CHAPTER 2

Thermodynamics – I

❖ Brief Resume of First and Second Law of Thermodynamics

There are four laws of thermodynamics that define the fundamental physical quantities like temperature, energy, and entropy that characterize thermodynamic systems at thermal equilibrium. These laws describe how these quantities behave under different conditions and rule out the possibility of some phenomena the perpetual motion. The zeroth law of thermodynamics states that If two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other; therefore, this law helps to define the concept of temperature. In this section, we will discuss the elementary ideas and mutual correlation between the first and second laws of thermodynamics.

➢ *First Law of Thermodynamics*

The first law of thermodynamics states that the energy can neither be created nor destroyed, but can be converted from one form to another.

The first law of thermodynamics is obtained on the experimental basis. In other words, we can say that the energy of an isolated system is always constant, which means that whenever some energy disappears from the system, an equal amount of energy in some other form is also produced. In 1847, Helmholtz explained this situation in his famous words, “it is impossible to construct a perpetual machine”. The term perpetual machine refers to a device that can work continuously without any energy consumption. Furthermore, we all know that heat is always produced whenever some mechanical work is done. These correlations were studied by Joule (1840 – 1880); and he found that mechanical work is directly proportional to the heat produced. Mathematically, we can say that

$$W \propto Q \quad or\ W = JQ \tag{1}$$

Where J represents the proportionality constant and is called as “Joule’s mechanical equivalent of heat”. If Q = 1, W = J; making J as the amount of mechanical work required to produce one calorie of heat. The experimental value for J was found to be 4.184 joules, which is a very popular relation (1 calorie = 4.184 joule). The first law of thermodynamics can also be deduced from the equivalence of heat and work. Suppose there is now an equivalence between the work and heat; and let Q heat is converted into work. Now when the same amount of work is done to produce the heat Q'; considering $Q \neq Q'$, we can say that Q is either greater or less than Q'. This would eventually mean that a certain amount of energy has been destroyed or created in this process, which is against the first law of thermodynamics.

The mathematical formulation of the first law thermodynamics can be obtained from the increase in the internal energy of the system. The internal energy of the system can be increased in two ways; one is doing work on the system, and the second one involves the supply of heat. Suppose that the initial internal energy of the system is E_1, after supplying heat q and doing work w on the system, the final amount of internal energy can be formulated as:

$$E_2 = E_1 + q + w \tag{2}$$

$$E_2 - E_1 = q + w \tag{3}$$

$$\Delta E = q + w \tag{4}$$

$$q = \Delta E - w \tag{5}$$

If the work is done by the system, putting $w = -P\Delta V$ in equation (5), we get

$$q = \Delta E - (-P\Delta V\,) \tag{6}$$

$$q = \Delta E + P\Delta V \tag{7}$$

The physical significance of the equation (7) is that heat absorbed by a given system is converted work done by the system and to raise its internal energy.

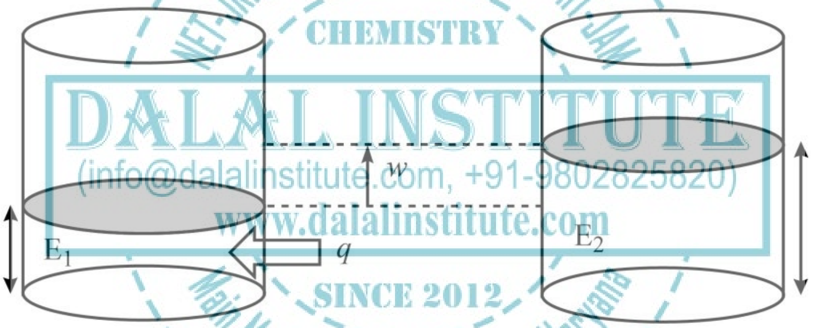

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Figure 1. The pictorial representation of the first law of thermodynamics.

It is also worthy to note that the general form of the first law of thermodynamics is applicable only in the case of chemical thermodynamics or physical processes. In 1905, Albert Einstein showed that energy and mass are just the faces of the coin, and can be transformed within each other. In other words, his findings showed that the mass can be converted into energy and the energy can back be converted into mass. Mathematically, the formulation is

$$E = mc^2 \tag{8}$$

Where m is the mass and c is the velocity of light. Since the velocity of light is a very large quantity (so the square), even the small disappearance of mass would generate a huge amount of energy. Such observations are pretty common in case of nuclear reactions and can be neglected here. Therefore, in a broad sense, it is the "law of energy-mass conservation".

➢ *Second Law of Thermodynamics*

The second law of thermodynamics states that it is impossible to convert the heat completely into work without leaving some effect elsewhere.

The second law of thermodynamics is actually a rational solution to the limitations of the first law. For instance, the first law talks about the exact equivalence between heat and work, but it is quite far from reality. In 1824, a French scientist Sadi Carnot showed that for every heat engine there is an upper limit to the efficiency of conversion of heat to work. In order to illustrate Carnot's conclusion, consider a locomotive engine that is supplied with a certain amount of heat; however, all of that heat will not be used to move the train but a part of it will always be consumed in some other processes like overcoming the friction. Let q_2 be the heat absorbed by the heat engine at temperature T_2, and w is the amount of the work done by the system; while q_1 is the heat returned to the sink at temperature T_1, then the Carnot's formulation can be given as:

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \tag{9}$$

Where η is the efficiency of the heat engine and is always less than one. Ideally, $\eta = 1$, which means that such a heat engine would convert 100% of the heat absorbed into work.

One more limitation of the first law is that it does not tell about the feasibility of the process, like whether the heat can flow from cold terminal to the hot one or not. It simply talks if the heat gained or heat lost but not the direction of the process. The second law of thermodynamics states that all the spontaneous processes are thermodynamically irreversible. The word "spontaneous" simply means a process that occurs by itself and external drive is required. In other words, we can also say that heat cannot flow from a cold body to hot, the water cannot uphill without any external drive.

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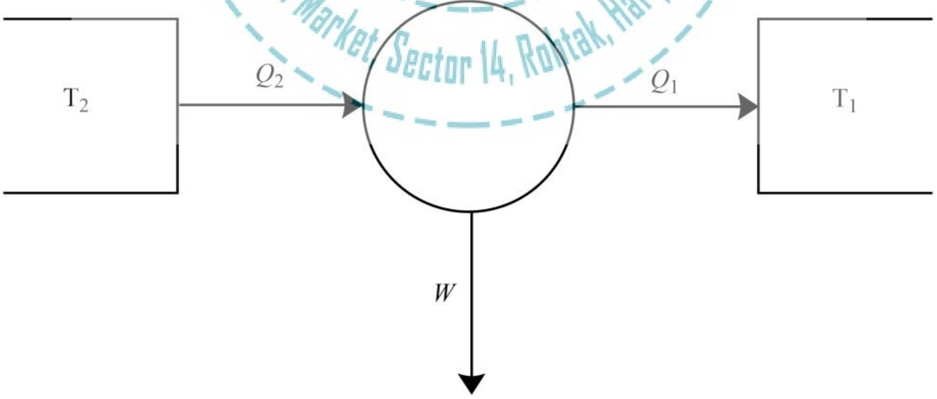

Figure 2. The pictorial representation of the second law of thermodynamics.

