THERMODYNAMICS

Topic: 4

Spontaneous processes and criteria for spontaneity, entropy as a state function.

VERY SHORT ANSWER QUESTIONS

1. State Hess's law?

Ans. Hess's law: The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps.

2. What is Gibbs energy?

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

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Where 'G' is known as Gibbs energy (or) Gibbs function.

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

SHORT ANSWER QUESTIONS

1. What is entropy?

Ans. Entropy: is taken as a measure of disorder of molecules (or) randomness of system. Greater the disorder of molecules in a system, the higher is the entropy.
Entropy is a state function. It depends on the temperature, pressure of the system.
For a spontaneous process in an isolated system the entropy change is positive.

2. **Define Gibbs energy.**

Ans: Gibbs energy ΔG: The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity reaction, Gibb's introduced thermodynamics function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G:)

This is given by the equation $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

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

ΔG_{sys} = negative for spontaneous reactions ($\Delta G < 0$)

ΔG_{sys} = positive for non – spontaneous reactions ($\Delta G > 0$)

ΔG_{sys} = Zero for equilibrium reactions ($\Delta G = 0$)

3. State third law of thermodynamics.

Ans. Third law of thermodynamics: "The entropy of a pure and perfectly crystalline substance is zero at the absolute zero of a temperature (-273^0C)

$$S_{\lim T \to 0} = 0$$

This law imposes a limitation on the value of entropy.

$$S_T = \int_0^T \frac{C_p}{T}\,dT$$

Thus entropy (S) of a substance at any temperature is calculated if the temperature dependence of 'C_p' is known as in evaluating absolute entropy of any substance.

Importance of this law: One of the most important applications of third law is the calculation. Of entropy changes in chemical reactions.

4. What is the importance of third law?

Ans: Importance of III law:

i) It imposes a limitation on the value of entropy

ii) Used in the calculation of entropy changes in chemical reactions.

iii) The overall (or) total entropy change (ΔS_{total}) must be positive for any spontaneous process (or) reaction.

$$\Delta S_{total} = \{\Delta S_{sys} + \Delta S_{surrounding}\} > 0$$

5. What is absolute entropy?

Ans: Absolute entropy (S^o): The entropy per mole amount of substance (or) ion in its standard state (i.e.,) at 298 K and 1 atm, pressure is called absolute entropy.

Ex:

Substance	Value of S^o ($JK^{-1} mol^{-1}$)
C (graphite)	5.7
C (diamond)	2.4
C (gas)	198
H_2O(liquid)	69.9
H_2O(gas)	188.8

Absolute entropy (S^o) is calculated using C_v value.

6. State and explain first law of thermodynamics.

Ans: I law of thermodynamics: The law of conservation of energy is taken as the first law of thermodynamics.

Statements:

i) "Energy can neither be created nor destroyed, although it can be transformed from one form to another".

ii) "It is impossible to construct a perpetual motion machine of first kind"

iii) "The total energy of the system and surroundings is constant".

Mathematical form of law of thermodynamics is

$$q = \Delta E + W$$

q = amount of heat absorbed by the system from surroundings

ΔE = increase in internal energy

W = work done

7. State and explain the significance of second law.

First law is unable to predict the feasibility of the change (or) direction of the change. The process which takes place on its own without any external agency is called spontaneous process.

All natural processes are spontaneous and thermodynamically irreversible.

. Second law of thermodynamics:

i) "It is impossible to construct a machine in cycles which transforms heat from a lower temperature to higher temperature region without intervention of any external agency"

ii) "Heat cannot flow from a colder body to a hotter body on its own".

iii) "All spontaneous processes are thermodynamically irreversible and entropy of system increases in all spontaneous processes".

8. Explain the terms 'entropy', 'Gibbs energy', with suitable examples.

Ans: Entropy (S): Entropy is taken as a measure of disorder of molecules (or) randomness of the system. Greater the disorder of molecules in a sytem, the higher is the entropy.

$$S_{gas} < S_{liquid} > S_{solid}$$

For a spontaneous process in an isolated system the entropy change is positive.

