Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	12: Thermodynamic criteria for non-equilibrium states
Module Tag	CHE_P10_M12

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1. Learning Outcomes

After studying this module you shall be able to:

- Know the significance of irreversible thermodynamics
- Differentiate between equilibrium and non-equilibrium thermodynamics.
- Learn postulates of non-equilibrium thermodynamics.
- Know about different laws of thermodynamics (first, second and third) laws.

2. Introduction

In classical thermodynamics, we have seen time dependent variation of thermodynamic quantities such as is internal energy (U), enthalpy (H), entropy (S),Gibb's free energy (G) etc. are not considered. Classical thermodynamics deals with transitions from one equilibrium state to another brought about by different mechanical or chemical methods. Non equilibrium thermodynamics is that branch of thermodynamics that deals with the system which are not in thermodynamic equilibrium. But such systems can be described by non-equilibrium state variables which represent an extrapolation of variables used to specify system in thermodynamic equilibrium.

All the natural processes occurring are not in thermodynamic equilibrium or irreversible in nature. Systematic macroscopic and general thermodynamics of irreversible process are obtained from Onsagertheorem.Irreversible thermodynamics essentially deals with qualitative and quantitative changes occurring with respect to time. Many physiochemical processeswhich are typically known as irreversible process include conduction of heat, diffusion of matter and chemical reactions.

3. Difference between equilibrium and non- equilibrium thermodynamics

- One basic difference between equilibrium and non-equilibrium thermodynamics lies in the behaviour of inhomogeneous systems which require knowledge of rate of reaction but this is not considered in equilibrium thermodynamics of homogeneous systems.
- Time courses of physical processes are ignored by equilibrium thermodynamics but irreversible thermodynamics explain the time courses of physical processes in continuous detail. Consequently, equilibrium thermodynamics permits those processes that pass through states far from thermodynamic equilibrium that cannot be described even by variables admitted for non-equilibrium thermodynamics like time rate of change of temperature and pressure.
- Equilibrium thermodynamics use the concept of quasi-static process. A quasi-static process is conceptually (timeless and physically impossible) mathematical passage along continuous path of states of thermodynamic equilibrium. But this concept of quasi-static process is not used by non-equilibrium thermodynamics.
- Non-equilibrium thermodynamics states that continuous time-courses, need its state variables to have a very close connection with those of equilibrium thermodynamics.

4. Postulates of Irreversible Thermodynamics

- The total entropy change dS of a system can be expressed as the sum of the entropy change arising from system ($d_{in}S$) and its interaction with surroundings ($d_{ex}S$)

$$dS_{total} = d_{ex}S + d_{in}S \qquad ....(1)$$

where,

$d_{ex}S$ = entropy change due to surroundings (external system)

$d_{in}S$ = entropy change within system (internal system)

dS_{total}= Total entropy

Entropy change within system can be equal to or greater than zero.

$d_{in}S=0$ in reversible system(or equilibrium)
$d_{in}S > 0$in irreversible process(non-equilibrium)

If $d_{ex}S=0$ (adiabatic transformation) then $dS_{total}=d_{in}S\geq 0$

There is no restriction on the sign of $d_{ex}S$, but $d_{in}S$ should always be positive (irreversible thermodynamics).

The quantity **$Td_{in}S$**is called the **uncompensated heat by Clausius**.

- The local entropy production ' σ ' is defined as the sum of product of fluxes and conjugate forces. The entropy production could always be isolated for any process. It is also equal to or greater than zero i.e.

$$\sigma \geq 0 \qquad \text{....(2)}$$

For the reversible process, entropy production is equal to zero.

- The dissipation factor ' ψ ' is defined as $\mathbf{T}\sigma$ (where T is absolute temperature). ψ is positive dissipation as it is natural consequence of irreversible process. σ can also be represented as $\frac{d_{in}S}{dt}$
- Onsager's formalism of irreversible thermodynamics states that "the entropy production vis–a–vis dissipation function can be represented as sum of fluxes and their conjugate forces".

$$\sigma = \sum_{i=1}^{n} J_i X_i \quad \ldots(3)$$

Where J_i = force of the i^{th} component

X_i = flux of the i^{th} component

n = total number of fluxes that are possible in a given system.

The linearity between fluxes & forces can be assumed to be valid as a first approximation for large class of systems.

In near equilibrium region:-

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \quad \ldots(4)$$

Where L_{ik} is the phenomenological coefficient.

$$X_i = \sum_{k=1}^{n} R_{ik} J_k \quad \ldots.(5)$$

Where R_{ik} is the resistance or resistivity coefficient.

5. Non- equilibrium state variables

Non-equilibrium thermodynamics need its state variables to describe continuous time courses so that it can connect to equilibrium thermodynamics. Non-equilibrium state variables are measured locally with same techniques which are used to measure thermodynamic state variables. These state variables are spatially and temporally non-uniform. Because of this spatial non-uniformity, non-equilibrium state variable that correspond to extensive thermodynamic state variable are need to be defined as spatial densities of the corresponding extensive equilibrium state variables. Occasionally, when the system is close to thermodynamic equilibrium, then intensive non-equilibrium state variables approaches equilibrium state variables like temperature and pressure. Moreover, non-equilibrium state variables should be mathematically related to each other in ways that resemble corresponding relations between equilibrium thermodynamic state variables.

6. Basic Concepts

Systems exhibiting non-equilibrium process are much more complex and they undergo fluctuations of more extensive quantities. Some boundary conditions which are imposed on them particularly intensive variables like temperature gradient or distorted collective motions are called **thermodynamics forces**. Now, discussing different laws of thermodynamics.

6.1 Zeroth law of thermodynamics

Zeroth-law of thermodynamics states that "if two bodies A and B having different temperature when come in contact with each other they both attain same temperature. In such system mass won't get exchanged but energy is exchanged. Thermometer is based on Zeroth Law.

6.2 First law of thermodynamics

The first law of thermodynamics is also known as law of conservation of energy i.e. energy can neither be created nor be destroyed.

This law states that if system absorbs heat from the surroundings, internal energy of the system increases. This rise in internal energy can be given back to surroundings in the form of work.

Mathematical form of first law is:-

$$q = \Delta U + w \qquad \ldots(6)$$

Where ΔU is change in internal energy, q is the heat absorbed, w is the work done.

We also know that work done is given by

$$w = P\Delta V$$

Substituting this in equation (6), we get

$$q = \Delta U + P\Delta V$$

Now the heat absorbed keeping the pressure of the system constant will be given by,

$$q_p = (U_2 - U_1) + P(V_2 - V_1)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \quad \ldots (7)$$

In the above equation U denotes the internal energy, P is pressure and V is the volume. All three U, P and V are state functions $\therefore$ the quantity U + PV should also be state function.

$\therefore$ The quantity U + PV = H is known as enthalpy and change in enthalpy will give amount of heat absorbed at constant pressure i.e.

$$q_P = H_2 - H_1 \quad \ldots (8)$$

Where H_1 is initial enthalpy and H_2 is the final enthalpy of the system. Then the equation (8) can be written as

$$\boxed{q_P = \Delta H}$$

where H is heat absorbed by system at constant pressure.

6.3 Second law of thermodynamics

The second law of thermodynamics forms the most important law in classical thermodynamics from which the criteria of spontaneity and equilibrium of a system are derived.From this law it can be deduced that at equilibrium, entropy of an isolated system reaches maximum. At equilibrium, sum of all components of entropy change is equal to zero.

$$\sum_i dS_i = 0 \qquad \text{...(9)}$$

For the spontaneous reaction which is moving towards equilibrium state, the sum of all components of entropy changes become greater than zero.

$$\sum_i \mathbf{dS_i > 0}$$

In steady state condition, macroscopic properties like pressure, composition remain same with time but dissipative process continues to change in a system.

Infinitesimal change in entropy is defined as:-

$$dS = \frac{\delta q_{rev}}{T} \qquad \text{...(10)}$$

For spontaneous process,

$$dS > \frac{\delta q}{T} \qquad \text{...(11)}$$

6.4 Third law of thermodynamics

The third law of thermodynamics states that the entropy of perfect crystal of any pure substance becomes equal to zero when the temperature is absolute zero. At this zero temperature, the system must be in the state possessing minimum thermal energy. This statement is correct only when system has only one state with minimum energy. That is at absolute zero temperature, the state is of perfect order, i.e. zero disorder and hence zero entropy.

$$\lim_{T \to 0} S = 0$$

The relation between entropy and number of microstates possible for a system is given by:

$$S = k_B \ln \Omega \qquad \ldots (12)$$

In the above equation k_B denotes the Boltzmann constant and Ω is the thermodynamic probability which is the number of microstates corresponding the given macrostate of the system.

This equation is known as Boltzmann entropy equation. It gives the quantitative definition of entropy as disorder.

7. Summary

- Thermodynamics of irreversible processes essentially deals with the qualitative and quantitative change occurring with respect to time. It is concerned with transport processes with the rate of chemical reactions.
- Equilibrium thermodynamics use the concept of "quasi-static process" whereas non-equilibrium thermodynamics does not use this concept rather need state variables to describe continuous time courses.
- Total entropy change of system is the sum of entropy change which arises from its interaction with surroundings and entropy change within the system.

$$dS = d_{in}S + d_{ex}S$$

- The local entropy production σ, is the sum of products of fluxes and conjugate forces, and is therefore,

$$\sigma \geq 0$$

- and according to Onsager's formalism

$$\sigma = \sum_{i=1}^{n} J_i X_i$$

J_i = conjugate force

X_i = flux

n = total number of fluxes.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	13: Thermodynamic potential
Module Tag	CHE_P10_M13

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1. Learning Outcomes

After studying this module you shall be able to

- Know about concept of uncompensated heat
- Learn about the thermodynamic potentials
- Derive relation between the chemical potential and thermodynamic potentials.

2. Uncompensated heat

A non-equilibrium or spontaneous process describe by equation of inequality, $dS > \frac{\delta q}{T}$ is based on the direction of spontaneous process.

Clausius suggested different form of second law of thermodynamics based on equality i.e.

$$dS - \frac{\delta q}{T} = \frac{\delta q'}{T} \qquad \ldots(1)$$

where $\delta q'$ is uncompensated heat. It is not the actual heat absorbed or evolved by the system but the heat that could have been absorbed in a reversible process in addition to non-equilibrium quantity δq in order to maintain equality.

Rewriting the above equation

$$dS = \frac{\delta q}{T} + \frac{\delta q'}{T} \qquad \ldots(2)$$

For reversible process $\delta q' = 0$while for irreversible process $\delta q' > 0$**.** Thus $\delta q'$ is always positive and is produced in the system as a result of non-equilibrium process resulting in an irreversible change.

Physical significance of uncompensated heat

Let the total entropy change of the system is sum of two components i.e., $d_{ex}S$ which is due to absorption of heat reversibly from outside and $d_{in}S$ which is due to irreversible changes occurring in interior of the system. This means:

$$dS = d_{in}S + d_{ex}S \qquad \ldots(3)$$

Comparing equation (2) and (3)

$$d_{ex}S = \frac{\delta q}{T} \qquad \ldots(4)$$

$$d_{in}S = \frac{\delta q'}{T} \qquad \ldots(5)$$

Rearranging the above equation

$$\delta q' = T d_{in}S \qquad \ldots(6)$$

Thus from equation (6), we can say that the uncompensated heat is related to the production of entropy as a result of some irreversible processes occurring within system. Such processes can be mixing of gases, diffusion of solute from higher to lower concentration. The randomness in the system increases as a result of increase in the disorder in state of system.

3. Thermodynamic potential

At equilibrium, the extensive parameters U, S, V,n_i are functions of state, and linear combinations of these parameters are also state functions. Helmholtz, Gibbs, and others have considered such combinations and have found that these are often more useful than the internal energy for describing systems under ordinary experimental conditions. Such combinations are called **thermodynamic potentials.** They are extensive quantities and must not be confused with the ordinary potentials, which are derivatives of the thermodynamic potentials and are intensive quantities.

Some of these thermodynamic potentials are:-

3.1 Helmholtz free energy

The Helmholtz free energy is given by:-

$$F = U - TS \qquad \ldots(7)$$

At constant temperature and volume conditions, we can write

$$(dF)_{T,V} = dU - TdS \qquad \ldots(8)$$

From first law of thermodynamics,

$$dU = TdS - dW \qquad \ldots(9)$$

Substituting (9) in (8)

$$(dF)_{T,V} = TdS - dW - TdS \qquad \ldots(10)$$

$$(dF)_{T,V} = -dW \qquad \text{or} \qquad -(dF)_{T,V} = dW \qquad \ldots(11)$$

Therefore, total reversible work performed by the system is equal to decrease in Helmholtz energy at constant temperature and volume.

Now, differentiating equation (7) without any restrictions

$$dF = dU - TdS - SdT \qquad \ldots(12)$$

Using expression for dU,

$$\mathbf{dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dn_i} \qquad \ldots(13)$$

Substituting (13) in (12)

$$\mathbf{dF = -PdV - SdT + \sum_{i=1}^{k} \mu_i dn_i} \quad \dots (14)$$

Equation (14) gives new definition of chemical potential

Therefore,

$$\boldsymbol{\mu_i = \left(\frac{dF}{dn_i}\right)_{V,T,n_k}} \quad \dots (15)$$

3.2 Gibbs Free Energy

Another important thermodynamic potential is Gibbs free energy (G).

Gibbs Free Energy is given by G = U – TS + P …(16)

Differentiating the above while keeping temperature and pressure constant

$$(dG)_{T,P} = dU - TdS + PdV \quad \dots.(17)$$

From First law of thermodynamics

$$dU = TdS - dW \quad \dots(18)$$

Substituting above equation in eq. (17)

$$(dG)_{T,P} = TdS - dW - TdS + PdV$$

$$= -dW + PdV$$

$$-(dG)_{T,P} = dW - PdV \dots (19)$$

Equation (19) shows that the decrease in G is equal to the total work minus the work of compression, which Gibbs called the useful work,dW – PdV = dW'; it is that part of the work which contributed by chemical reactions or by the transport of electricity. In the study of condensed systems such as solutions, living tissues, or solid material, PdV is usually small and generally does not contribute significantly to the total work, so that the choice of G as the characteristic potential is common practice.

Now, differentiating equation (16) without any restriction

$$dG = dU - TdS - SdT + PdV + VdP \quad \dots (20)$$

Since,

$$\mathbf{dU = TdS - PdV + \sum_{i=1}^{k} \mu_i dn_i} \quad \dots (21)$$

Substituting (21) in (20), we get

$$\mathbf{dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i} \quad \dots (22)$$

This expression defines the chemical potential in its most familiar form

$$\boldsymbol{\mu_i = \left(\frac{dG}{dn_i}\right)_{T,P,n_k}} \quad \dots (23)$$

3.3 Enthalpy

Another common thermodynamic potential is enthalpy, H.