The 2nd law of thermodynamics also states that the total entropy of an isolated system can never decline with time; in other words, combined entropy of a system and surroundings remains constant in ideal cases where the system is undergoing a reversible process. In all processes, including spontaneous processes, that occur, the total entropy of the system and surroundings increases and the process is irreversible in the thermodynamic frame. The entropy-increase accounts for the irreversibility of all the natural processes, and the asymmetry between the past and the future. Overall, the 2nd law of thermodynamics can be labeled as an empirical finding that was accepted as a truism of thermodynamic theory. The microscopic origin of the law can be explained by statistical mechanics.

❖ Entropy Changes in Reversible and Irreversible Processes

In order to understand the entropy change in reversible and irreversible processes, we need to understand the concept of entropy first. For a Carnot heat engine working at T_1 and T_2, it has been observed that the heat absorbed (q_2) and heat returned (q_1) are related as given below.

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \tag{10}$$

or

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \tag{11}$$

or

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} \tag{12}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \tag{13}$$

$$\frac{q}{T} = constant \tag{14}$$

Therefore, we can say that for any particular system, the ratio of heat absorbed or lost isothermally and reversibly to the absolute temperature at which this takes place is a constant parameter. If we consider q_1 as the heat absorbed at T_1, equation (13) becomes

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1} \tag{15}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0 \tag{16}$$

or

$$\sum \frac{q}{T} = 0 \tag{17}$$

Consider a reversible cyclic process, consists of many Carnot cycles. In going from point *A* to *B* and then back *A*, all the closed paths cancel each other that results in parent path *ABA*.

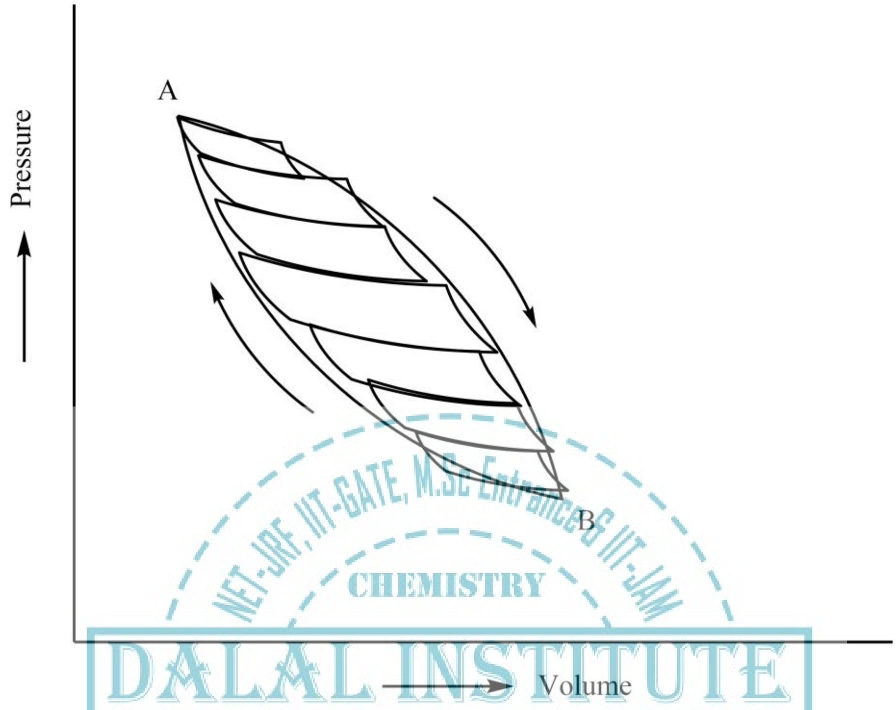

Figure 3. A cyclic process made of many Carnot cycles.

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For each cycle, we have equation (17), for an infinite number of cycles

$$\sum \frac{\delta q}{T} = 0 \tag{18}$$

Where δ*q* is the extremely small amount of heat absorbed at temperature *T* during the course of an isothermal and reversible process. Moreover, the total entropy change of the cyclic process *ABA* can be fragmented into two components as:

$$\sum \frac{\delta q}{T} = \sum_{A\to B} \frac{\delta q}{T} + \sum_{B\to A} \frac{\delta q}{T} = 0 \tag{19}$$

$$\sum_{A\to B} \frac{\delta q}{T} = -\sum_{B\to A} \frac{\delta q}{T} \tag{20}$$

or

$$\left(\frac{q}{T}\right)_{A\to B} = -\left(\frac{q}{T}\right)_{B\to A} \tag{21}$$

The physical significance of the equation (21) is that the value of q/T for the path $A{\rightarrow}B$ is the same as the path $B{\rightarrow}A$; which eventually means that the quantity q/T is actually a state function. This quantity i.e. q/T is called as entropy, and is generally labeled as S. If S_A and S_B are the entropies at point A and B, respectively; then we can say that

$$S_A - S_B = \frac{q}{T} \tag{22}$$

$$\Delta S = \frac{q}{T} \tag{23}$$

Hence, the entropy change may be defined as the amount of the heat absorbed isothermally and reversibly divided by the temperature at which the heat is absorbed. Being a state function, the change in entropy always depends upon the initial and final state and not upon the path followed. Moreover, since the heat is absorbed reversibly, it is better to use q_{rev} in equation (23) instead of simply q, therefore

$$\Delta S = \frac{q_{rev}}{T} \tag{24}$$

For an extremely minute change, the above equation becomes

$$dS = \frac{q_{rev}}{T} \tag{25}$$

The entropy is an extensive property measured in joule per Kelvin per mole ($\mathrm{JK^{-1}mol^{-1}}$). The most important significance of entropy is that it can be used to measure the randomness in the system.

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- ***Entropy Changes in Reversible Processes***

Suppose that the heat absorbed by the system and heat lost by the surrounding are under completely reversible conditions. In other words, q_{rev} is the heat absorbed and lost by the surrounding at temperature T, then we can say that the entropy change in the system will be given by the following relation.

$$\Delta S_{system} = \frac{q_{rev}}{T} \tag{26}$$

Similarly, the entropy change in the surrounding will be

$$\Delta S_{sorrounding} = -\frac{q_{rev}}{T} \tag{27}$$

Therefore, the total entropy change will be

$$\Delta S_{system} + \Delta S_{sorrounding} = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \tag{28}$$

Hence, we can conclude that the entropy change in an isolated system is always zero i.e. the sum of entropy change in system and entropy change in the surrounding is zero under reversible conditions.

