PHYSICAL CHEMISTRY

CHAPTER- SECOND LAW OF THERMODYNAMICS

LECTURE NO. 1

DATE:- 28, MAY, 2021

TIME: (3.00P.M.)

Thermodynamics is a physical science which deals with the study of quantitative relationship between heat energy and other forms of energy.

Process: - The transformation of system from one state to another state is called as process.

Or "The path or operation by which a system changes from one state to another state is called as process".

•Isothermal process: - The process in which temperature of the system remains constant throughout is called as Isothermal process.

$\therefore \Delta T = T_2 - T_1 = 0$, and $\Delta E = 0$.

(In this process, expansion takes place by absorption of heat while, the contraction takes place by evolution of heat).

2) Adiabatic process: - It is the process which does not involved exchange of heat between system and surrounding.

i.e. Heat is neither absorbed nor evolved by the system. i.e. $q = 0$, ($\Delta H = 0$), and $\Delta E \neq 0$.

(Adiabatic expansion occurs with decrease in temperature, while, adiabatic compression takes place with increase in temperature of the system).

3) Isobaric process: - The process during which pressure of the system remains constant is called as isobaric process. i.e. $\Delta P = 0$.

4) Isochoric process: - The process during which volume of the system remains constant is called as isochoric process. i.e. $\Delta V = 0$.

5) Cyclic process: - When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called as cyclic process.

When a system undergoes a series of changes and in the end returns to its original state is called a cyclic process.

Cycle is a series of operations in which the state of the system at the beginning and at the end is same.

(Since, E depends on state $\Delta E = 0$, $dH = 0$, $q = W$, or work done during all changes = Heat absorbed by the system).

Adiabatic process in ideal gases: - In an adiabatic process, there is no exchange of heat between system and surrounding. i.e q=0

According to the first law of thermodynamics $q=\Delta E+W$, but $q=0$

$\therefore W= -\Delta E$

i.e In an adiabatic process, work is done at the cost of internal energy .

As work is done by the system, the internal energy of the system decreases consequently temperature decreases. On the other hand, if the work is done on the system, the internal energy of the system increases and consequently the temperature increases.

PHYSICAL CHEMISTRY

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LECTURE NO. 2

DATE:- 4, JUNE, 2021

TIME: (3.00P.M.)

Scope of thermodynamics: -

1) The most important laws of physical chemistry i. e. Vant Hoff law of lowering of osmotic pressure, phase rule, distribution law are derived from thermodynamics.

2) It also tells whether a particular physical or chemical change can occur under the given set of conditions of temperature, pressure and concentration.

3) It is useful to predict how far the physical or chemical change proceed until the equilibrium condition is established.

Limitations of thermodynamics: -

1) It is applicable to macroscopic systems only.

2) It is not bother about the time factor. It is concerned with only initial and final states.

3) It does not provide the mechanism of a process.

4) It does not consider the internal structure of atoms and molecules.

First law of thermodynamics: -

1) Energy can neither be created nor be destroyed but it may be converted from one form to other form.

2) Energy of the universe is remains constant.

Mathematical expression of first law of thermodynamics is

$q = \Delta E + W$

Where, q = Heat absorbed, ΔE = Change in internal energy and W = Work done

Limitations of first law of thermodynamics: -

1) The law gives the equivalance between different forms of energy. But it does not give idea about the conditions under which the change is possible. The law does not give the extent to which the change is possible. i. e. Amount of one form of energy to other form of energy.

2) The law states that heat is converted into work but conversion of heat into work can be obtained only under limited conditions with great difficulties. Due to this conversion, there are permanent changes in system and surroundings. This cannot be explained by this law.

3) The law gives the relation between heat absorbed and work done by the system. However it does not give idea about source of heat and direction of the flow of heat.

Examples: - 1. A cup of hot coffee left in a cooler room eventually cools off. The reverse of this process- coffee getting hotter as a result of heat transfer from a cooler room does not take place.

2. Consider heating of a room by passage of electric current through an electric resistor. Transferring of heat from room will not cause electrical energy to be generated through the wire.

Spontaneous and Non Spontaneous Processes: -

A process that proceeds on its own accord i. e without being aided by any external agency is called as spontaneous or natural process.

While, the process that does not proceed by itself but needs the help of external agency is called as a non-spontaneous or unnatural process.

For example-

1: Flow of water: - Downhill flow of water is a spontaneous process. It occurs on its own. However, uphill flow of water is non spontaneous. (Water cannot flow by itself from lower level to higher level).