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamics function which involved both enthalpy (H) and entropy (S) functions. This is given by the equation,

$$G = H - TS$$

Where 'G' is known as Gibbs energy (or) Gibbs function.

9. What are the criteria for the spontaneous nature of chemical reaction? Give examples.

The spontaneity of a reaction and the algebraic signs of ΔH, ΔS, ΔG and the magnitude of 'T' can be related as follows.

ΔH	ΔS	ΔG	Nature of reaction
-	+	-	Spontaneous at all T values
-	-	-	Spontaneous at low T values
+	+	-	Spontaneous at high T values

All natural processes are spontaneous.

Ex: 1. Flowing of water from high level to low level
2. Expansion of gas from high pressure zone to low pressure zone
3. Flowing of heat from hot body to cold body.

LONG ANSWER QUESTIONS

1. What are C_p and C_v?

Ans: Heat capacity (C) : Heat capacity (C) of a substance is defined as the amount of heat required to raise its temperature through one degree.

(or)

It is the ratio of heat absorbed (q) to the resulting increase in temperature (dT).

$$\therefore C \quad \frac{q}{dT}$$

Heat capacity (C) is a state function. Hence to evaluate 'C', the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p)

from first law of thermodynamics,

$$q = dE + W = dE + P \cdot dV \quad (\because W = PV)$$

$$\therefore C \frac{q}{dT} = \frac{dE + P \cdot dV}{dT}$$

If the absorption of heat takes place at constant volume, C_v (i.e.,) dV = 0

$$\therefore C_v = \frac{q_v}{dT} = \frac{\partial E + O}{\partial T} = \frac{[\partial E]}{[\partial T]_v}$$

$$\therefore C_v = \frac{[\partial E]}{[\partial T]_v}$$

Definition for "C_v" : Heat capacity of a system at constant volume (C_v) may be defined as rate of change of internal energy with temperature at constant volume.

If heat is absorbed by the system at constant pressure, heat capacity is denoted by "C_p" and is called heat capacity at constant pressure.

$$C_P = \frac{q_P}{dT} = \frac{[\partial E]}{[\partial T]_P} + P \frac{[\partial v]}{[\partial T]_P} \qquad \text{----------(1)}$$

But $H = E + PV$

Differentiating this equation w.r.to T at constant pressure, we get

$$\frac{[\partial H]}{[\partial T]_p} = \frac{[\partial E]}{[\partial T]_p} + \frac{[\partial v]}{[\partial T]_p} \qquad \text{----------(2)}$$

From equations (1) and (2), we get

$$C_p = \frac{[\partial H]}{[\partial T]_p}$$

Definition for C_p: Heat capacity of a system at constant pressure (C_p) may be defined as rate of change of enthalpy with temperature at constant pressure.

2. How do you explain the spontaneous nature of an endothermic reaction? Illustrate with an example.

Ans. In endothermic reactions, Reactants on conversion into products go to higher energy state and temperature of the system falls. As a consequence, heat flows from surroundings into the system, the entropy of the surroundings decreases. If the disorder of the system raises sufficiently high and overall entropy increases is positive.

Total entropy change is positive: The reaction will be spontaneous an endothermic reaction is spontaneous only if the entropy of the system increases enough to overcome the decrease in entropy of the surroundings.

3. State and explain enthalpy and internal energy in terms of a substance.

Ans. Enthalpy (H) : Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature.

Mathematically, change in enthalpy $\Delta H = \Delta E + P.\Delta V$

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the initial and the final states.

$$\Delta H = [H_{products} - H_{reactants}]$$

Internal energy (E): "The total energy stored in the substance at constant temperature and pressure is called its internal energy (E)". It is a state function and is an extensive property

Internal energy change (ΔE) is considered as the difference between the internal energies of products and reactants.

$$\Delta E = (E_p - E_r)$$

In any path taken (Q – W) is equal to ΔE.

Where Q = heat and W = work.