➢ *Entropy Changes in Irreversible Processes*

Every reversible process becomes irreversible even if only one part of it becomes irreversible. To understand this, let us suppose that q_{irrev} heat lost by the surrounding. Although this heat would be absorbed by the system, the entropy of the system depends upon the heat absorbed reversibly. Therefore, entropy change of the system at an absolute temperature T will be

$$\Delta S_{system} = \frac{q_{rev}}{T} \tag{29}$$

Similarly, the entropy change of the surrounding will be

$$\Delta S_{sorrounding} = -\frac{q_{irrev}}{T} \tag{30}$$

The total entropy of the isolated system (system + surrounding) will be

$$\Delta S_{system} + \Delta S_{sorrounding} = \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \tag{31}$$

Furthermore, as we know that the $w_{rev} > w_{irrev}$, and internal energy is a state function that is independent of whether the process is reversible or irreversible. Mathematically, it is

$$\Delta E = q_{rev} - w_{rev} = q_{irrev} - w_{irrev} \tag{32}$$

we can conclude that,

$$q_{rev} > q_{irrev} \tag{33}$$

$$\frac{q_{rev}}{T} > \frac{q_{irrev}}{T} \tag{34}$$

or

$$\frac{q_{rev}}{T} + \frac{q_{irrev}}{T} > 0 \tag{35}$$

After comparing equation (35) with equation (31), we get

$$\Delta S_{system} + \Delta S_{sorrounding} > 0 \tag{36}$$

The physical interpretation of the above equation lies in the fact that all irreversible processes occur via a net increase in entropy. In other words, the total entropy change of an isolated system in any irreversible process is always greater than zero. The results of equation (28) and equation (36) can be combined to give a more generalized form as:

$$\Delta S_{system} + \Delta S_{sorrounding} \geq 0 \tag{37}$$

Where the sign of '=' stands from reversible and '>' stands for irreversible phenomena, respectively.

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The entropy change in the irreversible process like the flow of heat from the hot end (T_2) to cold end (T_1) can be calculated using the following relation.

$$\Delta S_{total} = -\frac{q_{rev}}{T_2} + \frac{q_{rev}}{T_1} = q_{rev}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{38}$$

Where q_{rev} is the amount of heat transferred from T_2 to T_1.

Furthermore, the Clausius inequality can also be proved from equation (36) which governs that all the irreversible processes are accompanied by a net increase in the entropy.

$$\Delta S_{system} > \Delta S_{sorrounding} \tag{39}$$

This can be illustrated with the help of the following examples.

i) Irreversible isothermal expansion of an ideal gas: Suppose an ideal gas expanding isothermally and irreversibly against vacuum. The condition isothermal means $\Delta T = 0$, which in turn implies that $\Delta U = 0$. Hence from the first law of thermodynamics, we have $dq = 0$ i.e. no heat is transferred from, or to the surrounding giving $dS_{\text{surrounding}} = 0$.

However, since the $dS_{\text{system}} = R \ln (V_2/V_1)$. Since V_2 is definitely greater than V_1, therefore

$$dS_{total} = dS_{system} + dS_{sorrounding} = dS_{system} + 0 \geq 0 \tag{40}$$

ii) Heat flow from hot to the cold end: Suppose dq is the amount of heat transferred from temperature T_2 to T_1. The entropy change at the source will be

$$dS_{source} = -\frac{dq}{T_2} \tag{41}$$

Similarly, the entropy change at the sink will be

$$dS_{sink} = \frac{dq}{T_1} \tag{42}$$

The total entropy change of the system can be calculated as

$$dS_{total} = dS_{source} + dS_{sink} = \frac{dq}{T_1} - \frac{dq}{T_2} \tag{43}$$

or

$$dS_{total} = dq\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{44}$$

Now because the source is always at a higher temperature than sink ($T_2 > T_1$), dS_{total} will be positive for sure, proving that transfer of heat from a hot body to the cold body occurs via a net entropy increment.

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❖ Variation of Entropy with Temperature, Pressure and Volume

Consider one mole of ideal gas filled in a chamber fitted with a weightless and frictionless piston. If the system absorbs a very small amount of heat δq_{rev} isothermally and reversibly at temperature T, the total entropy change in the system can be given by the following relation.

$$dS = \frac{\delta q_{rev}}{T} \tag{45}$$

Also, from the first law of thermodynamics

$$\delta q = dE - \delta w \tag{46}$$

The above equation may be written in the following form if the process is carried out under reversible conditions.

$$\delta q_{rev} = dE - \delta w \tag{47}$$

After putting the value of work of expansion ($-PdV$), the equation (47) becomes

$$\delta q_{rev} = dE - (-PdV) = dE + PdV \tag{48}$$

Using equation (48) in equation (45), we get

$$dS = \frac{dE + PdV}{T} \tag{49}$$

or

$$TdS = dE + PdV \tag{50}$$

Moreover, for one mole of an ideal gas, the value of heat capacity at constant volume (C_v) is

$$C_v = \frac{dE}{dT} \tag{51}$$

$$dE = C_v dT \tag{52}$$

Also

$$PV = RT \tag{53}$$

$$P = \frac{RT}{V} \tag{54}$$

Where R is the gas constant; while P, T and V are the pressure, temperature and volume, respectively. Now putting the value of equation (52) and (54) in equation (50), we get

$$TdS = C_v dT + \frac{RT}{V} dV \tag{55}$$

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V} \tag{56}$$

Now consider that the initial state (T_1, V_1) is converted to the final state (T_2, V_2), the total entropy will be calculated by the following relation

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_v \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \tag{57}$$

$$\int_{S_1}^{S_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} \tag{58}$$

or

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{59}$$

Since, from the ideal gas equation, the following also true for the initial and final state of the system.

$$P_1V_1 = RT_1 \tag{60}$$

$$P_2V_2 = RT_2 \tag{61}$$

Dividing equation (61) by equation (60), we get

$$\frac{P_2V_2}{P_1V_1} = \frac{RT_2}{RT_1} \tag{62}$$

or

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1} \tag{63}$$

After putting the value of (63) in equation (59), we get

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1T_2}{P_2T_1} \tag{64}$$

As we know that $C_p - C_v = R$; therefore, after putting $C_v = C_p - R$ in equation (64), we get

$$\Delta S = (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1T_2}{P_2T_1} \tag{65}$$

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$$= C_p \ln\frac{T_2}{T_1} - R\ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2} + R\ln\frac{T_2}{T_1} \tag{66}$$

or

$$\Delta S = C_p \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2} \tag{67}$$

The equation (59) and equation (67) formulate the variation of entropy with temperature-volume and temperature-pressure, respectively.