It is defined by H = U + PV ...(24)

For closed system, $dn_i = 0$

Differentiating equation (24) keeping pressure constant,

$(dH)_{P=} dU + PdV$

If $dn_{i\,=}\, 0$

$dU + PdV = (dq)_p$ and hence

$(dH)_{P\,=}\,(dq)_P$

Now, differentiating equation (24) without any restriction

$$dH = dU + PdV + VdP$$

Substituting expression of dU

$$\mathbf{dH = VdP + TdS + \sum_{i=1}^{k} \mu_i dn_i}$$

$$\boldsymbol{\mu_i = \left(\frac{dH}{dn_i}\right)_{S,P,n_k}}$$

Substituting equation H = U + PV into equation G = U – TS + PV, we find that the free energy is related to enthalpy by the expression G = H – TS.

3.4 Entropy

In natural or spontaneous processes energy is conserved while entropy is not conserved. In such processes, entropy of the reaction increases. Entropy of the system is extensive property. The total entropy is sum of total entropies of each individual part of system consisting of several parts i.e. if system is divided into ‘r’ different part, then total entropy is:-

$$dS = d_{in}S^1 + d_{in}S^2 + d_{in}S^3 + \cdots + d_{in}S^r \qquad ...(25)$$

Generally, $d_{in}S^k$ is entropy production of the k^{th} part, and

$$d_{in}S^k > 0 \text{ for every k part} \qquad ...(26)$$

This states that in irreversible processes the entropy production is positive in every part and this statement is stronger than the classical statement of second law that entropy of an isolated system can only increases or remain unchanged.

4. Summary

• The total entropy of the system is sum of two components: $d_{ex}S$and $d_{in}S$which are the entropy change due to change in heat in exterior and interior of system respectively.

• The relation between change in entropy and uncompensated heat is given by:

$$d_{in}S = \frac{\delta q'}{T}$$

Where $\delta q'$ stands for the uncompensated heat which is related as the production of entropy within the system because of some irreversible process occurring within the system.

• The thermodynamic potential are:

$\mu_i = \left(\frac{dF}{dn_i}\right)_{V,T,,n_k}$ Chemical potential in terms of change in Helmholtz free energy

$\mu_i = \left(\frac{dG}{dn_i}\right)_{P,T,,n_k}$ Chemical potential in terms of change in Gibbs free energy

$\mu_i = \left(\frac{dH}{dn_i}\right)_{S,P,,n_k}$ Chemical potential in terms of change in Enthalpy

• The entropy produced in every irreversible process is positive for every part of the system i.e.

$d_{in}S^k > 0$ for every k^{th} part of the system.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	14: Entropy
Module Tag	CHE_P10_M14

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1. Learning Outcomes

After studying this module you shall be able to

- Know briefly about the concept of entropy
- Study the entropy produced due to heat flow
- Derive entropy produced in chemical reaction
- Analyze the dependence of rate of the reaction on the rate of entropy production

2. Entropy

In thermodynamics, entropy is the measure of number of microstates corresponding to specified macroscopic variables in thermodynamic system. It is the measure of degree of randomness of molecule in the macroscopic system. Second law states that entropy of an isolated system does not decreases while for a non-isolated system entropy may decreases, provided entropy of their environment increases by at least that amount. In natural or spontaneous processes energy is conserved while entropy is not conserved. In such processes, entropy of the reaction increases. Entropy of the system is extensive property. The total entropy is sum of total entropies of each individual part of system consisting of several parts i.e. if system is divided into 'r' different part, then total entropy is:-

$$dS = d_{in}S^1 + d_{in}S^2 + d_{in}S^3 + \cdots + d_{in}S^r \qquad \text{….(1)}$$

Generally, $d_{in}S^k$ is entropy production of the k^{th} part , and

$$d_{in}S^k > 0 \text{ for every k part} \qquad \text{…(2)}$$

This states that in irreversible processes the entropy production is positive in every part and this statement is stronger than the classical statement of second law that entropy of an isolated system can only increases or remain unchanged.

3. Entropy Law

The change in entropy i.e. dS is divided into two parts which are $d_{ex}S$and$d_{in}S$. $d_{ex}S$is flow of entropy due to interactions with exterior of the system and $d_{in}S$is the change in entropy inside the system. Total change in entropy is given by:

$$dS = d_{in}S + d_{ex}S \qquad \ldots(3)$$

and

$d_{in}S = 0$ for reversible processes

$d_{in}S > 0$ for irreversible processes

But $d_{in}S$ cannot be in negative.

4. Entropy production due to heat flow

According to second law of thermodynamics, the entropy change is given by:-

$$dS = \frac{dq}{T} \qquad \ldots(4)$$

Where,

T = temperature

dq= heat from the surroundings

dS = entropy change which is an intensive property and is positive.

Now consider the system consisting of two phases I and II which are at uniform temperature T^{I} and T^{II} respectively. For the whole system consisting of these phases, the total entropy is given by:-

$$dS = dS^{I} + dS^{II} \qquad \dots (5)$$

Now, corresponding heat received from the surroundings by each phase is:-

$$d_q^{I} = d_{ex}^{I}q + d_{in}^{I}q \qquad \dots (6)$$

$$d_q^{II} = d_{ex}^{II}q - d_{in}^{II}q \qquad \dots (7)$$

Where subscript ex and in stands for external and internal. $d_{ex}^{I}q$is the heat flow from the exterior to the phase I and $d_{in}^{I}q$ is the heat flow from the internal system (phase I) to surroundings.

(As energy of the system is conserved therefore $d_{in}^{I}q + d_{in}^{II}q = 0$)

Now the corresponding entropy change of two phases is:-

$$d^{I}S = \frac{d_q^{I}}{T^{I}} = \frac{d_{ex}^{I}q}{T^{I}} + \frac{d_{in}^{I}q}{T^{I}} \qquad \dots (8)$$

$$d^{II}S = \frac{d_q^{II}}{T^{II}} = \frac{d_{ex}^{II}q}{T^{II}} - \frac{d_{in}^{II}q}{T^{II}} \qquad \dots (9)$$

Substituting eq. (8) and eq. (9) in eq. (5), which gives

$$dS = \frac{d_{ex}^{I}q}{T^{I}} + \frac{d_{ex}^{II}q}{T^{II}} + d_{in}^{I}q\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) \qquad \dots (10)$$

The first two terms of above equation corresponds to$d_{ex}S$while the third term corresponds to$d_{in}S$. This term gives entropy production as heat is transferred from phase II to phase I due to temperature difference $T^{II} - T^{I}$.

Therefore,

$$d_{in}S = d^{I}_{in}q\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) \quad \ldots (11)$$

From the above expression we see that if the temperature of phase II i.e., T^{II} is greater than the temperature of phase I, then $d_{in}S > 0$ as $d^{I}_{in}q > 0$

Now if $T^{I} > T^{II}$, then the quantity inside the parenthesis in the equation (11) will be less than zero, but $d_{in}S$ will still be greater than zero since $d^{I}_{in}q$ will also be less than zero.

But if $T^{I} = T^{II}$ i.e., at thermal equilibrium, entropy production will be zero.

The entropy production per unit time is given by:

$$\sigma = \frac{d_{in}S}{dt} = \frac{d_{in}q}{dt}\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) > 0 \quad \ldots (12)$$

i.e., rate of entropy production is the product of the rate of heat transfer $\left(\frac{d^{I}_{in}q}{dt}\right)$ and difference of state functions $\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right)$. This term act as the driving force for the heat transfer which can be considered as flux or flow or a consequence of driving force.

The total change of entropy for whole system,)

$$\frac{d_{in}S}{dt} = \frac{d_{in}q}{dt}\left(\frac{T^{II} - T^{I}}{T^{I}T^{II}}\right) \quad \ldots (13)$$

5. Entropy production in reaction

Consider chemical reaction occurring at condition of constant temperature &pressure. Let dH be an infinitesimal small quantity of enthalpy absorb by the surrounding at temperature T. Then infinitesimal change in entropy of the surrounding is $d_{ex}S = \frac{dH}{T}$ and infinitesimal entropy change arising from chemical reaction is $d_{in}S$.

So,

$$dS = d_{in}S + d_{ex}S \quad \ldots(14)$$

Substituting$d_{ex}S = \frac{dH}{T}$ in equation (14)

$$dS = d_{in}S + \frac{dH}{T} \ldots (15)$$

or $-Td_{in}S = dH - TdS$ … (16)

From classical thermodynamics,

$$dG = dH - TdS \quad \ldots (17)$$

Comparing eq. (16) and (17), we get

$$d_{in}S = -\frac{dG}{T} \quad \ldots (18)$$

Thus, the rate of entropy production is given by:-

$$\sigma = \frac{d_{in}S}{dt} = -\frac{1}{T}\left(\frac{dG}{dt}\right) \quad \ldots(19)$$

This states that as the Gibb's free energy increases then the rate of entropy production decreases.

Relation given by Clausius for the uncompensated heat is

$$d_{in}q = TdS - d_{ex}q \quad \ldots (20)$$

$d_{ex}q$ is the heat exchanged with the surroundings and dS is amount of entropy change of the system.

Now $dS = d_{in}S + d_{ex}S$

$$dS = \frac{d_{in}q}{T} + \frac{d_{ex}q}{T} \ldots (21)$$

or $TdS = d_{in}q + d_{ex}q$ … (22)

For the chemical reaction of an open system having 'c' components (i = 1,2,3,….c) the thermodynamic relation is given by:-

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad \ldots (23)$$

in which n_i is the number of moles of i^{th} component

μ_i is the chemical potential of the i^{th} component

At constant temperature & pressure conditions, the above equation becomes:-

$$(dG)_{T,P} = \sum_i \mu_i dn_i \quad \ldots (24)$$

From eq. (19) and (24) we get,

$$\sigma = \frac{d_{in}S}{dt} = -\frac{1}{T}\sum_i \mu_i \frac{dn_i}{dt} \quad \ldots (25)$$

Substituting for dn_i, we have

$$\frac{d_{in}S}{dt} = -\frac{1}{T}\frac{d\xi}{dt}\sum_i \nu_i\mu_i \quad .. (26)$$

Where ν_i is the stoichiometric coefficient of the ith component and ξ is is the extent of the reaction.

Now, as defined by De Donder, the affinity 'A' of a chemical reaction is:-

$$A = -\sum_i \nu_i\mu_i \quad \ldots (27)$$

From eq. (26) and (27)

$$d_{in}S = \left(\frac{A}{T}\right) d\xi > 0 \quad \ldots (28)$$

or $$\frac{d_{in}S}{dt} = \left(\frac{A}{T}\right)\left(\frac{d\xi}{dt}\right) > 0 \quad \ldots (29)$$

The rate of the reaction, r in terms of extent of reaction ξ is

$$r = \frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \dots (30)$$

The molar concentration of the i^{th} component is:-

$$c_i = \frac{n_i}{V} \qquad \dots (31)$$

Where n_i is the number of moles of i^{th} component dissolved in V litres.

Differentiating;

$$\frac{dc_i}{dt} = \frac{d}{dt}\frac{n_i}{V} = \frac{1}{V}\frac{dn_i}{dt} - \frac{n_i}{V^2}\frac{dV}{dt} \qquad \dots (32)$$

Let volume during the reaction remains constant, we get

$$\frac{dc_i}{dt} = \frac{1}{V}\frac{dn_i}{dt} = \frac{1}{V}\nu_i\frac{d\xi}{dt} \qquad \dots (33)$$

From eq. (29) and (30), we get

$$\sigma = \frac{d_{in}S}{dt} = \frac{1}{T}Ar > 0$$

or

$$T\sigma = Ar > 0 \qquad \dots (34)$$

As T is positive $\therefore$ A and r must have same sign. On comparing eq. (12) and (34) we can say that the role of driving force $\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right)$ is played by affinity A.

So the expression for entropy production is product of the force (A) and flow (r)

$$\sigma = \frac{Ar}{T} \qquad \dots (35)$$

For f reactions (ρ = 1, 2, 3….f) occurring simultaneously, the eq. (29) can be extended to:-

$$d_{in}S = \frac{1}{T}\sum_{\rho} A_{\rho} d\xi_{\rho} > 0 \qquad \ldots (36)$$

Where A_{ρ} is the affinity of ρ^{th} reaction, it is given by

$$A_{\rho} = -\sum_{i} \nu_{i\rho}\mu_{i} \qquad \ldots (37)$$

But at equilibrium, all affinities are zero, that is

$$A_1 = A_2 = \ldots.. = A_{\rho} = 0$$

The entropy production per unit time is now given by

$$\frac{d_{in}S}{dt} = \frac{1}{T}\sum_{\rho} A_{\rho} r_{\rho} > 0 \quad \ldots (38)$$

i.e. The entropy production per unit time is the sum of entropy production due to various reactions. The entropy production of all simultaneous reactions is positive.

If in a system two reactions are occurring simultaneously such that

$$A_1 r_1 < 0 \quad and \; A_2 r_2 > 0$$

And the sum of these two terms is

$$A_1 r_1 + A_2 r_2 > 0 \qquad \ldots(39)$$

Then both these two reactions are said to be **coupled reactions.**

8. Summary

- Entropy is the measure of degree of randomness of molecule in the macroscopic system. The total entropy of the system is the sum of entropies of the individual parts of the system.
- The total change in entropy is the sum of two components

  $dS = d_{in}S + d_{ex}S$

  where $d_{in}S$is the change in entropy inside the system and $d_{ex}S$is the flow of entropy due to interactions with exterior of the system
- The change in entropy in terms of heat exchange from the surroundings according to second law of thermodynamics is given by:

  $dS = \frac{dq}{T}$
- Where dq is the amount of heat exchange from the surroundings at temperature T.
- The total change in entropy due to the heat flow from the surroundings is given by

$$\sigma = \frac{d_{in}S}{dt} = \frac{d_{in}q}{dt}\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right)$$

  Where $\frac{d_{in}q}{dt}$ is the rate of heat transfer and $\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right)$ is the difference between state functions which is acting as driving force for the heat transfer.
- The entropy produced due to chemical reaction which is occurring at constant temperature and pressure conditions is given by:

$$\frac{d_{in}S}{dt} = \frac{1}{T}\sum_{\rho} A_{\rho} r_{\rho}$$

in which A_ρ stands for the affinity of the ρ^{th} reaction having r_ρ as the rate of

- reaction at temperature T.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	15, Entropy production
Module Tag	CHE_P10_M15

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1. Learning Outcomes

After studying this module you shall be able to

- Derive the relationship between rate of entropy production and the affinity of the reaction in an open system.
- Know the relation between entropy production and strength of current.
- Determine how entropy is produced during the mixing of gases

2. Introduction

Entropy is always created in the interior of open or closed system when irreversible changes occur, i.e. $d_{in}S \geq 0$. Also, for open as well as closed systems, we represent an entropy balance as

$$dS = d_{in}S + d_{ex}S \qquad \ldots(1)$$

where $d_{in}S$ is the entropy produced within the system and $d_{ex}S$ is the entropy brought into the system during a time dt from the surroundings. If a given system is not uniform with respect to temperature, then it must be split into small volume elements with a constancy of temperature and the total entropy must be evaluated by integration, i.e.

$$S = \int_v \bar{S}_v dV \qquad \ldots(2)$$

Where S_v is the local entropy per unit volume in each volume element. The rate of entropy production per unit volume of a system, σ_v is given by:

$$\sigma_v = \frac{1}{v}\frac{d_{in}S}{dt} \qquad \ldots(3)$$

Assuming that the only irreversible process is a chemical reaction, we have

$$\sigma_v(\text{chem}) = \frac{A\, r_v}{T} \geq 0 \qquad \ldots(4)$$

Where A is the affinity of the chemical reaction and r_v is the rate per unit volume, i.e.

$$r_v = \left(\frac{1}{v}\right)\frac{d\xi}{dt} \qquad \dots (5)$$

If several reactions occur simultaneously, then equation (4) can be generalized as

$$\sigma_v = \sum_R A_R \frac{r_v R}{T} \geq 0 \qquad \dots (6)$$

The summation implies that it is extended over all reactions.