2. Flow of heat:- If a bar of metal is hot at one end and cold at the other end then heat flows spontaneously from the hot end to cold end, until both the ends assumes same temperature. But the reverse flow of heat from cold end to hot end on its own accord is impossible.(but the same is possible on using refrigerating device, wherein heat is pumped from the cold end to hot end)

3. Diffusion of solution: - The diffusion of a solute from more concentrated solution to the less concentrated solution proceeds spontaneously when these are brought in contact with each other till the equilibrium is attained. However the reverse flow does not occur spontaneously.

4. Rolling of ball: - A ball rolls down from higher level to lower level on its own. But it does not roll uphill naturally.

5. Expansion of gas: - When a gas at higher pressure is connected to an evacuated vessel, the gas expands and occupies all the space spontaneously. It gets uniformly spread. But the same gas cannot return back to its original container.

6. Diffusion of gases: - Two gases irrespective of their densities and temperature readily and spontaneously diffuse into one another forming a homogenous mixture. But separation of gases from their mixture is not self possible. It is thus a non spontaneous process.

7. Precipitation: - If aqueous solution of NaCl is added to $AgNO_3$ solution, precipitate of AgCl is formed. It is thus a spontaneous process.

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

But $AgNO_3$ and NaCl cannot be produced back. Thus the reverse course of reaction is non spontaneous.

8. Flow of electricity: - Electricity flows from a point at higher potential to the point at lower potential spontaneously while the reverse process is non spontaneous.

From the above examples, we conclude that-

•Spontaneous process is always uni-directional and instantaneous and fast.

•Every spontaneous process bears the capacity of doing work and the capacity ceases at the attainment of its equilibrium with the surroundings. Hence, a spontaneous process is a source of energy.

•Every spontaneous process shifts from: -

•Non equilibrium state to equilibrium state

•Less probable state to more probable state

•Less random state to more random state i.e from more ordered state to less ordered state.

•Every non spontaneous process is in a state of equilibrium whereas a spontaneous process is in a state of non equilibrium.

•A spontaneous change is accompanied by decrease of internal energy or enthalpy.

•It implies that only such reactions will occur which are exothermic. But the melting of ice and evaporation of rainwater are endothermic processes which proceed spontaneously. Clearly, there is some other factor in addition to ΔH which governs spontaneity. It is the second law of thermodynamics, which introduces this new factor that is called entropy.

PHYSICAL CHEMISTRY

CHAPTER- SECOND LAW OF THERMODYNAMICS

LECTURE NO. 3

DATE:- 5, JUNE, 2021

TIME: (9.00A.M.)

Second law of thermodynamics: -

•All naturally occurring processes are spontaneous and are thermodynamically irreversible.

•Heat cannot flow on its own accord from a cold body to a hot body. (R. Clausius).

•All natural and spontaneous processes tend to proceed to a state of equilibrium.

•It is highly impossible to convert entire heat into work without producing changes in the system. (R. Clausius-Kelvin).

•It is highly impossible to construct a machine working in a cyclic manner and convert heat completely into work without producing changes in the system. (Plank).

•Whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe (Sound of water and generation of electricity).

•Every irreversible process leads to the dissipation of energy. Because of difference in driving and opposing force is more. For maximum work, difference must be low. (Kelvin).

Entropy: - The thermodynamic functions such as internal energy, enthalpy, work are not able to explain the spontaneity of the reaction. Therefore, the new thermodynamic function is introduced by R. Clausius known as entropy denoted by 'S'.

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

e. g. serially arranged playing cards and then shuffled cards.

Like internal energy and enthalpy, the entropy is a state function which depends on the initial and final states of the system.

The change in entropy = $\Delta S = S_2 - S_1$

Where, $S_2 \rightarrow$Entropy of the final state

And $S_1 \rightarrow$Entropy of the initial state

See word file

Thus, the entropy change is defined as the ratio of heat change during reversible process to the absolute temperature.

Or “It is the heat evolved or absorbed per unit absolute temperature.”

Entropy is an extensive property and its value depends on quantity of matter present in the system.

- For endothermic process, $q_{rev.}$ is positive, hence, ΔS is positive.
- For exothermic process, $q_{rev.}$ is negative, hence, ΔS is negative.
- For adiabatic process, $q_{rev.} = 0$, hence, $\Delta S = 0$.

Unit of entropy: - We know,

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

$$= \frac{\text{Calories per mole}}{\text{Degree}}$$

$= Cal.deg^{-1}.mol^{-1}.$

Thus, the unit of entropy change is cal/deg/mol, which is also called as entropy unit (eu).

SI unit of entropy is Joules/Kelvin/mole = $J.K^{-1}.mol^{-1}$. Or $J.mol^{-1}.deg^{-1}$.