The variation of entropy with temperature, pressure or volume in isothermal, isobaric and isochoric processes is discussed below.

1. Entropy change in isothermal process: Provided that the temperature of the system is kept constant ($T_2 = T_1 = T$), equation (59) and (67) are reduced to the following.

$$\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2} \tag{68}$$

2. Entropy change in isochoric process: Provided that the volume of the system is kept constant ($V_2 = V_1 = V$), equation (59) is reduced to the following.

$$\Delta S = C_v \ln\frac{T_2}{T_1} \tag{69}$$

3. Entropy change in isobaric process: Provided that the pressure of the system is kept constant ($P_2 = P_1 = P$), equation (67) is reduced to the following.

$$\Delta S = C_p \ln\frac{T_2}{T_1} \tag{70}$$

It is also worthy to note that if this reversible expansion takes place adiabatically, then $q_{rev} = 0$, and therefore, the change entropy will also be zero.

❖ Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction

The entropy change during the course of a process can be used to rationalize the unavailable energy as well as its spontaneity or feasibility. In this section, we will first discuss the entropy concept as a measure of unavailable energy and then we will study the spontaneity of a process in terms of entropy change.

➢ *Entropy Concept as a Measure of Unavailable Energy*

In order to understand the connection between entropy and unavailable energy, consider a heat source at temperature T_2 placed in an atmosphere or surrounding at temperature T_0. The surrounding plays the role of heat sink here. Now if Q is the heat transferred from the source to a Carnot heat engine working between T_2 and T_0, then from Carnot's theorem, we have

$$\frac{W_{max,T_2,T_0}}{Q} = \frac{T_2 - T_0}{T_2} \tag{71}$$

$$W_{max,T_2,T_0} = Q\left(1 - \frac{T_0}{T_2}\right) \tag{72}$$

Where W_{max,T_2,T_0} is the maximum work that can be obtained from a heat engine working between T_2 and T_0 temperatures. It is worthy to note that only a part of the heat transferred can be turned into work i.e. available to be used as work.

Now suppose that the same amount of heat is first transferred directly from the source at T_2 to another source at $T_1 < T_2$. In other words, the heat Q is now first transferred from hot source to a cold source without any Carnot bridging. Now the maximum work that can be obtained from a heat engine working between T_1 and T_0 temperatures will be

$$W_{max,T_1,T_0} = Q\left(1 - \frac{T_0}{T_1}\right) \tag{73}$$

Where W_{max,T_1,T_0} is the maximum work that can be obtained after the direct heat transfer, since the heat engine is now working between T_1 and T_0 temperatures. Now before the irreversible heat transfer ($T_2 \rightarrow T_1$), the magnitude of energy that could have been transformed into work is:

$$E_{unavailable} = \left(W_{max,T_2,T_0}\right) - \left(W_{max,T_1,T_0}\right) \tag{74}$$

$$= \left[Q\left(1 - \frac{T_0}{T_2}\right)\right] - \left[Q\left(1 - \frac{T_0}{T_1}\right)\right] \tag{75}$$

$$= Q\left[\left(1 - \frac{T_0}{T_2}\right) - \left(1 - \frac{T_0}{T_1}\right)\right] \tag{76}$$

$$= Q\left(\frac{T_0}{T_1} - \frac{T_0}{T_2}\right) \tag{77}$$

$$= T_0\left(\frac{Q}{T_1} - \frac{Q}{T_2}\right) \tag{78}$$

Since $-Q/T_2$ and Q/T_1 are the entropy loss and gain of sources at T_2 and T_1, respectively; the equation (78) reduces to the following.

$$E_{unavailable} = T_0\left(\Delta S_{source\ at\ T_1} + \Delta S_{source\ at\ T_2}\right) \tag{79}$$

$$= T_0\, \Delta S_{irreversible\ heat\ transfer} \tag{80}$$

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Where $E_{unavailable}$ is lost work or the energy which is no longer available to do any useful work.

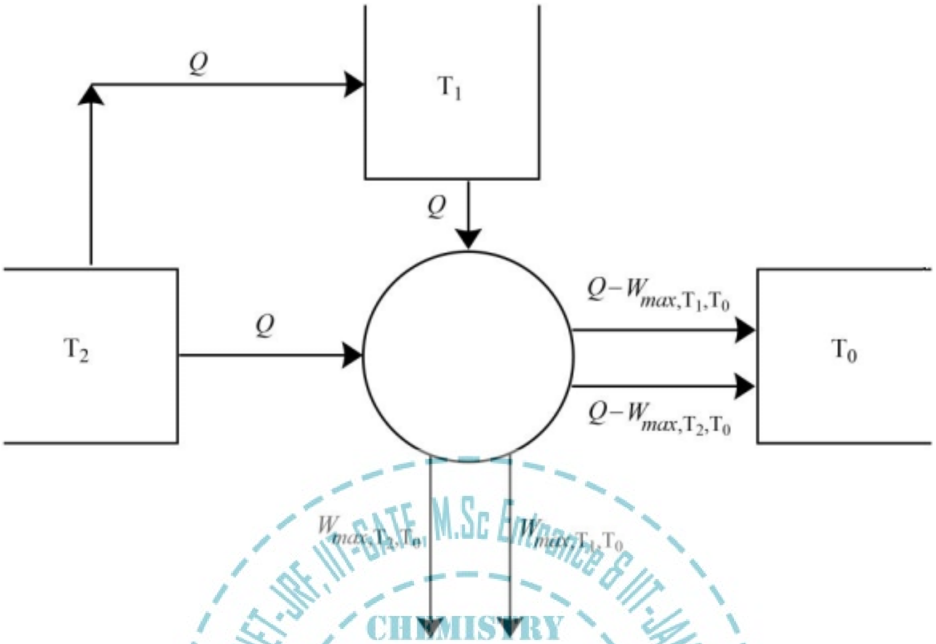

Figure 4. The pictorial representation of the entropy–unavailable-energy.

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The physical significance of equation (80) can also be demonstrated using a live example. Let us consider a Carnot engine working between 800K and 200K is supplied with a heat (Q) of 5000 joules. The efficiency of such an engine will be

$$\eta = \frac{T_2 - T_0}{T_2} = \frac{800 - 200}{800} = 0.75 \tag{81}$$

The maximum work obtained will be

$$W = \eta Q = 0.75 \times 5000\, J = 3750 \tag{82}$$

Now if this 5000 joules of heat is first transferred to the reservoir at 500K, and then it is fed to a Carnot engine working obviously between "500K" and 200K. The efficiency of such an engine will be

$$\eta = \frac{T_1 - T_0}{T_1} = \frac{500 - 200}{500} = 0.6 \tag{83}$$

The maximum work obtained will be

$$W = \eta Q = 0.6 \times 5000\, J = 3000 \tag{84}$$

Comparing the results of equation (82) and (84), we can say that there is 750 J less work from the same heat transfer in the second process.