3. Entropy production and entropy flow in open system

We now consider the change in dS in an open system in terms of matter exchange with surroundings or that formed due to chemical changes occurring within the system. Let us consider an open system consisting of two phases I and II so that both energy and matter can be exchanged:-

From classical thermodynamics;

$$dU = TdS - PdV + \sum_i \mu_i dn_i \qquad \dots (7)$$

or $TdS = dU + PdV - \sum_i \mu_i dn_i$ … (8)

and recalling following equation

$dU = dq – PdV$ and $dn_i = \nu_i d\xi$ … (9)

Equation (8) becomes:

$$dS = \frac{dq}{T} - \frac{1}{T}\sum_i^k \mu_i \nu_i \, d\xi \qquad \dots (10)$$

As affinity $A = -\sum_i \mu_i \nu_i$, in which ν_i is the stoichiometric coefficient of the i^{th} component, then Equation (10) becomes

$$dS = \frac{dq}{T} + \frac{A}{T} d\xi \qquad \dots (11)$$

Now, as we have considered an open system in which both energy and matter are exchanged. ∴ From equation (11) dq is replaced by $d\phi$, where $d\phi$ represents the flow of energy due to heat transfer and exchange of matter. Now also considering entropy exchange with surroundings i.e.

$$d_{ex}S = \frac{d\phi}{T} - \sum_i \frac{\mu_i}{T} d_{ex}n_i \qquad \dots (12)$$

Equation (11) can be written as

$$dS = \frac{d\phi}{T} - \sum_i \frac{\mu_i}{T} d_{ex}n_i + \frac{A}{T} d\xi \qquad \dots (13)$$

For both the phases I and II, total entropy produced will be

$$dS = \frac{d^I\phi}{T^I} + \frac{d^{II}\phi}{T^{II}} - \sum_i \left(\frac{\mu_i^I}{T^I} - \frac{\mu_i^{II}}{T^{II}}\right) d_{ex}n_i^I + \frac{A^I}{T^I} d\xi^I + \frac{A^{II}}{T^{II}} d\xi^{II} \qquad \dots (14)$$

Where A^I and A^{II} are affinities of reactions which are occurring in phase I and II respectively. $d_{ex}n_i^I$ is the number of moles of i component transferring from phase II to phase I.

For energy flow we can write:

$$\frac{d^I\phi}{T^I} = \frac{d_{ex}^I\phi}{T^I} + \frac{d_{in}^I\phi}{T^I} \qquad \dots (15)$$

$$\frac{d^{II}\phi}{T^{II}} = \frac{d_{ex}^{II}\phi}{T^{II}} + \frac{d_{in}^{II}\phi}{T^{II}} \qquad \dots (16)$$

Substituting eq. (15) and (16) in eq. (14)

$$dS = \frac{d_{ex}^I q}{T^I} + \frac{d_{ex}^{II} q}{T^{II}} + d_{in}^I\phi\left(\frac{1}{T^I} - \frac{1}{T^{II}}\right) - \sum_i \left(\frac{\mu_i^I}{T^I} - \frac{\mu_i^{II}}{T^{II}}\right) d_{ex}n_i^I + \frac{A^I d\xi^I}{T^I} + \frac{A^{II} d\xi^{II}}{T^{II}} \qquad \dots (17)$$

In above equation, the first two terms represent entropy flow$d_{ex}S$ due to the exchange of heat between closed system and external surroundings. The remaining terms represent entropy production$d_{in}S$. The third term represents entropy change due to exchange of energy between phases I and II, fourth term represents the change in entropy due to exchange of matter between the phases I and II; and the last two terms represents change in entropy due to chemical reactions taking place in each phase.

Now finding rate of entropy production:

$$\sigma = \frac{d_{in}S}{dt} = \frac{d^{I}\phi}{dt}\left(\frac{1}{T^{I}} - \frac{1}{T^{II}}\right) - \sum_i \left(\frac{\mu_i^{I}}{T^{I}} - \frac{\mu_i^{II}}{T^{II}}\right)\frac{d_{ex}n_i^{I}}{dt} + \left(\frac{A^{I}}{T^{I}}\right) r^{I} + \left(\frac{A^{II}}{T^{II}}\right) r^{II} \geq 0 \qquad \dots (18)$$

where r is the corresponding rate of the reaction.

In the equation (18) coefficients of rate flow i.e. terms inside the parenthesis are the force terms. Thus, the rate of entropy production is represented as the sum of product of generalizedforces (affinities) denoted by X_i and corresponding fluxes (flows) which is denoted by J_i.

Therefore,

$$\sigma = \frac{d_{in}S}{dt} = \sum_i J_i X_i > 0 \qquad \dots (19)$$

4. Entropy production due to flow of current in electrical conductor

Let the current of strength i passes through electric conductor of length ll' during a time t. Then the charge i.t then flows through a potential difference $(\phi^{l'} - \phi^{l})$where$\phi^{l'}$is potential at l' and ϕ^{l} is potential at l. Then the electric work done in the process is: $W_{elec} = i.t(\phi^{l'} - \phi^{l})$ … (20)

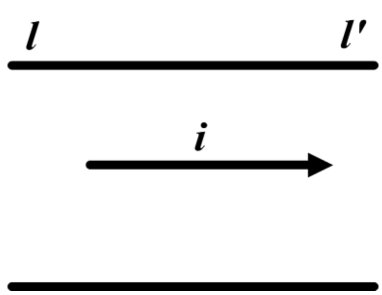

Figure illustrates the direction of flow of current i.e. from *l* to *l'*

According to ohm's law$(\phi^{l'} - \phi^{l})$ can be written as:-

$\phi^{l'} - \phi^{l} = -i.R$ … (21)

Where R is the resistance of the conductor ll'. Since $\phi^{l'} - \phi^{l}$ is negative $\therefore$ negative sign is represented in above expression.

Substituting eq. (21) in (20) we get

$W_{elec} = -i.t * i.R = -i^2Rt$ … (22)

Applying first law of thermodynamics;

$q = \Delta U + w = -i^2Rt$ (Since there is no change in the system therefore ΔU = 0) … (23)

Similarly, change in entropy dS = 0 for the given system and it is given by

$dS = d_{ex}S + d_{in}S = \frac{q}{T} + d_{in}S$ … (24)

Or rearranging the above equation

$d_{in}S = dS - \frac{q}{T} = -\frac{q}{T}$ (since dS = 0) … (25)

Substituting equation (23) in (25), we get:

$d_{in}S = -\frac{q}{T} = \frac{i^2Rt}{T} > 0$ … (26)

Or using equation (21) equation (26) can be written as:

$d_{in}S = \frac{i.t}{T}(\phi^{l'} - \phi^{l}) > 0$ … (27)

Thus, the electrical force $\frac{1}{T}(\phi^{l'} - \phi^{l})$ is responsible for the occurrence of flow of charge i.e. flux i.t.

5. Entropy production during mixing of gases

Let us consider a system of ideal gases, kept in a vessel, which do not interact with each other and separated from each other by partition.

Total entropy of the system suggested by Glasstone when gases were separated is given by:-

$$S_1 = \sum_i n_i (C_v \ln T + R \ln v_i + S_i) \quad \text{… (28)}$$

Before mixing

Gas 1	Gas 2	Gas 3
P	P	P
V_1	V_2	V_3
n_1	n_2	n_3

After mixing

Gas 1 + Gas 2 + Gas 3
P, V, T
$n_1 + n_2 + n_3 = n$

In the above equation S_i is an integration constant at constant temperature. We now calculate the entropy of the mixture of gases S_2, after the removal of partitions.

Entropy of mixture of gases S_2 is:-

$$S_2 = \sum n_i (C_v \ln T + R \ln V + S_i) \quad \text{…(29)}$$

where each of the gases occupies total volume V. Let individual gas were at same pressure P before mixing. Therefore,

$$P = \frac{n_1 RT}{v_1} = \frac{n_2 RT}{v_2} = \frac{n_3 RT}{v_3} \quad \text{… (30)}$$

And

$$P = \frac{(n_1+n_2+n_3)RT}{v_1+v_2+v_3} = \frac{nRT}{V} \quad \text{… (31)}$$

Thus

$$\frac{n_1}{v_1} = \frac{n_2}{v_2} = \frac{n_3}{v_3} = \frac{n}{V} \quad \text{.. (32)}$$

This equation can also be written as:-

$$\frac{n_1}{n} = N_1 = \frac{v_1}{V} \qquad \dots (33)$$

General Expression:-

$$\frac{n_i}{n} = N_i = \frac{v_i}{V} \qquad \dots (34)$$

where N_i = mole fraction of the component i in the mixture of gases.

Substituting (34) in (28)

$$S_1 = \sum n_i \left(C_v \ln T + R \ln N_i + R \ln V + S_i\right) \qquad \dots (35)$$

Thus entropy of mixing is:-

$$S_2 - S_1 = \Delta S_m = -\sum_i n_i R \ln N_i = -R \sum_i n_i \ln N_i \qquad \dots (36)$$

As ln N_i is negative $\therefore \Delta S_m$ is positive. Thus for irreversible process, entropy is produced.

For one mole of mixture of ideal gases entropy of mixing can be written as

$$\Delta S_m = -R \sum_i \frac{n_i}{n} \ln N_i = -R \sum_i N_i \ln N_i$$

The above equation is valid only at constant temperature and total volume (i.e. there is no net volume change on mixing.)

6. Summary

1. The rate of entropy production is given by the sum of the product of forces (affinities) i.e. X_i and corresponding fluxes (flows) i.e. J_i.

$$\sigma = \frac{d_{in}S}{dt} = \sum_i J_i X_i$$

2. The rate of entropy production per unit volume of the irreversible process is always greater than zero and its expression is given by:

$$\sigma_v = \sum_R A_R \frac{r_v R}{T} \geq 0$$

Here σ_v is the rate of entropy production per unit volume, A_R is the affinity of the reaction, R is the total number of reactions occurring simultaneously, r_v is the rate of the reaction per unit volume at temperature T.

3. The entropy produced within the electric conductor is affected by two factors:

- electrical force i.e.$\frac{1}{T}\left(\phi^{l'} - \phi^{l}\right)$
- flux i.e. i.t

The expression for change in entropy within the electrical conductor ll' is given by:

$$d_{in}S = \frac{i.t}{T}\left(\phi^{l'} - \phi^{l}\right)$$

where ' i ' is the amount of current flowing at temperature T through a conductor having the potential difference $\phi^{l'} - \phi^{l}$.

4. The change in entropy produced in one mole of a mixture of ideal gas having the components i is given by:

$$\Delta S_m = -R\sum_i \frac{n_i}{n}\ln N_i = -R\sum_i N_i \ln N_i$$

where R is the gas constant and N_i is the mole fraction of component i.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	16, Transformation of fluxes and forces, non-equilibrium stationary states and Phenomenological equations and laws
Module Tag	CHE_P10_M16

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1. Learning Outcomes

After studying this module, you shall be able to:

- Know about the entropy balance equation
- Learn how entropy production is related to affinity of the reaction
- Learn how fluxes and forces are transformed
- Learn about phenomenological laws
- Find out the relationship between the rate of entropy production and coefficient of thermal conductivity

2. Entropy balance equation

The basic equation for non-equilibrium thermodynamics is entropy balance equation. This balance equation for entropy can be derived using the concept of conservation of energy and the balance equation for the concentration. This equation depicts the relationship between three thermodynamic quantities: the entropy change, the entropy production and the entropy flow. The change in entropy is the time derivative of the entropy of the system, and it is the sum of two integrals (entropy production and entropy flow) for a given system. The expression is given by:

$$\frac{dS}{dt} = \frac{d_{in}S}{dt} + \frac{d_{ex}S}{dt} \qquad \ldots(1)$$

The expression $\frac{d_{in}S}{dt}$ denotes the entropy production and is written by $\frac{d_{in}S}{dt} = \int \sigma dV$. This time derivative of the entropy denotes the entropy produced within the system. The time derivative $\frac{d_{ex}S}{dt}$ denotes the entropy flow and the expression is given by

$\frac{d_{ex}S}{dt} = \int(-div\,J)dV$. It is the time derivative of that entropy which comes from or goes out to the environment across the boundary of the system.
Tus the final expression for change in entropy is given by:

$$\frac{dS}{dt} = \int(\sigma - div\,J)dV \quad \ldots(2)$$

For a reaction-diffusion system, the entropy production comprises of two components: the entropy production of chemical reactions and diffusions i.e. $\int \sigma_R dV$ and $\int \sigma_D dV$ respectively.
The total entropy production can be written as:

$$\int \sigma dV = \int \sigma_R dV + \int \sigma_D dV = \int \sum_{\rho} k_B ln \frac{r_{\rho,+}}{r_{\rho,-}}(r_{\rho,+} - r_{\rho,-})dV + \int k_B \sum_{j} \frac{D_j}{c_j}(\nabla c_j)^2 dV$$

In the above equation, k_B denotes the Boltzmann constant, $r_{\rho,+}$ and $r_{\rho,-}$represents the rate of forward and backward reactions of the ρ^{th}chemical reaction, D_j and c_j represent diffusion coefficient and the concentration of the j^{th} component respectively.

