is a process which may take place by itself or after initiation under some given set of conditions. It means any process which has a tendency or urge to take place by itself is called spontaneous process. Spontaneous process can not reverse of it's own. All natural process are spontaneous process.

For a spontaneous process in isolated system, the change in entropy (ΔS) should be positive. For the process which is carried out in open vesel, total entropy change (ΔS_{total}) is taken into account i.e. $\Delta S_{total} = (\Delta S_{system} + \Delta S_{surroundings}) > 0$ (Zero).
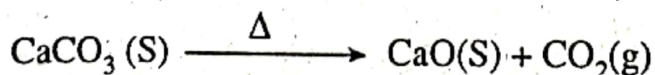
e.g.

(a) Process that takes place by themselves:
   (i) Evaporation of water kept in an open vessel.
   (ii) Dissolution of common salt/sugar in water.

(b) Process that takes place after initiation:
   (i) Decomposition of $CaCO_3$ on heating into CaO and CO_2.

$$CaCO_3 (S) \xrightarrow{\Delta} CaO(S) + CO_2(g)$$

   (ii) Combustion of methane into $CO_2(g) + H_2O (\ell)$ after ignition.

$$CH_4 (g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2H_2O(\ell)$$