➢ *Entropy Concept as the Criteria for the Spontaneity of Reaction*

The second law of thermodynamics states that all the spontaneous processes are thermodynamically irreversible, and accompanied by a net increase in entropy. The entropy change for a reversible process is,

$$\Delta S_{system} + \Delta S_{sorrounding} = 0 \tag{85}$$

And the entropy change for a spontaneous or irreversible process is

$$\Delta S_{system} + \Delta S_{sorrounding} > 0 \tag{86}$$

The results of equation (85) and equation (86) can be combined to give a more generalized form as:

$$\Delta S_{system} + \Delta S_{sorrounding} \geq 0 \tag{87}$$

Where the sign of '=' stands from reversible and '>' stands for irreversible or spontaneous reaction, respectively.

Nevertheless, the criteria from equation (87) is not very much practical as ΔS_{system} and $\Delta S_{sorrounding}$ are not easy to determine. Therefore, some other criteria must be deduced which requires only the knowledge of the change in some simple thermodynamic parameters. In order to do so, write down the equation (87) for infinitesimally small changes as given below.

$$dS_{system} + dS_{sorrounding} \geq 0 \tag{88}$$

If δq is the heat lost by the surrounding reversibly and isothermally at temperature T, then we can say that

$$dS_{sorrounding} = -\frac{q_{rev}}{T} \tag{89}$$

Also, from the first law of thermodynamics, we have

$$\delta q_{rev} = dU + PdV \tag{90}$$

After putting the value from equation (90) in equation (89), we have

$$dS_{sorrounding} = -\frac{dU + PdV}{T} \tag{91}$$

Now putting the value of $dS_{sorrounding}$ from equation (91) into equation (88), we get

$$dS_{system} - \frac{dU + PdV}{T} \geq 0 \tag{92}$$

$$TdS_{system} - dU - PdV \geq 0 \tag{93}$$

$$TdS \geq dU + PdV \tag{94}$$

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Where $dS_{system} = dS$ i.e. change in the entropy of the system. For a spontaneous or irreversible process TdS must be greater the sum of internal energy change and pressure-volume work.

However, the above relation is reduced to the following if the internal energy and volume of the system are kept constant i.e. $dU = 0$ and $dV = 0$.

$$(TdS)_{U,V} \geq 0 \tag{95}$$

or

$$(dS)_{U,V} \geq 0 \tag{96}$$

Here it is worthy to recall that the sign '=' is for reversible reactions whereas '>' condition is applicable to spontaneity or irreversibility of a reaction.

Besides, the spontaneity of equation (94) can also be written in the form of internal energy change,

$$dU \leq TdS - PdV \tag{97}$$

the above relation is reduced to the following if the internal energy and volume of the system are kept constant i.e. $dS = 0$ and $dV = 0$.

$$(dU)_{S,V} \leq 0 \tag{98}$$

Again it should be noted that the sign '=' is for reversible reactions whereas '<' condition is applicable to spontaneity or irreversibility of a reaction.

❖ Free Energy, Enthalpy Functions and Their Significance, Criteria for Spontaneity of a Process

The thermodynamic free energy and enthalpies are extremely useful concepts in the field of chemical thermodynamics. The decrease or increase in free energy is the maximum amount of work that a thermodynamic system can perform in a process at a constant temperature. The sign of thermodynamic free energy simply indicates whether a process is thermodynamically forbidden or feasible. The thermodynamic free energy is a state function, like internal energy and enthalpy. In this section, we will discuss the significance of enthalpy and free energy functions, and the corresponding spontaneity of a process.

➢ *Enthalpy or Heat Content*

As most of the reactions are carried out in open vessels where the atmospheric pressure remains the same, it must be very interesting to study the heat change that occurs during the course of a chemical reaction. The work-done by gas in the piston-fitted chamber against constant pressure (P) with ΔV volume change is

$$w = -P\Delta V \tag{99}$$

From the first law of thermodynamics, we know that

$$q = \Delta U - w \tag{100}$$

Where q is the heat absorbed and ΔU is the change in the internal energy of the system respectively. After putting the value of work of expansion from equation (99) in equation (100), we get

$$q_p = \Delta U - (-P\Delta V) \tag{101}$$

$$q_p = \Delta U + P\Delta V \tag{102}$$

The symbol q_p is used instead of q because the whole process is carried out at constant pressure. Now suppose that this heat absorbed increases the internal energy from U_1 to U_2 and volume from V_1 to V_2 i.e.

$$\Delta U = U_2 - U_1 \tag{103}$$

$$\Delta V = V_2 - V_1 \tag{104}$$

After putting the values from equation (103) and (104) into equation (102), we get

$$q_p = (U_2 - U_1) + P(V_2 - V_1) \tag{105}$$

or

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \tag{106}$$

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The quantity $U + PV$ is now defined as the enthalpy of the system; and since U, P and V all are state functions, the quantity $U + PV$ must also be a state function. Mathematically, the enthalpy can be shown as

$$H = U + PV \tag{107}$$

Therefore, if the enthalpy changes initial state H_1 to the final state H_2 at constant pressure, we have

$$H_1 = U_1 + PV_1 \tag{108}$$

$$H_2 = U_2 + PV_2 \tag{109}$$

After putting the values from equation (108) and (109) in equation (106), we get

$$q_p = H_2 - H_1 \tag{110}$$

$$q_p = \Delta H \tag{111}$$

Hence, we can conclude that the enthalpy change of a system is simply the amount of heat absorbed at constant pressure. Besides, if we compare equation (102) and equation (111), we have

$$\Delta H = \Delta U + P\Delta V \tag{112}$$

Therefore, the enthalpy change of a reaction may also be defined as the sum of its internal energy change and pressure-volume work done.

The physical significance of enthalpy: There is a certain amount of energy stored in every substance or material called internal energy. This energy comprises of many forms like kinetic, rotational, vibrational or inter-particle interactions. Moreover; like pressure, volume and internal energy; the enthalpy function is also an extensive property. Now recalling the expression of enthalpy again

$$H = U + PV \tag{113}$$

We can say that the enthalpy is nothing but the internal energy that is available for the conversion into heat; which is why the enthalpy is also called as "heat content". Furthermore, like internal energy, the heat content or enthalpy is also not obtainable absolutely. However, like some other thermodynamic quantities, the parameter that is needed in the various analysis is enthalpy change which can be derived experimentally.