3. Transformation of generalized fluxes and forces

The rate of entropy production for an irreversible process is given by:-

$$\sigma = \frac{d_{in}S}{dt} = \sum_i J_i X_i > 0 \ldots(3)$$

For a single chemical reaction occurring at a given rate, the above expression can be written as

$$\frac{d_{in}S}{dt} = J_{ch}X_{ch} > 0$$

σ does not depend on the reaction sequence but depends on linear combination of forces and flows. In the above equation, the flux J is identified with the rate r and generalized forces X is identified with affinity.
Consider a consecutive type of reaction:-

$$A \longrightarrow B \quad \ldots(i)$$

$$B \longrightarrow C \quad \ldots(ii)$$

For the reaction (i), the affinity is given by:-

$$A_1 = -(\mu_B - \mu_A) = \mu_A - \mu_B \quad \text{(since } r_A = r_B = 1) \quad \ldots(4)$$

Similarly for reaction (ii), the affinity is given by:-

$$A_2 = -(\mu_C - \mu_B) = \mu_B - \mu_C \quad \text{(since } r_B = r_C = 1) \quad \ldots(5)$$

The change in number of moles of A per unit time or rate of a reaction is given by:-

$$-\frac{dn_A}{dt} = r_1 \qquad \text{or} \; \frac{dn_A}{dt} = -r_1 \qquad \ldots(6)$$

Similarly, the change in number of moles of C per unit time is given by:-

$$\frac{dn_C}{dt} = r_2 \qquad \ldots(7)$$

Hence, the change in number of moles of B per unit time is given by:-

$$\frac{dn_B}{dt} = -\frac{dn_A}{dt} - \frac{dn_C}{dt} = r_1 - r_2 \qquad \ldots(8)$$

We know that the rate of entropy production for reaction (i) and (ii) is given by:-

$$\frac{Td_{in}S}{dt} = Ar_1 + Ar_2 \ldots(9)$$

Now, consider different chemical reaction;

$$A \longrightarrow C \qquad \ldots(i')$$

$$B \longrightarrow C \qquad \ldots(ii')$$

The corresponding affinities of the reactions (i') and (ii') are:-

$$A_1' = \mu_A - \mu_C = A_1 + A_2 \qquad \ldots(10)$$

$$A_2' = \mu_B - \mu_C = A_2 \ldots(11)$$

Therefore,

$$\frac{dn_A}{dt} = -r_1' \; ; \; \frac{dn_B}{dt} = -r_2' \; ; \; \frac{dn_C}{dt} = r_1' + r_2' \ldots(12)$$

By comparing equations (6,7,8) with equation (12) this, we find that

$$r_1 = r_1' \text{ and } r_2 = r_1' + r_2' \qquad \ldots(13)$$

For this reaction, the rate of entropy production is given as:-

$$\frac{Td_{in}S}{dt} = A_1'r_1' + A_2'r_2' \qquad \ldots(14)$$

$$\frac{Td_{in}S}{dt} = (A_1 + A_2)r_1 + A_2(r_2 - r_1') \qquad \ldots(15)$$

$$\frac{Td_{in}S}{dt} = (A_1 + A_2)r_1 + A_2(r_2 - r_1) = A_1r_1 + A_2r_2 \qquad \ldots(16)$$

$$\text{Thus,} \frac{Td_{in}S}{dt} = \sum A_1'r_1' = \sum A_1r_1 \qquad \ldots(17)$$

The above equation suggests that the newly generated set of equations for entropy production are also same. Thus, the transformation properties of the fluxes $J_i$and the generalized forces X_i are such that linear combination of forces and fluxes give a new set of fluxes J_i' and new set of forcesX_i'. Thus, the equation holds good.

$$\sum_i J_iX_i = \sum_i J_i'X_i' \qquad \ldots(18)$$

There are three types of transformations in linear irreversible thermodynamics.
Now we will discuss about non- stationary states.

4. Non-Equilibrium stationary states

Non equilibrium stationary states are state variables which are independent of time. In this case entropy production is different from zero and there is no transport of mass i.e. $J_m = 0$. Whereas equilibrium states are states in which entropy production is zero. A stationary state arises when the concentrations of the intermediate components not vary with time.

Considering a one-component system in which there exists temperature gradient (X_{th}) as well as concentration gradient (X_m). Near equilibrium, entropy production per unit time can be written as:-

$$\frac{d_{in}S}{dt} = J_{th}X_{th} + J_mX_m > 0 \qquad \ldots(19)$$

And the linear phenomenological laws (which are discussed in detail later) are:-

$$J_{th} = L_{11} X_{th} + L_{12}X_m \qquad \ldots(20a)$$

$$J_m = L_{21} X_{th} + L_{22}X_m \qquad \ldots(20b)$$

Where L_{11} and L_{22} are the coefficient of thermal conductivity and diffusion coefficient respectively. L_{12} is the coefficient of heat flow related to a concentration gradient. L_{21} is coefficient of mass flow associated with a temperature gradient.

Stationary states may be characterized by **extremum principle**. This principle states that in the stationary state, the minimum amount of entropy is produced compatible with some auxiliary conditions to be specified in each case. Thus an equation may be derived that specify condition that entropy production has minimum value for given value of X_{th}. Thus using the equations (19) and (20) and Onsager reciprocal relation ($L_{12} = L_{21}$), the rate of entropy production becomes

$$\frac{d_{in}S}{dt} = L_{11}X_{th}^2 + 2L_{12}X_{th}X_m + L_{22}X_m^2 > 0$$

Taking the derivative of equation (19) with respect to X_m keeping X_{th} constant, thus we get

$$\frac{\partial}{\partial X_m}\left(\frac{d_{in}S}{dt}\right) = 2(L_{12}X_{th} + L_{22}X_m) = 2J_m$$

In the situation of steady state i.e., when $J_m = 0$, it means that the rate of entropy production has an extreme value in the steady state. This extreme is minimum which can be shown by taking the second derivative of equation (19).

As in the steady state we know that $\frac{\partial}{\partial X_m}\left(\frac{d_{in}S}{dt}\right) = 0$, thus we get

$$\frac{\partial^2}{\partial X_m^2}\left(\frac{d_{in}S}{dt}\right) = \frac{\partial}{\partial X_m}(2J_m) \qquad \text{(at constant } X_{th}\text{)}$$

$$= 2\frac{\partial}{\partial X_m}(L_{21}X_{th} + L_{22}X_m)$$

$$= 2L_{22}$$

Since, L_{22} has positive value thus the second derivative is also positive so that the extremum is a minimum. This statement also furnishes the statement of Prigogine's principle of minimum entropy production. This principle states that at the steady state all the flows corresponding to unrestricted forces vanish.This can be generalized to the case of n independent affinities X_1 .... X_n out of which certain number k, $X_1 \ldots \ldots X_k$ are kept constant. For such case, stationary state,

$$J_{k+1} \ldots \ldots .. = J_n = 0$$

Such conditions are equivalent to minimum conditions for entropy production, i.e.,

$$\frac{\partial}{\partial X_j}\left(\frac{d_{in}S}{dt}\right) = 0 \qquad \text{(j= k+1,……n)}$$

Prigogine stated that the time variations of rate of entropy production i.e. $\frac{d}{dt}\left(\frac{d_{in}S}{dt}\right)$ is split into two parts:-

- Due to the irreversible processes which are occurring inside the system and
- Due to the flow of entropy from the system to the surroundings.

Because of the irreversible processes, occurring in the system the rate of entropy production decreases until the state is reached when it becomes minimum. When the system is in non-equilibrium steady state, then a system cannot come out this state despite being spontaneous irreversible state. But if some perturbations occur that disturb the system from steady state, then there occur some internal changes which bring back the system to the steady state.

5. Phenomenological Equations and laws

The principle of microscopic reversibility states that under equilibrium conditions, any molecular process and its reverse will proceed at the same rate. According to this principle, the rates or velocities of the various types of process (i.e. fluxes) are linearly related to the thermodynamic forces. Thus these forces are responsible for the fluxes that occur. Example,

Force (X)	Flux (J)
1. Temperature gradient	Heat flow
2. Gradient of chemical potential	Diffusion of matter
3. Gradient of electrical potential	Flow of charge

In irreversible processes, the transport of heat, mass, momentum and electric charge occurs. In all such cases, a quantity flux is transported as a result of driving force which is divided from gradient of some physical property of the system.

For transport of heat, driving flux is temperature gradient; for transport of mass driving flux is the concentration gradient; for electric current flux is the potential gradient.

The transport phenomenon of one dimensional system is:-

$$J = LX \qquad \ldots(21)$$

Linear law of this kind are referred to as phenomenological law, where J is flux (flow per unit area), X is the driving force (or gradient) which is responsible for the flow and L is proportionality constant called transport coefficient

Various transport processes can be written in following relationships: -

1) Fourier's Law: For heat transfer

$$J_Q = -\kappa \frac{dT}{dx} \qquad \ldots(22)$$

2) Fick's Law: For mass transfer

$$J_m = -D\frac{dc}{dx} \qquad \ldots(23)$$

3) Newton's Law: For momentum transfer

$$J_M = -\mu\frac{du}{dx} \qquad \ldots(24)$$

4) Ohm's Law: For electricity flow

$$J_e = -\lambda \frac{dE}{dx} \quad \text{…(25)}$$

In above equations, J_is represent corresponding fluxes.

i.e., J_Q = heat flux

J_m = mass flux

J_M = momentum flux

J_e = electric flux

and κ, D, μ, λ are corresponding transport coefficients which depend upon the material properties of the system. The above laws are called **phenomenological laws** which are used to define transport processes.

The forces X drive the flows, a gradient of $\left(\frac{1}{T}\right)$ causes the flow to heat. But at equilibrium, all the forces and flows vanish. Forces drive the flows, but a flow does not depend entirely on forces; flows can depend on other factors such as presence of catalyst. Catalyst can affect the rate of reaction. When two or more processes occur simultaneously in the same system, it is assumed that each of the flows depend on both the forces which cause the flow.

For small deviation in the forces from their equilibrium value of zero, the flows are expected to be linear function of forces. Lord Rayleigh expressed the linear dependence of all mechanical flows on all mechanical forces in a system. But Onsager in 1931 extended this concept and included all thermodynamic flows and forces. The resulting phenomenological equations are:-

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + \text{.....}\ L_{1n}X_n$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 + \text{.....}\ L_{2n}X_n$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 + \text{.....}\ L_{3n}X_n \quad \text{…(26)}$$

$$\vdots$$

$$J_n = L_{n1}X_1 + L_{n2}X_2 + L_{n3}X_3 + \text{.....}\ L_{nn}X_n \quad \text{…(27)}$$

Or

$$J_i = \sum_{k=1}^{n} L_{ik}X_k \qquad \text{(where i = 1, 2, 3, ….n)} \quad \text{…(28)}$$

The significance of the above equations can be explained as follows. Let consider a system in which n simultaneous flows or processes i.e., $J_1, J_2, ... J_n$ occur. To each flow, corresponding conjugate force $X_1, X_2, ... X_n$ were assigned. The choice of conjugate force is made in such a way that the dimension of the product $J_i X_i$ should be as that of dimension of entropy production or decrease in free energy with time.

According to Fick, Fourier, Ohm it is concluded that each flow is proportional to conjugate force, the proportionality constant be straight coefficient L_{ii}. All these straight coefficients appear on the diagonal of the matrix of forces on right hand side of set of equations given above. But from equation we also state that the flow J_1 is also driven by forces $X_2, X_3, ... X_n$ if the "coupling coefficients" or "cross coefficients" i.e., $L_{12}, L_{13}, ... L_n$ are different from zero i.e., force X_j contribute to flow J_i $(i \neq j)$ only when $L_{ij} \neq 0$. This shows that dependence of flows on non-conjugated forces is also linear. And this linearity holds true only for sufficiently slow processes occurring when the system is not too distant from a state of equilibrium.

Now consider two flows, J_1 and J_2 where

J_1 = flow of heat

J_2 = flow of matter

$\therefore$ X_1 = Temperature gradient

X_2 = concentration gradient

And $J_1 \propto X_1$ $\quad$ $J_2 \propto X_2$

If two processes occur simultaneously and system is close to equilibrium, the flow and fluxes are related by the phenomenological equations:

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad \text{…(29)}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad \text{…(30)}$$

Where L_{11}, L_{22} are 'direct or diagonal coefficients' and are always positive

L_{12}, L_{21} are 'off diagonal coefficients', that describes the interference or coupling of the two irreversible processes 1 and 2 (heat flow and matter flow). It may be positive or negative.

L_{12} = heat flow arising due to concentration gradient

L_{21} = flow of matter arising due to temperature gradient

Now, in general

$$J_i = L_{ii}X_i + L_{ik}X_k + \cdots$$

$$J_k = L_{ki}X_i + L_{kk}X_k + \cdots \qquad \ldots(31)$$

According to law of irreversible thermodynamics;

$$\frac{d_{in}S}{dt} = \sum_k J_k X_k > 0 \qquad \ldots(32)$$

Considering the above condition,

$$\frac{d_{in}S}{dt} = J_1X_1 + J_2X_2 \qquad \ldots(33)$$

Substituting (29) and (30) in eq. (33)

$$\frac{d_{in}S}{dt} = (L_{11}X_1 + L_{12}X_2)X_1 + (L_{21}X_1 + L_{22}X_2)X_2 > 0 \qquad \ldots(34)$$

$$\frac{d_{in}S}{dt} = L_{11}X_1^2 + (L_{12} + L_{21})X_1X_2 + L_{22}X_2^2 > 0 \qquad \ldots(34a)$$

Equation (34a) will be positive if both X_1 and X_2 have the same sign. Further, inequality condition will also be satisfied if $L_{11} > 0$, $L_{22} > 0$ and $(L_{12} + L_{21})^2 < 4L_{11}L_{22}$ which may be shown as follows:

The R.H.S. of the equation (34a) may be written as:

$$= L_{11}\left\{X_1^2 + \frac{(L_{12} + L_{21})}{L_{11}}X_1X_2 + \frac{L_{22}}{L_{11}}X_2^2\right\} > 0 \qquad \ldots(35)$$

Substituting $\frac{L_{12} + L_{21}}{L_{11}} = 2d$

And add and subtract $d^2X_2^2$ in equation (35)

$$= L_{11}\left\{X_1^2 + 2dX_1X_2 + d^2X_2^2 + \frac{L_{22}}{L_{11}}X_2^2 - d^2X_2^2\right\} > 0$$

$$= L_{11}\left\{(X_1 + dX_2)^2 + \frac{L_{22}}{L_{11}}X_2^2 - \left(\frac{L_{12} + L_{21}}{2L_{11}}\right)X_2^2\right\} > 0$$

$$= L_{11}\left\{(X_1 + dX_2)^2 + \left(\frac{4L_{11}L_{22} - (L_{12} + L_{21})^2}{4L_{11}^2}\right)X_2^2\right\} > 0 \qquad \ldots(36)$$

In the above equation the term $(X_1 + dX_2)^2$ will always be positive, now for the term to be greater than zero $4L_{11}L_{22}$ should be greater than $(L_{12} + L_{21})^2$. Therefore $L_{11} > 0$ and $L_{22} > 0$. Thus the diagonal coefficient L_{11}, L_{22} are always positive, whereas the off diagonal coefficient may be positive or negative their exact value being dependent on equation (36).

An alternative form of equations in which forces are represented as linear function of flows can be expressed as :

$$X_1 = R_{11} J_1 + R_{12} J_2 + R_{13} J_3 + ... + R_{1n} J_n$$

$$X_2 = R_{21} J_1 + R_{22} J_2 + R_{23} J_3 + ... + R_{2n} J_n \qquad \ldots(37)$$

$$X_3 = R_{31} J_1 + R_{32} J_2 + R_{33} J_3 + ... + R_{3n} J_n$$

$$X_n = R_{n1} J_1 + R_{n2} J_2 + R_{n3} J_3 + ... + R_{nn} J_n \qquad \ldots(38)$$

Or

$$X_i = \sum_{k=1}^{n} R_{ik}J_k$$

(where i = 1, 2, 3, ….n) …(39)

Above set of equations are obtained by solving equations (26), (27) for the forces. The coefficients $L_{ik} = \left(\frac{J_i}{X_k}\right)_{X_j}$ have dimension of flows per unit force and have characteristics of mobilities or conductance.