Entropy change in an isolated system: -

The isolated system is thermally insulated from the surroundings so that it can exchange neither matter nor energy with the surroundings. Consider a cylinder with a working substance such as ideal gas. A cylinder is provided with a weightless and frictionless piston. The cylinder is enclosed in a large heat reservoir which is insulated from the surrounding. Such arrangement of a system and the heat reservoir adiabatically insulated from the surroundings is called an isolated system.

Statement of second law based on entropy:-

•We know that for isolated system, $\Delta S_i \geq 0$.

2. For any reversible process or cycle the total entropy change $\Delta S = 0$.

3. For spontaneous, natural and irreversible process or cycle $\Delta S > 0$.

i. e such process is associated with increase in entropy. Above considerations led R. Clausius to state the second law of thermodynamics on the basis of entropy change as, "All the process in nature are associated with increase in entropy and the direction of the change is such that it always leads to increase in entropy"

Or "Our stock source of available energy is decreasing and it is continuously converted into a disordered form of energy called heat and thereby the entropy of the universe is increasing"

In thermodynamics, the system and surroundings constitutes universe. Universe is an isolated system. The second law can be stated as "Entropy of the universe is all the while increasing or universe is expanding."

The entropy is unavailable part of energy which is continuously decreasing. Consequently free energy which is available energy for doing work is decreasing. Hence second law can be stated as "Free energy of the universe is continuously decreasing". All statements given earlier are simple qualitative and as such cannot be mathematically stated. This statement of entropy however is both qualitative and quantitative. Hence it can be expressed mathematically as seen earlier.

R. Clausius combined first and law of thermodynamics as "The total energy of the universe remains constant but the entropy of the universe is continuously increasing or always tends to be maximum".

The importance of second law is that provides the criteria for

1. Possibility of a given change.

2. Direction of the change if at all it is possible.

Physical significance of entropy:-

•Entropy is a measure of disorder of the system:→

In a crystalline solid, the atoms, ions or molecules are arranged in a definite geometrical pattern i. e orderly arrangement. Such solids have very low entropy. But when solid changes to liquid, the orderly arrangement is disturbed and disorder is increased. The entropy of a liquid is higher than solid. In case of gas, molecules go apart and randomness as well as entropy is highest. Thus when disorder increases, entropy also increases, hence the entropy is a measure of disorder or randomness in the system.

- Entropy is a measure of unavailable energy for work:→

Consider the example of work of expansion by steam. Let us consider one gram of water. It requires 540 calories of heat to get converted into vapor at its boiling point. Such a steam or vapor is not capable of giving any work of expansion. Because on expansion its temperature will fall down and it will be condensed to water. This indicates that, for 1 gram of steam to give work heat content must be above 540 calories. i. e excess of energy is converted into work. Thus, for 1 gram of water to remain in vapor state, 540 calories of heat is essential. This heat is in hidden form in vapor molecules and cannot be available to perform work. Therefore entropy is the measure of unavailable energy

•Entropy is a measure of thermodynamic probability:→

Spontaneous process always takes place with increase in entropy and proceeds from ordered state to disordered state. The ordered state is less probable and disordered state is more probable. Thus entropy (S) and probability (W) are related to each other as,

$S = f(W)$.

Thus S and W are directly proportional to each other. The state of equilibrium is the state of maximum probability. Any spontaneous process proceeds to a state of equilibrium. Therefore entropy is a measure of thermodynamic probability.

•Entropy is a measure of mixtupness:→

The electrical energy, mechanical energy and chemical energy are organized energies used to perform work. But heat is the form of energy due to random motion of atoms or molecules in a body. Thus heat is unorganized or chaotic in nature. When useful forms of energies are used to perform work and converted into heat mixtupness or chaos of the system increases. The process also takes place with increase in entropy. Therefore entropy is regarded as the measure of mixtupness of chaos of the system.

Entropy change in physical transformation:-

Physical transformation means change of substance from one phase to another phase for e.g. Fusion (solid to liquid), solidification (liquid to solid), evaporation (liquid to vapor), condensation (vapor to liquid) and transition (one crystalline form to another) etc represents physical transformation.

The entropy change ΔS_t for all types of physical transformation is given by

$$\Delta S_t = S_2 - S_1$$

The transition from one phase to another takes place at constant temperature and pressure at which both phases are in equilibrium. All the physical transformations take place with change in the quantity of heat. Since the entropy change of the system depends on quantity of heat evolved or absorbed hence with a change in physical state, entropy change also takes place.

Thank You.

Stay Home, Stay Safe.