Enthalpy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$H = U + PV \tag{114}$$

After differentiating the equation (114), we get

$$dH = dU + VdP + PdV \tag{115}$$

$$dH - VdP = dU + PdV \tag{116}$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \tag{117}$$

Now after putting the value of $dU + VdP$ from equation (116) in equation (117), we get

$$TdS \geq dH - VdP \tag{118}$$

or

$$dH \leq TdS + VdP \tag{119}$$

For a spontaneous or irreversible process dH must be less than the sum of multiplication of temperature and entropy change, and pressure-volume work.

However, the above relation is reduced to the following if the entropy and pressure of the system are kept constant i.e. $dS = 0$ and $dP = 0$.

$$(dH)_{S,P} \leq 0 \tag{120}$$

Here it is worthy to recall that the sign '=' is for reversible reactions whereas '<' condition is applicable to spontaneity or irreversibility of a reaction.

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➢ *Helmholtz Free Energy or Work Function*

The Helmholtz free energy is typically denoted by the symbol '*A*', which is derived from the German word "Arbeit" meaning work. The Helmholtz free energy can be defined mathematically as

$$A = U - TS \tag{121}$$

Where T, S and U are temperature, entropy, and internal energy, respectively. Moreover; like U, T and S; free energy *A* is also a state function. Since A is independent of its previous state, we can say that

$$A_1 = U_1 - TS_1 \tag{122}$$

$$A_2 = U_2 - TS_2 \tag{123}$$

Where the subscript 1 and 2 represent the initial and final state. The change in Helmholtz free energy in going from initial to final state can obtain by subtracting equation (122) from equation (123) as

$$A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1) \tag{124}$$

$$\Delta A = (U_2 - U_1) - T(S_2 - S_1) \tag{125}$$

$$\Delta A = \Delta U - T\Delta S \tag{126}$$

Where *ΔU* and *ΔS* are the change in internal energy and entropy, respectively. Therefore, the Helmholtz free energy change can be described as the difference of internal energy change and the multiplication of entropy change multiplied with the temperature at which the reaction is actually carried out.

The physical significance of Helmholtz free energy: From the definition of entropy change, we know that

$$\Delta S = \frac{q_{rev}}{T} \tag{127}$$

Also, from the first law of thermodynamics, for the work of expansion we have

$$\Delta U = q_{rev} - w_{max} \tag{128}$$

Putting the values of *ΔS* and *ΔU* from equation (127) and (128) in equation (126), we get

$$\Delta A = (q_{rev} - w_{max}) - T\left(\frac{q_{rev}}{T}\right) \tag{129}$$

$$= q_{rev} - w_{max} - q_{rev}$$

or

$$-\Delta A = w_{max} \tag{130}$$

Hence, the decrease in Helmholtz free energy at constant temperature is equal to the maximum work done by the system; that is why the Helmholtz free energy is also called as work function.

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Helmholtz free energy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$A = U - TS \tag{131}$$

After differentiating the equation (131), we get

$$dA = dU - TdS - SdT \tag{132}$$

$$TdS = dU - SdT - dA \tag{133}$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \tag{134}$$

Now after putting the value of TdS from equation (133) in equation (134), we get

$$dU - SdT - dA \geq dU + PdV \tag{135}$$

or

$$-SdT - dA \geq PdV \tag{136}$$

$$dA \leq -PdV - SdT \tag{137}$$

For a spontaneous or irreversible process, dA must be less than the negative sum of multiplication of pressure and volume change with the multiplication of entropy and temperature change.

However, the above relation is reduced to the following if the volume and temperature of the system are kept constant i.e. $dV = 0$ and $dT = 0$.

$$(dA)_{V,T} \leq 0 \tag{138}$$

Here it is worthy to recall that the sign '=' is for reversible reactions whereas '<' condition is applicable to spontaneity or irreversibility of a reaction.

- ***Gibbs Free Energy or Gibbs Function***

The Gibbs free energy is typically denoted by the symbol 'G', and can be defined mathematically as

$$G = H - TS \tag{139}$$

Where T, S and H are temperature, entropy, and enthalpy, respectively. Moreover; like H, T and S; the Gibbs free energy G is also a state function. Since G is independent of its previous state, we can say that

$$G_1 = H_1 - TS_1 \tag{140}$$

$$G_2 = H_2 - TS_2 \tag{141}$$

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Where the subscript 1 and 2 represent the initial and final state. The change in Gibbs free energy in going from initial to final state can obtain by subtracting equation (141) from equation (140) as

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1) \tag{142}$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1) \tag{143}$$

$$\Delta G = \Delta H - T\Delta S \tag{144}$$

Where ΔH and ΔS are the change in enthalpy and entropy, respectively. Therefore, the Gibbs free energy change can be described as the difference of enthalpy change and the multiplication of entropy change multiplied with the temperature at which the reaction is actually carried out.

The physical significance of Helmholtz free energy: From the definition of entropy change, we know that

$$\Delta S = \frac{q_{rev}}{T} \tag{145}$$

Also, at constant pressure, we have

$$\Delta H = \Delta U + P\Delta V \tag{146}$$

Putting the values of ΔS and ΔH from equation (145) and (146) in equation (144), we get

$$\Delta G = (\Delta U + P\Delta V) - T\left(\frac{q_{rev}}{T}\right) \tag{147}$$

$$= (\Delta U - q_{rev}) + P\Delta V \tag{148}$$

Also, from the first of thermodynamics, for the work of expansion we have

$$\Delta U - q_{rev} = -w_{max} \tag{149}$$

Now, after putting the value of equation (149) in equation (148), we get

$$\Delta G = -w_{max} + P\Delta V \tag{150}$$

$$-\Delta G = w_{max} - P\Delta V \tag{151}$$

Hence, the decrease in Gibbs free energy for the process occurring at constant pressure and constant temperature is equal to the "maximum net work" that can be obtained from the process. The term "maximum net work" refers to maximum work other than the work of expansion.

Gibbs free energy as the criteria for the spontaneity of reaction: The general expression for the enthalpy of a system is given below.

$$G = H - TS \tag{152}$$

Since $H = U + PV$, equation (152) takes the form

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$$G = U + PV - TS \tag{153}$$

After differentiating the equation (153), we get

$$dG = dU + PdV + VdP - TdS - SdT \tag{154}$$

$$TdS = dU + PdV + VdP - SdT - dG \tag{155}$$

Also as we know that, for the spontaneity of a process

$$TdS \geq dU + PdV \tag{156}$$

Now after putting the value of TdS from equation (155) in equation (156), we get

$$dU + PdV + VdP - SdT - dG \geq dU + PdV \tag{156}$$

or

$$VdP - SdT - dG \geq 0 \tag{157}$$

$$dG \leq VdP - SdT \tag{158}$$

For a spontaneous or irreversible process, dG must be less than the sum of negative multiplication of volume and pressure change with the multiplication of entropy and temperature change.