The coefficients $R_{ik} = \left(\frac{X_i}{J_k}\right)_{J_j}$ have dimension of force per unit flow and represents resistance or friction. It is possible to pass from one system of coefficients to other by rules of matrix algebra. For the simple case of two flows and two forces;

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad X_1 = R_{11}J_1 + R_{12}J_2 \qquad \ldots(40)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad X_2 = R_{21}J_1 + R_{22}J_2 \qquad \ldots(41)$$

The relation between the R_{ik} and L_{ik} are given by

$$R_{11} = \frac{L_{22}}{|L|},\ R_{12} = -\frac{L_{12}}{|L|},\ R_{21} = -\frac{L_{21}}{|L|},\ R_{22} = \frac{L_{11}}{|L|} \qquad \ldots(42)$$

In which the determinant $|L| = L_{11}L_{22} - L_{12}L_{21}$

In general, $R_{ik} = \frac{|L|_{ik}}{|L|}$ … (43)

In which $|L|$ is the determinant of the matrix of the coefficients L_{ik} and $|L|_{ik}$ is the minor of the determinant corresponding to the term L_{ik}.

5. Summary

- The rate of entropy production is given by:

$$\frac{dS}{dt} = \frac{d_{in}S}{dt} + \frac{d_{ex}S}{dt}$$

- In terms of entropy production and entropy flow, the rate of entropy production is given by:

$$\frac{dS}{dt} = \int (\sigma - div\, J) dV$$

Where $\frac{d_{in}S}{dt} = \int \sigma dV$ represents the entropy production and $\frac{d_{ex}S}{dt} = \int (\sigma - div\, J) dV$ represents the entropy flow.

- The transformation properties of the fluxes J_i and the generalized forces X_i are such that linear combination of forces and fluxes give a new set of fluxes J_i' and new set of forces X_i'.

- A stationary state is a state which arises when the concentrations of the intermediate components not vary with time.

- Extremum principle states that in the stationary state, the minimum amount of entropy is produced compatible with some auxiliary conditions to be specified in each case
- The transport process can be described by various laws. These are:

Fourier's Law: $J_Q = -\kappa \frac{dT}{dx}$

Fick's Law: $J_m = -D \frac{dc}{dx}$

Newton's Law: $J_M = -\mu \frac{du}{dx}$

Ohm's Law: $J_e = -\lambda \frac{dE}{dx}$

In above equations, κ, D, μ, λ are corresponding transport coefficients which depend upon the material properties of the system. J_i's are the corresponding fluxes.

- According to Fick, Fourier, Ohm it is concluded that each flow is proportional to conjugate force, the proportionality constant be straight coefficient L_{ii}. But the flow J_1 is also driven by forces $X_2, X_3, ... X_n$, i.e. force X_j contribute to flow J_i $(i \neq j)$, only when "coupling coefficients" or "cross coefficients" $L_{ij} \neq 0$. This shows that dependence of flows on non-conjugated forces is also linear.

- The relation between the R_{ik} and L_{ik} is given by

In general, $R_{ik} = \frac{|L|_{ik}}{|L|}$

In which |L| is the determinant of the matrix of the coefficients L_{ik} and $|L|_{ik}$ is the minor of the determinant corresponding to the term L_{ik}.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	17, Curie-prigogine principle
Module Tag	CHE_P10_M17

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1. Learning Outcomes

After studying this module you shall be able to:

- Learn about Curie-Prigogine Principle
- Relate scalar flows with vectorial forces and vice versa
- Know about the phenomenological equations
- Learn about principle of microscopic reversibility

2. Curie- Prigogine Principle

Consider the following equations:

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 + \cdots + L_{1n}X_n$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 + \cdots + L_{2n}X_n$$

.

.

.

$$J_n = L_{n1}X_1 + L_{n2}X_2 + L_{n3}X_3 + \cdots + L_{nn}X_n$$

$$J_n = L_{n1}X_1 + L_{n2}X_2 + L_{n3}X_3 + \ldots\ldots L_{nn}X_n$$

$$J_i = \sum_{k=1}^{n} L_{ik}X_k$$

And

$$X_1 = R_{11} J_1 + R_{12} J_2 + R_{13} J_3 + ... + R_{1n} J_n$$
$$X_2 = R_{21} J_1 + R_{22} J_2 + R_{23} J_3 + ... + R_{2n} J_n$$

$$X_3 = R_{31} J_1 + R_{32} J_2 + R_{33} J_3 + ... + R_{3n} J_n$$

$$X_n = R_{n1} J_1 + R_{n2} J_2 + R_{n3} J_3 + ... + R_{nn} J_n$$

or

$$X_i = \sum_{k=1}^{n} R_{ik} X_k$$

(wherei = 1, 2, 3, ….n)

In the above equations, J_i represent the flow and R_i represent corresponding forces.

The coefficient $L_{ik} = \left(\frac{J_i}{X_k}\right)_{X_j}$ are flows per unit force and $R_{ik} = \left(\frac{X_i}{J_k}\right)_{J_j}$ are force per unit flow.

In the above equations, the assumption was made that there is linear coupling between all forces and all flows which are taking part in irreversible processes occurring in a system. For different flows and forces there is requirement of different assumptions. The flow of chemical reaction and thermodynamic force associated with it and affinityof the reaction are scalar quantities while flow of heat and matter as well as their conjugated forces are vectors. Viscous phenomenon, which are omitted in this treatment are tensors of second order.

According to this Curie Principle, the dissipation function is given by:-

$$\phi = \sum J_s X_s + \sum J_v X_v \qquad \ldots(1)$$

Where

J_s are scalar flows and X_s are their conjugate forces

J_v are vectorial flows with X_v corresponding conjugate forces.

On simplification we can write above equation as:-

$\phi = \sum J_s X_s + \sum J_v X_v$ (s = 1, 2, …..k) & (v = k + 1, k + 2, ….h)

To know whether coupling exists between flows of one character and forces of another character, consider that x-component of any flow can be coupled with x-component of a force of any tensorial order. (A scalar is a tensor of zeroth order, vector is tensor of first order and tensors of higher order may also occur). According to this, we can write phenomenological equations as:-

$J_s = L_{ss} X_s + L_{sv} X_v$ …(3)

$J_v = L_{vs} X_s + L_{vv} X_v$ …(4)

In above set, L_{ss} relate the scalar force X_s to scalar flow J_s and it itself is scalar quantity.

The coefficient L_{sv} must be vector to give scalar flow through inner product with vectorial force X_v.

The coefficient L_{vs} must be vector in order to produce a vectorial resultant J_v, when multiplied by scalar X_s.

The coefficient L_{vv} is a tensor of second order, which transform the vectors X_v into vector J_v.

Such couplings occur in an anisotropic system in which these is no spatial symmetry. But for isotropic system in which the properties at equilibrium are same in all directions, all modes of couplings are not possible. Thus, flows and forces of different tensorial order are not coupled.

Therefore, for isotropic case, the above equation reduces to:-

$J_s = L_{ss} X_s$(Since L_{sv}in equation (3) is zero) …(5)

$J_v = L_{vv} X_v$ (L_{vs} in equation (4) is zero) …(6)

where the coefficient L_{vv} is scalar.

The reason for this behavior is that in isotropic system a reversal of sign of all coordinate axes must leave all phenomenological coefficients invariant.

Since L_{ss} is scalar which is also required, but the vectors L_{sv} and L_{vs} change their sign upon inversion of the coordinate system, L_{sv} and L_{vs} remain invariant only when both are equal to zero or if no coupling exists between scalar flows and vectorial forces and between vectorial flows and scalar forces. As L_{vv} should be invariant under any rotation of coordinate system leads to conclusion that L_{vv} must be scalar for isotropic system. Thus, the Curie-Prigogine principle states that there is no coupling between scalar and vectorial quantities. Since it is based on considerations of Curie regarding cause and effect relations in static systems of different symmetry, it was extended by Prigogine to irreversible system in flow.

Important conclusion from this principle is that simultaneous diffusion and chemical reaction cannot be coupled phenomenologically in an isotropic system.

3. Principle of Microscopic Reversibility

The principle of microscopic reversibility states that mechanical equations of motions of individual particle of a system of particles are invariant with respect to the transformation or reversal of time i.e. this principle of microscopic reversibility is a consequence of the invariance of the equations of motion under transformation of time which simply means that for every microscopic motion, if all the velocities of particles are reversed, then also solution is obtained.

Now generalizing the concept of correlational fluctuation. Consider a fluctuating parameter α_i which have the value $\alpha_i(t)$ at time t and fluctuation α_j after the time τ& then the product of both these quantities is taken. So, the average value of this product during a sufficiently long lapse of time is given by:-

$$\overline{\alpha_i(t)\,\alpha_j(t+\tau)} = \lim_{T\to\infty}\frac{1}{T}\int_0^T \alpha_i(t)\alpha_j(t+\tau)\,dt \qquad \ldots(7)$$

Equation (7) i.e., time average is also equal to the **ensemble average** according to ***ergodic theorem***.

This principle on microscopic level also states that processes which are going in one direction have the same probability to go in opposite direction. Or we can say that the arrow of time has no direction in microscopic realm.

If the fluctuations $\alpha_j(t)$ and $\alpha_i(t+\tau)$ are considered, the latter occurring after time interval τ then average value of the product $\alpha_j(t)$ and $\alpha_i(t+\tau)$ are found. This differs from equation (7) only in order of two fluctuations, or by substitution $t \longrightarrow -t$. Thus, the microscopic reversibility can be expressed as:-

$$\overline{\alpha_i(t)\,\alpha_j(t+\tau)} = \overline{\alpha_j(t)\,\alpha_i(t+\tau)} \qquad \ldots(8)$$

Subtracting $\alpha_i(t)\,\alpha_j(t)$ from both sides and then dividing by τ, then we have

$$\alpha_i(t)\frac{[\alpha_j(t+\tau) - \alpha_j(t)]}{\tau} = \alpha_j(t)\frac{[\alpha_i(t+\tau) - \alpha_i(t)]}{t} \qquad \ldots(9)$$

When τ approaches to zero, i.e. $\tau \rightarrow 0$ then we get

$$\overline{\alpha_i(t)\frac{d\alpha_j(t)}{dt}} = \overline{\alpha_j(t)\frac{d\alpha_i(t)}{dt}} \qquad \ldots(10)$$

τ are physically small for smaller values but they should be large enough compared to the time of single collision process τ_0, as it is the only case in which statistical average is applied. But if values of τ are very large then they should not be larger than the time required for the fluctuation to relax and disappear as at larger values of τ equation (8) become meaningless. Thus the relation should be $\tau_0 << \tau << \tau_r$.

Introducing Onsager hypothesis which states that rate of change of fluctuating parameter has same linear dependence on thermodynamic forces as observed in macroscopic flows. Mathematically it can be written as

$$J_i = \frac{\overline{d\alpha_i}}{dt} = \sum_k L_{ik} X_k \qquad \ldots(11)$$

in which L_{ik} are the overall macroscopic coefficients.

Now substituting eq. (11) in (10), we get

$$\sum_k L_{jk}\overline{\alpha_i X_k} = \sum_k L_{ik}\overline{\alpha_j X_k} \quad \ldots(12)$$

$$\text{Or } \sum_{k=1}^{n} L_{jk}\overline{\alpha_i X_k} = \sum_{k=1}^{n} L_{ik}\overline{\alpha_j X_k} \quad \ldots(13)$$

using result of fluctuation theory we get

$$\overline{X_\rho \alpha'_\rho} = -k\delta_{\rho'\rho} \quad \ldots(14)$$

where k is constant and $\delta_{\rho'\rho}$ is Kronecker-delta

i.e., $\delta_{\rho'\rho} = \begin{Bmatrix} 1, & \rho' = \rho \\ 0, & \rho' \neq \rho \end{Bmatrix}$

Thus from equation (12) and (14) we get

$$L_{ji} = L_{ij} \quad \ldots(15)$$

These are ***Onsager reciprocal relation***. Such relations are also valid for systems which have systematic deviations from equilibrium till the linear relationship between fluxes and forces is maintained. The extension of Onsager theory to complicated system has been done by Casimir and de Groot.

4. Summary

- According to this Curie Principle, the dissipation function is given by:-

$$\phi = \sum J_s X_s + \sum J_v X_v$$

where

J_s are scalar flows and X_s are their conjugate forces

J_v are vectorial flows with X_v corresponding conjugate forces.

- Flows and forces of different tensorial order are not coupled.
- Curie-Prigogine principle states that there is no coupling between scalar and vectorial quantities. Important conclusion from this principle is that simultaneous diffusion and chemical reaction cannot be coupled phenomenologically in an isotropic system.
- The principle of microscopic reversibility states that mechanical equations of motions of individual particle of a system of particles are invariant with respect to the transformation or reversal of time.
- The Onsager reciprocal relation is given by

$$L_{ji} = L_{ij}$$

Such relations are also valid for systems which have systematic deviations from equilibrium till the linear relationship between fluxes and forces is maintained.

Subject	Chemistry
Paper No and Title	10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
Module No and Title	18, Onsager relation
Module Tag	CHE_P10_M18

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1. Learning Outcomes

After studying this module you shall be able to:

- Know the general form of Onsager relation
- Know about the conditions imposed on phenomenological coefficients when the entropy production is greater than zero.
- Learn the role of chemical kinetics in finding the reciprocal relation
- Compare chemical kinetics and thermodynamics point of view in finding reciprocal relation

2. Onsager Relation

In phenomenological equations information regarding thermodynamically slow processes are given adequately but their applications have considerable difficulties. In simplest case of two forces and two flows, where there are four coefficients which are need to be determined by four independent experimental methods. Similarly for the case of three flows and forces, the number of coefficients which are need to be determined are nine, whose analysis through different experiment is extremely difficult.

But in 1931, Onsager showed that the matrix of phenomenological coefficients is symmetric i.e.

$L_{ik} = L_{ki}$ where $(i \neq k)$ …(1)

Onsager's relation chose the forces in such a way that when each flow J_i is multiplied by appropriate force X_i, the sum of these products is equal to the rate of creation of entropy per unit volume of the system θ, multiplied by temperature, T. Thus,

$$\sigma = T\theta = J_1X_1 + J_2X_2 + ... = \sum_i J_iX_i \quad ...(2)$$

Thus, evaluating the expression for entropy production is important. The equation (1) given above plays central role in the thermodynamics but this is applicable when eq. (2) is used to choose proper flows and forces for the phenomenological equations.

Equation (1) not only reduced the number of independent coefficients but also allows the correlations between flow and phenomenon that have great importance.The coefficients of the equations **(6-9)** are independent but the absolute magnitude of coupling coefficients is restricted by magnitude of straight coefficients because entropy production is always positive.