However, the above relation is reduced to the following if the pressure and temperature of the system are kept constant i.e. $dP = 0$ and $dT = 0$.

$$(dG)_{P,T} \leq 0 \tag{159}$$

Here it is worthy to recall that the sign ‘=’ is for reversible reactions whereas ‘<’ condition is applicable to spontaneity or irreversibility of a reaction.

❖ Partial Molar Quantities (Free Energy, Volume, Heat Concept)

So far we have discussed the variation of various thermodynamic properties with respect to temperature and pressure while the composition of the system was kept constant (closed system). In 1907, G.N. Lewis started the study of open systems i.e. the variation of various thermodynamic properties with respect to the composition of one or more components. In other words, he studied the behavior of a particular thermodynamic property of the system when a component is removed from or added to the system under consideration. Now since a variation like this is observable only for an extensive property, the general definition of partial molar properties can be given as given below.

A partial molar property may simply be defined as a thermodynamic quantity which indicates how an extensive property of a solution or mixture changes with the variation in the molar composition of the mixture at constant temperature and pressure.

Basically, it is the partial derivative of the extensive property with respect to the number of moles of the component under consideration. All extensive properties of a mixture have corresponding partial molar properties. In this section, we will discuss some very important partial molar quantities like partial molar free energy ($\overline{G_i}$), partial molar volume ($\overline{V_i}$) and partial molar enthalpy ($\overline{H_i}$).

➢ *Partial Molar Free Energy or Chemical Potential*

In order to derive the expression for partial molar free energy, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, the partial molar free energy depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$G = f(T, P, n_1, n_2, n_3 \dots) \tag{160}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar free energy as given below.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{161}$$

The first term on the right-hand side gives the change in the free energy with temperature at constant pressure and compositions; while the second term gives the change in the free energy with pressure at constant temperature and compositions. The terms afterward represent the variation in free energy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (161) takes the form

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{162}$$

Every term on the right-hand side of the equation (162) is partial molar free energy and is symbolized by a "bar" over it i.e.

$$(dG)_{T,P} = \overline{G_1}\, dn_1 + \overline{G_2}\, dn_2 + \overline{G_3}\, dn_3 \dots \tag{163}$$

For the *i*th component, we can say that

$$\overline{G_i} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_2,n_3\dots} \tag{164}$$

The equation (164) gives the general expression for "partial molar free energy" or the "chemical potential" of the *i*th species.

➢ *Partial Molar Volume*

In order to derive the expression for partial molar volume, consider a system that comprises of n types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$V = f(T, P, n_1, n_2, n_3 \ldots) \tag{165}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar volume as given below.

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_1,n_2\ldots} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_1,n_2\ldots} dP + \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \cdots \tag{166}$$

The first term on the right-hand side gives the change in the volume with the temperature at constant pressure and compositions; while the second term gives the change in the volume with pressure at constant temperature and compositions. The terms afterward represent the variation in volume with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (166) takes the form

$$(dV)_{T,P} = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} dn_2 + \left(\frac{\partial V}{\partial n_3}\right)_{T,P,n_1,n_2\ldots} dn_3 \ldots \tag{167}$$

Every term on the right-hand side of the equation (167) is partial molar volume and is symbolized by a “bar” over it i.e.

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} \tag{168}$$

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} \tag{169}$$

After putting the values from equations like (168 – 169) in equation (167), we get

$$(dV)_{T,P} = \overline{V_1}\, dn_1 + \overline{V_2}\, dn_2 + \overline{V_3}\, dn_3 \ldots \tag{170}$$

For the ith component, we can say that

$$\overline{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_2,n_3\ldots} \tag{171}$$

The equation (171) gives the general expression for the “partial molar volume” of the ith species.

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➢ ***Partial Molar Enthalpy or Partial Molar Heat Content***

In order to derive the expression for partial molar enthalpy, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, volume depends upon not only the temperature and pressure but also on the number of moles of different components, i.e.,

$$H = f(T, P, n_1, n_2, n_3 \ldots) \tag{172}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in molar enthalpy as given below.

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n_1,n_2\ldots} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n_1,n_2\ldots} dP + \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \cdots \tag{173}$$

The first term on the right-hand side gives the change in the enthalpy with the temperature at constant pressure and compositions; while the second term gives the change in the enthalpy with pressure at constant temperature and compositions. The terms afterward represent the variation in enthalpy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant i.e. $dT = 0$, $dP = 0$, the equation (173) takes the form

$$(dH)_{T,P} = \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} dn_2 + \left(\frac{\partial H}{\partial n_3}\right)_{T,P,n_1,n_2\ldots} dn_3 \ldots \tag{174}$$

Every term on the right-hand side of the equation (174) is partial molar enthalpy and is symbolized by a "bar" over it i.e.

$$\overline{H_1} = \left(\frac{\partial H}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} \tag{175}$$

$$\overline{H_2} = \left(\frac{\partial H}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} \tag{176}$$

After putting the values from equations like (175 – 176) in equation (174), we get

$$(dH)_{T,P} = \overline{H_1}\, dn_1 + \overline{H_2}\, dn_2 + \overline{H_3}\, dn_3 \ldots \tag{177}$$

For the *i*th component, we can say that

$$\overline{H_i} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_2,n_3\ldots} \tag{178}$$

The equation (178) gives the general expression for the "partial molar enthalpy" of the *i*th species.

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❖ Gibb's-Duhem Equation

In order to derive the expression for Gibbs's-Duhem equation, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, the partial molar free energy depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$G = f(T, P, n_1, n_2, n_3 \dots) \tag{179}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar free energy as given below.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{180}$$

The first term on the right-hand side gives the change in the free energy with the temperature at constant pressure and compositions; while the second term gives the change in the free energy with pressure at constant temperature and compositions. The terms afterward represent the variation in free energy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant, i.e., $dT = 0$, $dP = 0$, the equation (180) takes the form

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{181}$$

Every term on the right-hand side of the equation (181) is partial molar free energy or simply the "chemical potential" i.e.