Considering two flows and two forces, the entropy production is given by:-

$$\sigma = J_1X_1 + J_2X_2 \quad ...(3)$$

Now substituting for $J_1 = L_{11}X_1 + L_{12}X_2$ and $J_2 = L_{21}X_1 + L_{22}X_2$, we obtain:

$$\sigma = L_{11}X_1^2 + (L_{12} + L_{21})\,X_1X_2 + L_{22}X_2^2 > 0 \quad ...(4)$$

Since, either X_1 or X_2 made to be vanish, we require that:-

$$L_{11}X_1^2 \geq 0,\ L_{22}X_2^2 \geq 0 \quad ...(5)$$

So that L_{11} and L_{22} i.e. both straight coefficients must be positive. In eq. (4); the quadratic form will remain positive only when the determinant is equal to or greater than 0.

$$\begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} = L_{11}L_{22} - L_{12}L_{21} \geq 0 \quad ...(6)$$

which gives the restriction on the possible magnitudes of the coupling coefficients L_{12} and L_{21}. Using Onsager's condition equation (1) i.e., $L_{ik} = L_{ki}$this condition becomes:-

$$L_{11}L_{22} \geq L_{12}^2$$

General case for any number of flows and forces where entropy production is greater than 0, impose two conditions on the phenomenological coefficients:-

(i) $L_{ii} \geq 0$ …(7)

(ii) $$\begin{vmatrix} L_{11} & L_{12} & \cdots\cdots & L_{1n} \\ L_{21} & L_{22} & \cdots\cdots & L_{2n} \\ \vdots & & & \\ L_{n1} & L_{n2} & \cdots\cdots & L_{nn} \end{vmatrix} = |L| \geq 0 \qquad \text{…(8)}$$

So that

$$L_{ii}L_{jj} \geq L_{ij}^2$$

3. Onsager relation by chemical kinetics point of view

In finding reciprocal relation, chemical kinetics played a crucial role. For this, relation between kinetic and thermodynamic descriptions of chemical reaction rate is required. In chemical kinetics, classically the rate of the reaction is proportional to concentration or their powers. While phenomenological equation states that reaction velocity be proportional to thermodynamic force or affinity which in turn depends on the logarithms of concentration. To rectify it, consider phenomenological description in the neighborhood of equilibrium when the rate of chemical change is very slow.

Considering simple mononuclear transformation;

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

The rate of the reaction given by kinetic theory are:-

$$\frac{dc_A}{dt} = -k_1c_A + k_{-1}c_B \qquad \text{…(9)}$$

$$\frac{dc_B}{dt} = k_1c_A - k_{-1}c_B \qquad \text{…(10)}$$

Where

c_A is concentration of A

c_B is concentration of B.

The two reaction flows, characterized by two constants can be distinguished by chemical treatment, but there is only one macroscopic flow of reaction from left to right, so that

$$J = -\frac{dc_A}{dt} = \frac{dc_B}{dt} = 0 \qquad \ldots(11)$$

At equilibrium, the flow vanishes and

$$k_1\overline{c_A} = k_{-1}\overline{c_B} \qquad \ldots(12)$$

or $$\frac{k_{-1}}{k_1} = \frac{\overline{c_A}}{\overline{c_B}} = K \qquad \ldots(13)$$

Where

$\overline{c_A}$ and $\overline{c_B}$ are equilibrium concentration of A and B respectively

K is the equilibrium constant of the reaction.

Now considering deviations α_i , of concentration from equilibrium values i.e.

$$\alpha_A = c_A - \overline{c_A} \qquad \ldots(14)$$

$$\alpha_B = c_B - \overline{c_B} \qquad \ldots(15)$$

and restricting range of concentration close to equilibrium, so that

$$\frac{\alpha_A}{\overline{\overline{C_A}}} << 1,\ \frac{\alpha_B}{\overline{\overline{C_B}}} << 1 \qquad \ldots(16)$$

Since the reaction proceeds without any exchange of matter with surroundings, therefore

$$C_A + C_B = \overline{C_A} + \overline{C_B} \qquad \ldots(17)$$

and $$\alpha_A + \alpha_B = 0$$

or $$\alpha_A = -\alpha_B \qquad \ldots(18)$$

Substituting equation (14) and (15) in (9) and (10)

$$J = k_1(\overline{c_A} + \alpha_A) - k_{-1}(\overline{c_B} + \alpha_B) \quad \text{...(19)}$$

$$J = k_1\bar{c}_A + k_1\alpha_A - k_{-1}\bar{c}_B - k_{-1}\alpha_B$$

Using equation (12)

$$J = k_1\bar{c}_A + k_1\alpha_A - k_1\bar{c}_A - k_{-1}\alpha_B$$

$$= k_1\alpha_A - k_{-1}\alpha_B \quad \text{...(20)}$$

Using equation (18) i.e. $\alpha_A = -\alpha_B$ the equation becomes

$$J = k_1\alpha_A + k_{-1}\alpha_A$$

$$J = (k_1 + k_{-1})\alpha_A \quad \text{...(21)}$$

$$J = k_1\alpha_A\left(1 + \frac{k_{-1}}{k_1}\right)$$

Using equation (13), the rate becomes

$$J = k_1\alpha_A\,(1 + K) \quad \text{...(22)}$$

Considering thermodynamic point of view, the driving force for the reaction is affinity. The affinity of the reaction is given by:

$A = \sum_{i=1}^{2} \nu_i\mu_i = \mu_A - \mu_B$ where ν_i is the stoichiometric coefficient ...(23)

At equilibrium, affinity of the reaction becomes zero, so

$$\overline{\mu_A} = \overline{\mu_B} \quad \text{...(24)}$$

where bar denotes equilibrium value of chemical potential.

Since, we already know that the chemical flow is proportional to force;

$$J = LA = L(\mu_A - \mu_B) \quad \text{...(25)}$$

For ideal solution which is under the condition of constant temperature and pressure, the chemical potential is

$$\mu_i = \mu_i^\circ + RT\ \ln c_i \qquad \ldots(26)$$

Substituting equation (26) in (23)

$$A = \mu_A^\circ + RTc_A - \mu_B^\circ - RT\ \ln c_B \qquad \ldots(27)$$

$$A = \left(\mu_A^\circ - \mu_B^\circ\right) + RT\ \ln\frac{c_A}{c_B} \qquad \ldots(28)$$

Using eq. (14) and (15)

$$A = \left(\mu_A^\circ - \mu_B^\circ\right) + RT\ln\frac{\alpha_A + \overline{c_A}}{\alpha_B + \overline{c_B}} \qquad \ldots(29)$$

Solving this equation further,

$$A = \left(\mu_A^\circ - \mu_B^\circ\right) + RT\ \ln(\alpha_A + \overline{c_A}) - RT\ \ln(\alpha_B + \overline{c_B})$$

$$A = \left(\mu_A^\circ - \mu_B^\circ\right) + RT\ \ln\overline{c_A}\left(1 + \frac{\alpha_A}{\overline{c_A}}\right) - RT\ \ln\overline{c_B}\left(1 + \frac{\alpha_B}{\overline{c_B}}\right) \qquad \ldots(30)$$

$$A = \left(\mu_A^\circ - \mu_B^\circ\right) + RT\ \ln\overline{c_A} + RT\ \ln\left(1 + \frac{\alpha_A}{\overline{c_A}}\right) - RT\ \ln\overline{c_B} - RT\ \ln\left(1 + \frac{\alpha_B}{\overline{c_B}}\right) \qquad \ldots(31)$$

At equilibrium, $\mu_A^\circ = \mu_B^\circ$

$$A = RT\left[\ln\left(1 + \frac{\alpha_A}{\overline{c_A}}\right) - \ln\left(1 + \frac{\alpha_B}{\overline{c_B}}\right)\right] \qquad \ldots(32)$$

If $\frac{\alpha_A}{\overline{c_A}} \ll 1, \frac{\alpha_B}{\overline{c_B}} \ll 1$; ; the logarithmic terms may be expanded in series, and retaining only first term in the above equation (32) which then becomes;

$$A = RT\left(\frac{\alpha_A}{\overline{c_A}} - \frac{\alpha_B}{\overline{c_B}}\right) = RT\frac{\alpha_A}{\overline{c_A}}\left[1 - \frac{\alpha_B}{\overline{c_B}} \times \frac{\overline{c_A}}{\alpha_A}\right] \qquad \ldots(33)$$

Using eq. (13) and (18) in eq. (33)we get

$$A = RT\frac{\alpha_A}{\overline{c_A}}(1 + K) \qquad \ldots(34)$$

Substituting equation (34) in (25);

$$J = \frac{LRT}{\overline{c_A}}\alpha_A(1 + K) \qquad \ldots(35)$$

For obtaining the above equation, we should consider that the reaction is close to equilibrium so that deviations of concentration from equilibrium value i.e., terms α_A and α_B are small.

Thus, two methods i.e., **thermodynamic approach** and **kinetic approach** give same result for slow reactions near equilibrium.

i.e. Thermodynamic treatment gives:-

$$J = \frac{LRT}{\overline{c_A}}\alpha_A(1 + K) \qquad \ldots(36)$$

Chemical kinetic point of view gives:-

$$J = k_1\alpha_A\ (1 + K) \qquad \ldots(37)$$

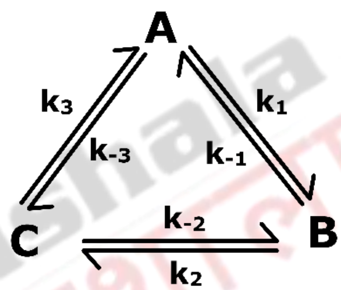
Thus, relating the above equations, we get

$$L = \frac{\overline{c_A}k_1}{RT} \qquad \ldots(38)$$

The above expression states that coefficient for chemical reaction L is not constant but it is dependent on equilibrium concentration $\overline{C_A}$. Similarly phenomenological coefficient is not a constant but it is dependent on characteristic parameters of the system.

4. Onsager proof

Using considerations of the previous section, a more complicated reaction system can be analyzed. Onsager considered a cyclic reaction for deriving the symmetry of phenomenological coefficients. The reaction was:–



The rate of three given reaction can be written as:-

$$J_1 = k_1 c_A - k_{-1} c_B$$

$$J_2 = k_2 c_B - k_{-2} c_C \quad \text{...(39)}$$

$$J_3 = k_3 c_C - k_{-3} c_A$$

But according to the phenomenological description, the rate of the reaction can also be defined only by two independent flows. The affinities of the three reactions are:-

$$A_1 = \mu_A - \mu_B$$

$$A_2 = \mu_B - \mu_C$$

$$A_3 = \mu_C - \mu_A \quad \text{.....(40)}$$

But these affinities are also dependent on each other by following relation:–

$$A_3 = -(A_1 + A_2) \quad \text{.....(41)}$$

Considering the dissipation function for the reaction system indicates that these are also two independent flows:

$$T\sigma = J_1A_1 + J_2A_2 + J_3A_3 \quad \text{.....(38)}$$

$$= (J_1 - J_3)A_1 + (J_2 - J_3)A_3$$

$$= J_1A_1 - J_3A_1 + J_2A_2 - J_3A_2 \quad \text{.....(42)}$$

The phenomenological equations for the above equations are

$$J_1 - J_3 = L_{11}A_1 + L_{12}A_2$$

$$J_2 - J_3 = L_{21}A_1 + L_{22}A_2 \quad \text{.....(43)}$$

At equilibrium, the chemical potentials become equal.

$$\bar{\mu}_A = \bar{\mu}_B = \bar{\mu}_C \quad \text{.....(44)}$$

Hence form the equation (39), the affinities become:-

$$A_1 = 0$$

$$A_2 = 0 \quad \text{.....(45)}$$

Thus, $J_1 - J_3 = 0$

$$J_2 - J_3 = 0 \quad \text{.....(46)}$$

So $J_1 = J_2 = J_3$ .....(47)

Thus according to thermodynamic point of view, at equilibrium all the flows become equal to each other rather than vanishing. The reaction may therefore, circulate indefinitely without producing entropy and without violating classical thermodynamics.

5. Summary

- In 1931, Onsager showed that the matrix of phenomenological coefficients is symmetric i.e.

$L_{iK} = L_{Ki}$ where $(i \neq K)$

- Using Onsager's relation the rate of entropy production is given by

$$\sigma = T\theta = J_1X_1 + J_2X_2 + \ldots\ldots = \sum_i J_iX_i$$

- On chemical kinetic point of view, the rate of entropy production is given by

$$J = K_1\,\alpha_A\,(1 + K)$$

- On thermodynamic point of view the rate of entropy production is given by

$$J = \frac{LRT}{\overline{C}_A}\,\alpha_A\,(1 + K)$$

- On comparing the two theories i.e. chemical kinetic and thermodynamic point of view we get $L = \frac{\overline{C}_A K_1}{RT}$ as a coefficient of chemical reaction.

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TABLE OF CONTENTS

1. Learning Outcomes

After studying this module you shall be able to:

- Know about various Electro kinetic phenomenon
- Understand various laws in which linear relationship between flux and its conjugate force is maintained.
- Learn about Saxen relations
- Differentiate between Soret effect and Dufour effect
- Derive the relationship Soret coefficient and heat of transport.

2. Electrokinetic Effect

In this section, electro-kinetic phenomenon such as electro-osmosis and streaming potential are considered. Electrokinetic phenomenon are due to the coupling between the electric current and matter flow, i.e. such processes have coupled influence of multiple types of forces or potentials (electrical, pressure, gravity etc.) on the transport behavior of multicomponent system. These type of processes are described by relationships known as Onsager reciprocity relations. Such physical phenomenon are regulated by transport processes in which linear relationship between a flux and corresponding driving force is maintained. Gradient of potential like concentration, chemical potential, temperature, pressure, electric potential etc. act as a driving force. Such transport processes in which linear relationship between a flux and its conjugate during force is maintained are:–

✶ **Molecular diffusion**, where diffusive flux is due to concentration gradient (Fick's law)

✶ **Thermodynamic conduction**, where heat flow is due to temperature gradient (Fourier's law)

✶ **Fluid flow**, in which rate of flow of fluid is proportional to the pressure gradient (Newton' law)

✶ **Electrical conduction**, in which current is related to the applied potential gradient (Ohm's law)

Thus flux is directly proportional to conjugated driving force and can be stated as:–

$$J_i = L_i X_i \qquad ...(1)$$

where J_i = flux

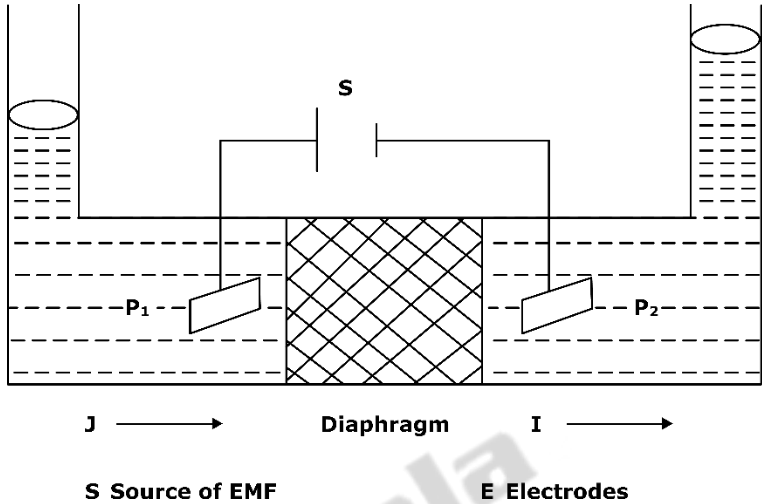
X_i = conjugate driving force

L_i = proportionality constant or transport coefficient.

Presence of driving force in such processes shows deviation from equilibrium. The electro kinetic transport processes cannot be explained in the relationship of single driving force and corresponding flux.

Now we will study electro kinetic effect in detail.

Consider a system consisting of two chambers I and II containing electrolytes. These electrolyte communicate through porous diaphragm or through capillary. On either side of diaphragm, platinum electrode is placed. It is supposed that the temperature and concentrations are uniform throughout the whole system. Both phases differ only with respect to pressure and electrical potential. This is shown in the following figure:



If the potential V is applied between the two chambers, then the current will flow until a stage is reached when the pressure difference ΔP is established at steady state. This pressure difference is also known as **electro-osmotic pressure**. If by the help of piston the fluid flow J from one chamber to another, then an electric current I, also known as streaming current flows through electrodes. Thermo-dynamical explanation for these effects are given in terms of entropy production. In the given case the system is discontinuous since there is no gradients but difference in chemical potential between two chambers. For such system, entropy production per unit volume σ is replaced by total entropy production $\frac{d_{in}S}{dt}$.

The entropy production due to flow of constituents from chamber 1 to chamber 2 can be assumed as a chemical reaction for which the difference in electrochemical potential becomes affinity.

Thus, entropy production is given by:–

$$d_{in}S = \frac{1}{T}\sum_i \tilde{A}_i d\xi_i = -\frac{1}{T}\sum_i \tilde{A}_i dn_i^I \qquad ...(2)$$

Where $\widetilde{A}_i$ is the electrochemical affinity due to the transfer of the component i from phase I to phase II.

It can be written as:-

$$\widetilde{A}_i = A_i + Z_i F(\varphi^I - \varphi^{II}) \quad ...(3)$$

$$= (\mu_i^I + Z_i F\varphi^I) - (\mu_i^{II} + Z_i F\varphi^{II}) \quad ...(4)$$

In these equations superscripts refer to the two chambers, Z_i is the charge number (electrovalence) of the ionic component i which is being transferred. F is the Faraday constant and φ is the electrical potential.

System is assumed to be closed and the degree of advancement of phase change is given by:-

$$-dn_i^I = dn_i^{II} = d\xi_i \quad ...(5)$$

Equation (4) can be written simply as:-

$$\widetilde{A}_i = (\mu_i^I - \mu_i^{II}) + Z_i F(\varphi^I - \varphi^{II}) \quad ...(6)$$

$$= \Delta\mu_i + Z_i F\Delta\varphi \quad ...(7)$$

Since the temperature and composition in both chambers are same, then for small difference in the pressure between two chambers, we may write

$$\Delta\mu_i = V_{mi}\Delta P \quad ...(8)$$

in which V_{mi} is specific molar volume of component i. Equation (2) can be rewritten as

$$\frac{d_{in}S}{dt} = -\frac{1}{T}\sum_i V_{mi}\frac{dn_i^I}{dt}\Delta P - \frac{1}{T}\sum_i Z_i F\frac{dn_i^I}{dt}\Delta\phi \quad ...(9)$$

But the fluxes can be defined as

$J = -\sum_i V_{mi}\frac{dn_i^I}{dt}$ is the volume flow or flow of matter. ...(10)

$I = -\sum_i Z_i F \frac{dn_i^I}{dt}$ is the electric current due to the transfer of charges from chamber I to chamber II ...(11)

Thus, the entropy production (2) becomes

$$\frac{d_{in}S}{dt} = \frac{J\Delta P}{T} + \frac{I\Delta Q}{T} \quad ...(12)$$

and the phenomenological equations are given by

$$I = L_{11}\frac{\Delta\phi}{T} + L_{12}\frac{\Delta P}{T} \quad ...(13)$$

$$J = L_{12}\frac{\Delta\phi}{T} + L_{22}\frac{\Delta P}{T} \quad ...(14)$$

In which Onsager relation i.e. $L_{12} = L_{21}$ holds good.

Thus, the two irreversible effects are considered i.e. the transfer of matter under combined influence of difference of pressure and flow of electrical current due to the difference of electrical potential. Also, due to the interference of two irreversible processes, the cross effect between the coefficient is developed i.e. $L_{12} = L_{21}$.

Now defining four electrokinetic effects i.e. streaming potential, electro osmosis, the electro-osmotic pressure and streaming current as follows:

- **Streaming potential (SP)** $\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = -\frac{L_{12}}{L_{11}}$ ...(15)
- **Electro osmosis (EO)** $\left(\frac{J}{I}\right)_{\Delta P=0} = \frac{L_{21}}{L_{11}}$ ...(16)
- **Electro Osmotic pressure (EOP)** $\left(\frac{\Delta P}{\Delta\phi}\right)_{J=0} = \frac{-L_{21}}{L_{22}}$ ...(17)
- **Streaming Current (SC)** $\left(\frac{I}{J}\right)_{\Delta\phi=0} = \frac{L_{12}}{L_{22}}$ ...(18)

From the above expressions we can say that the streaming potential is defined as the potential difference per unit pressure different in the state with zero electrical current. Similarly from eq. (16) EO is defined as the flow of matter per unit electrical current in the state with uniform pressure. From eq. (17) we can say that Electro-Osmotic Pressure is known as difference in pressure per unit potential difference when the flow J = 0. Eq (18) states that steaming current is defined as electric current flux per unit matter flux when electrical potential difference becomes equal to zero.

As the consequence of reciprocal relation i.e. $L_{12} = L_{21}$, the following relations are obtained

$$\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = -\left(\frac{J}{I}\right)_{\Delta P=0} \quad \text{i.e.} \quad \mathbf{SP = -EO} \qquad \ldots(19)$$

And

$$\left(\frac{\Delta P}{\Delta\phi}\right)_{J=0} = -\left(\frac{I}{J}\right)_{\Delta\phi=0} \quad \text{i.e.} \quad \mathbf{EOP = -SC} \qquad \ldots(20)$$

The above two relations are called Saxen relations.

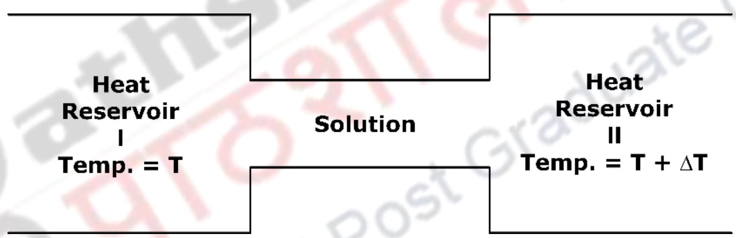
3. Thermal Diffusion

The interaction between heat and matter flows gives two effects, the Dufour effect and the soret effect. The Dufour effect refers to the flux of heat caused by a concentration gradient while Soret effect corresponds to thermal diffusion i.e. flux of matter caused by temperature gradient. It is also referred as thermal osmosis when a flux of matter occurs across a membrane under a temperature gradient.

3.1 *Dufour and Soret Effects*

Consider a solution having the solvent component 1 and a solute component 2. Suppose there exists the temperature gradient in a solution of unit cross section and unit length due to supply of heat at its ends from two heat reservoirs maintained at temperatures T and $T + \Delta T$ (shown in figure).

Due to temperature gradient, continuous flux of heat occurs from heat reservoirs II (warmer) to heat reservoir I (colder) shown in figure from right to left and concentration gradient also develops in the solution which originally has even distribution of solute. After a long interval of time a stationary state is ultimately reached during which period the temperature gradient is balanced by the gradient of chemical potential.



There are two types of fluxes in system of a dilute solution taking the solvent as a frame of reference. These fluxes are:–

- ✓ Heat flux J_{hf}
- ✓ Flux of solute J_2

The phenomenological equations for the above fluxes can be written as:–

$$J_{hf} = -l_{11}\, d\ln T - l_{12} d\mu_2 \qquad ...(21)$$

$$J_2 = -l_{21}\, d\ln T - l_{22} d\mu_2 \qquad ...(22)$$

where the coefficient l_{11} is related to thermal conductivity l_{22} is related to isothermal diffusion coefficients, D.

When the chemical potential of the solute becomes constant i.e. $d\mu_2 = 0$, then flux becomes

$$J_{hf} = -l_{11}\, d\ln T = \frac{-l_{11}}{T} dT = -\lambda dT \qquad \ldots(23)$$

λ in the above equation is the thermal conductivity which is equal to $\frac{l_{11}}{T}$.

At constant temperature, dT = 0

$$\therefore \qquad J_2 = -l_{22}\, d\mu_{2,T} \qquad \ldots(24)$$

$$= -l_{22} RT \frac{dc_2}{c_2} = -Ddc_2 \qquad \ldots(25)$$

Here $D = l_{22}RT/c_2$ and c_2= concentration of solute

The thermal diffusion coefficient, D_T is given as

$$D_T = \frac{l_{21}}{c_2 T} \qquad \ldots(26)$$

Now substituting the expression of D and D_T in equation (22)

$$J_2 = -D_T . c_2 dT - Ddc_2$$

Soret effect is the effect in which flux of the solute is generated because of the temperature difference. Soret coefficient (S_T) is given by the ratio of thermal diffusion coefficient to the ordinary diffusion coefficient.

$$S_T = \frac{-D_T}{D} = \left(\frac{dc_2}{c_2 dT}\right)_{J_2=0} \qquad \ldots(27)$$

The above condition is valid only at stationary state condition of $J_2 = 0$.

Now finding 'heat of transport' q_i for non-isothermal system i.e. heat transport coupled to the transport of the component i when temperature difference is zero. i.e.

$$q_2 = \left(\frac{J_{hf}}{J_2}\right)_{dT=0} = \frac{l_{12}}{l_{22}} \qquad \ldots(28)$$

Now finding **relationship between** q_2 **and** S_T

$$S_T = \frac{-D_T}{D} = \frac{-l_{21}}{c_2 T} \cdot \frac{c_2}{l_{22}RT} = \frac{-l_{21}}{l_{22}} \frac{1}{RT^2}$$

$$= \frac{-l_{21}}{l_{22}\,RT^2} \qquad \ldots(29)$$

or $$S_T = -\frac{q_2}{RT^2} \qquad \ldots(30)$$

3.2 Thermal Diffusion in Continuous System

The phenomenon of thermal diffusion is studied by Ludwig in 1856. In this phenomenon, flow of matter is done by non-conjugated force called temperature gradient. Now understanding this phenomenon in thermodynamic terms. Consider the entropy produced in continuous, non-isothermal system of diffusing substances i.e. expression for σ is given by:

$$\sigma = J_q \,.\, \text{grad}\frac{1}{T} + \sum_{i=1}^{n} J_i \,.\, \text{grad}\left(-\frac{\mu_i}{T}\right) \qquad \ldots(31)$$

Whereas the force gradient can be written as

$$\text{grad}\left(\frac{-\mu_i}{T}\right) = \frac{1}{T}\text{grad}(-\mu_i) - \mu_i \text{grad}\frac{1}{T} \qquad \ldots(32)$$

Thermodynamically, the chemical potential can be written as

$$d\mu_i = -\overline{S_i}dT + \overline{V_i}dP + \sum_{i=1}^{n} \mu_i^c dn_i \qquad \ldots(33)$$

Accordingly, the equation becomes

$$\text{grad}\,\mu_i = -\overline{S}_i\,\text{grad}T + \overline{V}_i\,\text{grad}\,P + \text{grad}\,\mu_i^c \qquad \ldots(34)$$

where μ_i^c part of chemical potential which is concentration dependent

Let the system is in mechanical equilibrium, gradP = 0, the equation becomes

$$\text{grad}\,\mu_i = -\overline{S}_i\,\text{grad}T + \text{grad}\,\mu_i^c \qquad \ldots(35)$$

Substituting (35) in (32) and also using the equation

$$\overline{H}_i = -T\overline{S}_i + \mu_i$$

We get

$$\text{grad}\left(-\frac{\mu_i}{T}\right) = -\overline{H}_i\text{grad}\frac{1}{T} + \frac{1}{T}\text{grad}(-\mu_i^c) \qquad \ldots(36)$$

Now equation (31) becomes

$$\sigma = \left(J_q - \sum_{i=1}^{n}\overline{H}_i J_i\right)\text{grad}\frac{1}{T} + \sum_{i=1}^{n}\frac{J_i\,\text{grad}(-\mu_i^c)}{T} \qquad \ldots(37)$$

In terms of dissipation function

$$\phi = T\sigma = \frac{J'_q\,\text{grad}(-T)}{T} + \sum_{i=1}^{n} J_i\,\text{grad}(-\mu_i^c) \qquad \ldots(38)$$

where $$J'_q = J_q - \sum_{i=i}^{n}\overline{H}_i J_i \qquad \ldots(39)$$

The thermal flow J'_q has been called the "reduced" heat flow. It is the difference between "total" heat flow and heat flow caused by flow of matter. Expression for Gibb'sDuhem equation is

$$\sum_{i=1}^{n-1} c_i \, grad \, \mu_i^c = -c_w \, grad \, \mu_w^{\circ} \qquad \ldots(40)$$

In which the subscript w denotes the solvent, then using equation (40) into (38) and rearranging, we get:

$$\phi = \frac{J'_q \mathrm{grad}\,(-T)}{T} + \sum_{i=1}^{n-1}\left(J_i - \left(\frac{c_i}{c_w}\right) J_w\right) . \mathrm{grad}\,(-\mu_i^c) \ldots(41)$$

In above equation, the flows $\left(J_i - \left(\frac{c_i}{c_w}\right) J_w\right)$ are the flows of the solutes relative to the solvent, J_i^d, so,

$$\phi = \frac{J'_q \, . \, \mathrm{grad}\,(-T)}{T} + \sum_{i=1}^{n-1} J_i^d \, \mathrm{grad}\,(-\mu_i^c) \qquad \ldots(42)$$

For binary solution, the equation reduced to

$$\phi = \frac{J'_q \, . \, \mathrm{grad}\,(-T)}{T} + J_s^d \, . \, \mathrm{grad}\,(-\mu_s^c) \qquad \ldots(43)$$

where J_s^d is the flow of solute relative to solvent.

Using this, the phenomenological equations become:

$$J_s^d = -L_{11} \, \mathrm{grad}\mu_s^c - L_{iq} \frac{\mathrm{grad}\,T}{T} \qquad \ldots(44)$$

$$J'_q = -L_{q1} \, \mathrm{grad}\mu_s^c - L_{qq} \frac{\mathrm{grad}\,T}{T} \qquad \ldots(45)$$

Reciprocal relation is $L_{1q} = L_{q1}$ …(46)

Relation between $\mathrm{grad}\,\mu_s^c$ and grad c_s is

$$grad\ \mu_s^c = \frac{\partial \mu_c}{\partial c_s}, \qquad grad\ c_s = \mu_{ss}\ grad\ c_s \qquad \ldots(47)$$

The equation for solute flow becomes

$$J_s^d = -L_{11}\mu_{ss}\ grad c_s - L_{1q}\frac{grad\ T}{T} \qquad \ldots(48)$$

The total flow of solute has two terms; ordinary diffusional flow which is proportional to concentration gradient and thermal diffusion flow which is dependent on temperature gradient. The coefficient of grad $c_s$in the equation (48) is the diffusion coefficient, D of the solute. Generally, L_{1q} is linearly proportional to the solute concentrationc_s, so, the thermal diffusion coefficient D^T is given by

$$\frac{L_{1q}}{T} = c_s D^T \qquad \ldots(49)$$

Eq. (48) becomes

$$J_s^d = -D\ grad c_s - c_s D^T grad\ T \qquad \ldots(50)$$

The thermal diffusion can also be represented in terms of Soret coefficients S_T which is defined as the ratio of the thermal diffusion coefficient to ordinary diffusion coefficient

$$S_T = \frac{D^T}{D} = \frac{L_{1q}}{Dc_s T} \qquad \ldots(51)$$

This Soret coefficient is a measure of the concentration gradient of the solute which is maintained because of temperature gradient at steady state, which is defined by condition $J_s^d = 0$, grad T = constant.

Equation (50) becomes

$$\frac{grad\ c_s}{grad\ T} = -\frac{c_s D^T}{D} \qquad \ldots(52)$$

So, the Soret coefficient, becomes

$$-S_T = \frac{grad\ ln\ c_s}{grad\ T}$$

Thermal diffusion can also be represented in terms of the amount of heat transfer Q* which is defined as the reduced heat flow per unit flow of matter at uniform temperature. Thus from eq. (44) and (45)

$$\left(\frac{J_q{}'}{J_s^d}\right)_{grad\ T\ =\ 0} = Q^* = \frac{L_{q1}}{L_{11}} \qquad \ldots(53)$$

From eq. (53) and with Onsager relation eq. (46), then equation (48) may be written as:

$$J_s^d = -L_{11}\mu_{ss}\ gradc_s - L_{11}Q^*\frac{grad\ T}{T} \qquad \ldots(54)$$

The thermal diffusion coefficient is given by

$$D^T = \frac{L_{11}Q^*}{c_sT} \qquad \ldots(55)$$

The Soret coefficient is given by

$$S_T = \frac{D^T}{D} = \frac{L_{11}Q^*}{c_sT} \qquad \ldots(56)$$

As $D = L_{11}\mu_{ss}$ the relation between Soret coefficient and heat of transport is

$$S_T = \frac{Q^*}{c_s\mu_{ss}T} \qquad \ldots(57)$$

For dilute solutions

$$\mu_{ss} = \frac{\partial\mu_s}{\partial c_s} = \frac{\partial}{\partial c_s}(RT\ lnc_s) = \frac{RT}{c_s} \qquad \text{...(58)}$$

Or $\qquad c_s\mu_{ss} = RT \qquad \ldots(59)$

For the ideal case, the Soret coefficient is

$$S_T = \frac{Q^*}{RT^2} \qquad \ldots(60)$$

Hence, the constancy of the Soret coefficient S_T implies a constant heat of transfer Q^*.

4. Summary

➢ Electrokinetic phenomenon are due to the coupling between the electric current and matter flow, i.e. such processes have coupled influence of multiple types of forces or potentials (electrical, pressure, gravity etc.) on the transport behavior of multicomponent system

➢ Entropy production is given by:–

$$d_{in}S = \frac{1}{T}\sum_i \tilde{A}_i d\xi_i = -\frac{1}{T}\sum_i \tilde{A}_i dn_i^I$$

➢ The four electrokinetic effects i.e. streaming potential, electro osmosis, the electro-osmotic pressure and streaming current as follows:

- **Streaming potential (SP)** $\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = -\frac{L_{12}}{L_{11}}$
- **Electro osmosis (EO)** $\left(\frac{J}{I}\right)_{\Delta P=0} = \frac{L_{21}}{L_{11}}$
- **Electro Osmotic pressure (EOP)** $\left(\frac{\Delta P}{\Delta\phi}\right)_{J=0} = \frac{-L_{21}}{L_{22}}$
- **Streaming Current (SC)** $\left(\frac{I}{J}\right)_{\Delta\phi=0} = \frac{L_{12}}{L_{22}}$

➢ There are two types of fluxes in system of a dilute solution taking the solvent as a frame of reference. These fluxes are:–

- ✓ Heat flux J_{hf}
- ✓ Flux of solute J_2

➢ **Relationship between q_2 and S_T**

$$S_T = -\frac{q_2}{RT^2}$$

Where q_2 is the heat transport at temperature T (in kelvins) and S_T is the Soret coefficient.

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TABLE OF CONTENTS

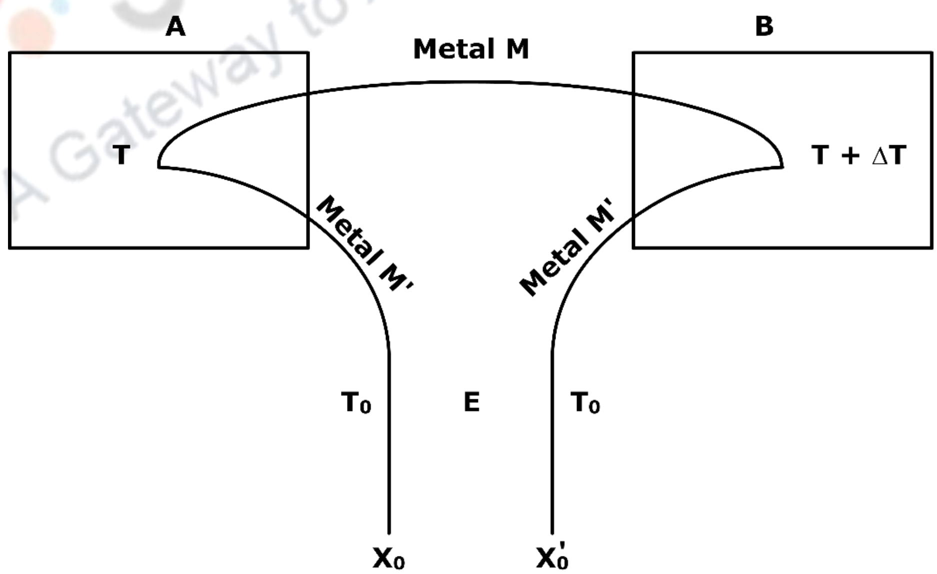
1. Learning Outcomes

After studying this module you shall be able to:

- Learn about various thermoelectric phenomenon
- Derive equation of thermoelectricity or Kelvin equation
- Compare Seebeck effect and Peltier effect
- Know the applications of irreversible thermodynamics in biological system

2. Thermoelectric Phenomenon

Thermoelectric phenomenon include the effects which arise when the junctions of two metals of thermocouple are kept at two different temperatures. Suppose a thermocouple consisting of two metals M and M' whose junctions in electrical contact are kept at temperatures T and $T + \Delta T$ (as depicted). Because of this temperature difference at the two junctions, potential and thermal gradients are developed and heat and electric charge will flow.



Now the thermoelectric phenomenon will be discussed in detail.

3. Types of thermoelectric phenomenon

There are number of thermoelectric effects but we will consider only three effects in details.

- Seebeck effect
- Peltier Effect
- Thomson effect

3.1 Seebeck Effect

In Seebeck effect, one junction of a bimetallic couple is heated and other junction is cooled so that an electromotive force is generated in the circuit i.e. e.m.f. is developed between the ends of junctions of two metals because of the temperature gradient at the two metal junction. In this effect e.m.f. between junctions A and B is measured when no current is flowing at these points. Potentiometrically, the e.m.f. is measured at the terminals X_0 and X'_0. These terminals are at same temperature to avoid thermoelectric emfs inside the measuring system.

Thus, EMF E, can be written as

$$E = -\int_{X_0}^{X'_0} \left(\frac{d\phi}{dx}\right)_{I=0} dx \qquad ....(1)$$

where ϕ is the electric potential.

The thermoelectric power is derivative of electric potential w.r.t. temperature and is given by

$$\frac{dE}{dt} = -\frac{d\phi}{dX}\cdot\frac{dX}{dt} = -\frac{d\phi}{dt} \qquad ....(2)$$

3.2 Peltier Effect

In 1834, Peltier found that when an electric current passes through bimetallic circuit, then absorption of heat takes place at one junction and liberation of heat at another junction. For maintaining constant temperature, the rate at which heat must be supplied to or removed from the junctions is proportional to the current and reverses sign when the direction of the current is reversed. Thus, absorption or liberation of heat depends upon the direction of current flow. In this effect, two junctions are kept at the same temperature and current I passes through wire. Thus, some amount of heat q_H is absorbed at one junction and some amount of $-q_H$ is released at other junction. The heat flow per unit current at constant temperature is called Peltier heat Π i.e.

$$\Pi = \frac{\text{heat added or removed}}{I} \quad \text{.....(3)}$$

Or we can write it as

$$\Pi = \left(\frac{q_H}{I}\right)_{dT} = 0 \quad \text{.....(4)}$$

This Peltier heat Π is dependent on temperature and if the junctions are held at different temperature then there will be a net influx or efflux of heat from or to the surroundings.

In this case two irreversible effects are observed. These are

- Flow of heat due to temperature gradient
- Flow of current due to potential gradient.

Then the rate of entropy production or dissipation function is given by

$$T\frac{d_{in}S}{dt} = T\sigma = q_H\left(-\frac{1}{T}\cdot\frac{dT}{dX}\right) + I\left(-\frac{d\phi}{dX}\right) \quad \text{.....(5)}$$

where q_H and I are the flows and terms within brackets are corresponding forces.

The relevant phenomenological equations are given by

$$q_H = L_{11}\left(-\frac{1}{T} \cdot \frac{dT}{dX}\right) + L_{12}\left(-\frac{d\phi}{dX}\right) \qquad \text{.....(6)}$$

$$I = L_{21}\left(-\frac{1}{T} \cdot \frac{dT}{dX}\right) + L_{22}\left(-\frac{d\phi}{dX}\right) \qquad \text{.....(7)}$$

In the above equation, the term $\left(-\frac{1}{T} \cdot \frac{dT}{dX}\right) = -\frac{\text{grad } T}{T}$

and $$-\frac{d\phi}{dX} = -\text{grad } \phi \qquad \text{.....(8)}$$

Now, as in Seebeck experiment current flow I = 0

then from equation (7) the following expression is obtained

$$\frac{-\left(\frac{d\phi}{dX}\right)}{-\left(\frac{1}{T}\frac{dT}{dX}\right)} = -\frac{L_{21}}{L_{22}} \qquad \text{.....(9)}$$

or $$-\left(\frac{d\phi}{dT}\right)_{I=0} = \frac{dE}{dT} = \frac{L_{21}}{L_{22}}\left(\frac{1}{T}\right) \qquad \text{.....(10)}$$

Using dT = 0, the Peltier heat expression becomes

$$\Pi = \left(\frac{q_H}{I}\right)_{dT=0} = \frac{L_{21}}{L_{22}} \qquad \text{.....(11)}$$

or $$\frac{\Pi}{(dE/dT)} = T\frac{L_{12}}{L_{21}} \qquad \text{.....(12)}$$

By using Onsager reciprocal relation $L_{12} = L_{21}$, above expression becomes

$$\Pi = T\left(\frac{dE}{dT}\right) \qquad \text{.....(13)}$$

The above equation is equation for thermoelectricity and is referred as known **Kelvin Equation.**

3.3 Thomson effect

The Thomson effect was predicted by Lord Kelvin in 1851. This effect describes heating and cooling of a current-carrying conductor with a temperature gradient.

Let the current density J passes through the homogeneous conductor, then the Thomson effect predicts the rate of heat production per unit volume i.e. $\frac{dq}{dt}$

$$\frac{\mathrm{dq}}{\mathrm{dt}} = -\kappa\,\mathrm{J}\cdot\Delta\mathrm{T}$$

Where κ is the Thomson coefficient and ΔT is the temperature gradient. Thomson effect takes place in the steady state system rather than equilibrium system. But when the direction of flow of current is reversed then the direction of Thomson heat flow is also reversed.

Comparison between Seebeck , Peltier and Thomson effect

CAUSE	EFFECT	MANIFESTATION
Temperature gradient at the junction of two metals	Seebeck (1821)	Development of EMF between the ends of junctions of the two metals
Passage of current from an external source through a circuit consisting of two different metals	Peltier (1834)	Heat absorption or liberation depending upon the direction of current flow
Maintaining a temperature gradient in a wire of homogeneous material	Thomson (1854)	Heat must be supplied to or extracted from the wire to maintain a temperature

through which current flows		gradient (Thomson heat)

4. Irreversible thermodynamics for biological system and coupled reactions

Biological systems are the open systems i.e. both matter and energy are exchanged with the environment. The growth of living organism or cell is characterized by transitions resulting in greater order and thus decrease of entropy from the initial state. For an isolated system, entropy of the system increases due to spontaneous change and hence resulting in increase of disorder. Thus, if biological system is treated as an isolated system instead of open system, then basic principles of thermodynamics are violated. Global behavior of living organisms can be better understood by theory of non-equilibrium stationary states as it has also been suggested by Prigogine. The evolution of living organism up to the stationary state may be considered as taking place under a certain number of constraints determined by the outside world, constraints such as the concentrations of some substances in the outside world which are transformed inside the living organisms. The stationary state can be regarded as the state of minimum entropy production per unit time regardless of the nature of the constant parameters. In a biological system, mainly process of metabolism contribute to the entropy production $\frac{d_i s}{dt}$ whereas the assimilated food is degraded into simple substances such as CO_2 which is accompanied by liberation of energy. As the organism grows, the total rate of entropy produced is negative although $\frac{d_i s}{dt}$ is positive but$d_e s/dt$ is negative and greater than $\frac{d_i s}{dt}$. This reduction in entropy indicates greater order (or organization) in the organisms. During the growth of the organism, it is subjected to several fixed constraints exerted by the outside world, so that the maturation of organism is accompanied by decrease in entropy (when steady state or stationary state of the biological system is reached, then the total rate of entropy production i.e. $\frac{ds}{dt} = 0$ as at stationary state $\frac{d_i s}{dt} = \frac{d_e s}{dt}$) The system remains stable to external perturbations in the steady state. In the steady state, a system loses minimum amount of free energy and it is most economical in terms of energetic stand point. Thus it states that physical principal behind the evolution of phenomenon of life is the concept of least dissipation of energy. But the living systems are equipped with the series of regulating mechanism that maintain the steady state and bring organism back to its unperturbed condition similar to the action of the restoring force coming into play in any fluctuation from stationary state in a physical system.

5. Summary

- Thermoelectric phenomenon include the effects which arise when the junctions of two metals of thermocouple are kept at two different temperatures.
- Seebeck effects, Peltier effects and Thomson effect are the types of thermoelectric effects.
- In Seebeck effect e.m.f. is measured between junction of thermocouple when no current is flowing through it while in Peltier effect e.m.f. is measured when the current I is flowing through it.
- Emf is written as

$$E = -\int_{x_0}^{x'_0} \left(\frac{d\phi}{dx}\right)_{I=0} dx$$

- Peltier heat Π is given as

$$\Pi = \frac{\text{heat added or removed}}{I}$$

$$\text{or} \quad \Pi = \left(\frac{q_H}{I}\right)_{dT} = 0$$