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} \tag{182}$$

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} \tag{183}$$

$$\mu_3 = \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} \tag{184}$$

$$\mu_4 = \left(\frac{\partial G}{\partial n_4}\right)_{T,P,n_1,n_2\dots} \tag{185}$$

$$\mu_5 = \left(\frac{\partial G}{\partial n_5}\right)_{T,P,n_1,n_2\dots} \tag{186}$$

After putting the values from equations like (182 – 186) in equation (181), we get

$$(dG)_{T,P} = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \mu_4\, dn_4 + \mu_5\, dn_5 \ldots \quad (187)$$

Now, if the system composition is definite, the integration of the above equation gives

$$G_{T,P,N} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4\, dn_4 + \mu_5\, dn_5 \ldots \quad (188)$$

The differentiation of equation (188) at constant temperature and constant pressure but changing composition gives the following relation

$$(dG)_{T,P} = (n_1 d\mu_1 + \mu_1 dn_1) + (n_2 d\mu_2 + \mu_2 dn_2) + (n_3 d\mu_3 + \mu_3 dn_3) + (n_4 d\mu_4 + \mu_4 dn_4) + (n_5 d\mu_5 + \mu_5 dn_5) \ldots \quad (189)$$

or

$$(dG)_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \mu_4 dn_4 + \mu_5 dn_5 \ldots) + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + n_4 d\mu_4 + n_5 d\mu_5 \ldots) \quad (190)$$

After comparing the equation (187) and (190), we can conclude that the content included in the second bracket must be equal to zero. Mathematically, we can say that

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 \ldots = 0 \quad (191)$$

or

$$\sum n_i d\mu_i = 0 \quad (192)$$

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Which is the popular Gibbs-Duhem equation, and is applicable to the systems under constant temperature-pressure conditions.

The physical significance of the Gibbs-Duhem equation can be understood by taking the example of binary solutions i.e. a system of two components only. The Gibbs-Duhem equation for such systems is

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (193)$$

or

$$n_1 d\mu_1 = -n_2 d\mu_2 \quad (194)$$

or

$$d\mu_1 = -\frac{n_2}{n_1}\, d\mu_2 \quad (195)$$

Hence, the chemical potential of one constituent is not independent of another component in binary solutions. In other words, the chemical potentials or partial molar free energies of two components of the binary system are mutually dependent; and if the one increases the other one decreases.

It is also worthy to note that if the number of moles of different constituents remains constant (closed system), i.e., $dn_i = 0$; equation (180) reduces to the following.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \tag{196}$$

Also, for a closed system, we know that

$$dG = VdP - SdT \tag{197}$$

Which means that

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad and \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \tag{198}$$

Which is the variation of free energy with temperature and pressure in closed systems. These two relations can further be used to deduce the variations of chemical potentials with temperature and volume.

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❖ Problems

Q 1. Define the first law of thermodynamics with pictorial description.

Q 2. Discuss the limitations of the first law of thermodynamics and the need for the second law.

Q 3. What is entropy? How does it behave in reversible and irreversible reactions?

Q 4. Comment on the statement “all spontaneous processes are thermodynamically irreversible”.

Q 5. Derive the relation showing the variation of entropy with temperature and pressure.

Q 6. What do you mean by “unavailable energy” or the “lost work”?

Q 7. Discuss the spontaneity of a process in terms of entropy change.

Q 8. What is Gibbs free energy? What are its significances?

Q 9. Define the work function and discuss the related spontaneity science.

Q 10. What are partial molar quantities? Discuss with the special reference of chemical potential.

Q 11. Derive Gibbs-Duhem equation.

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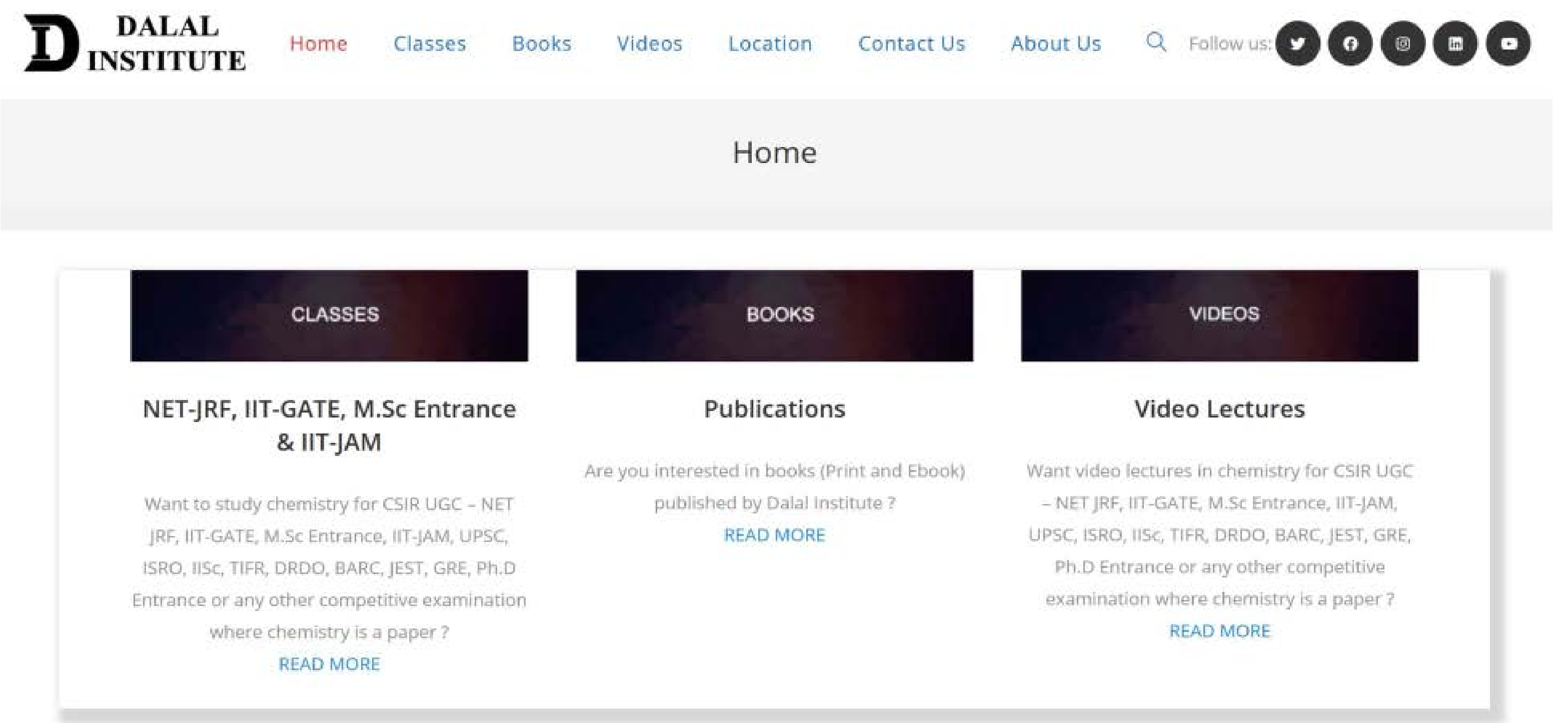

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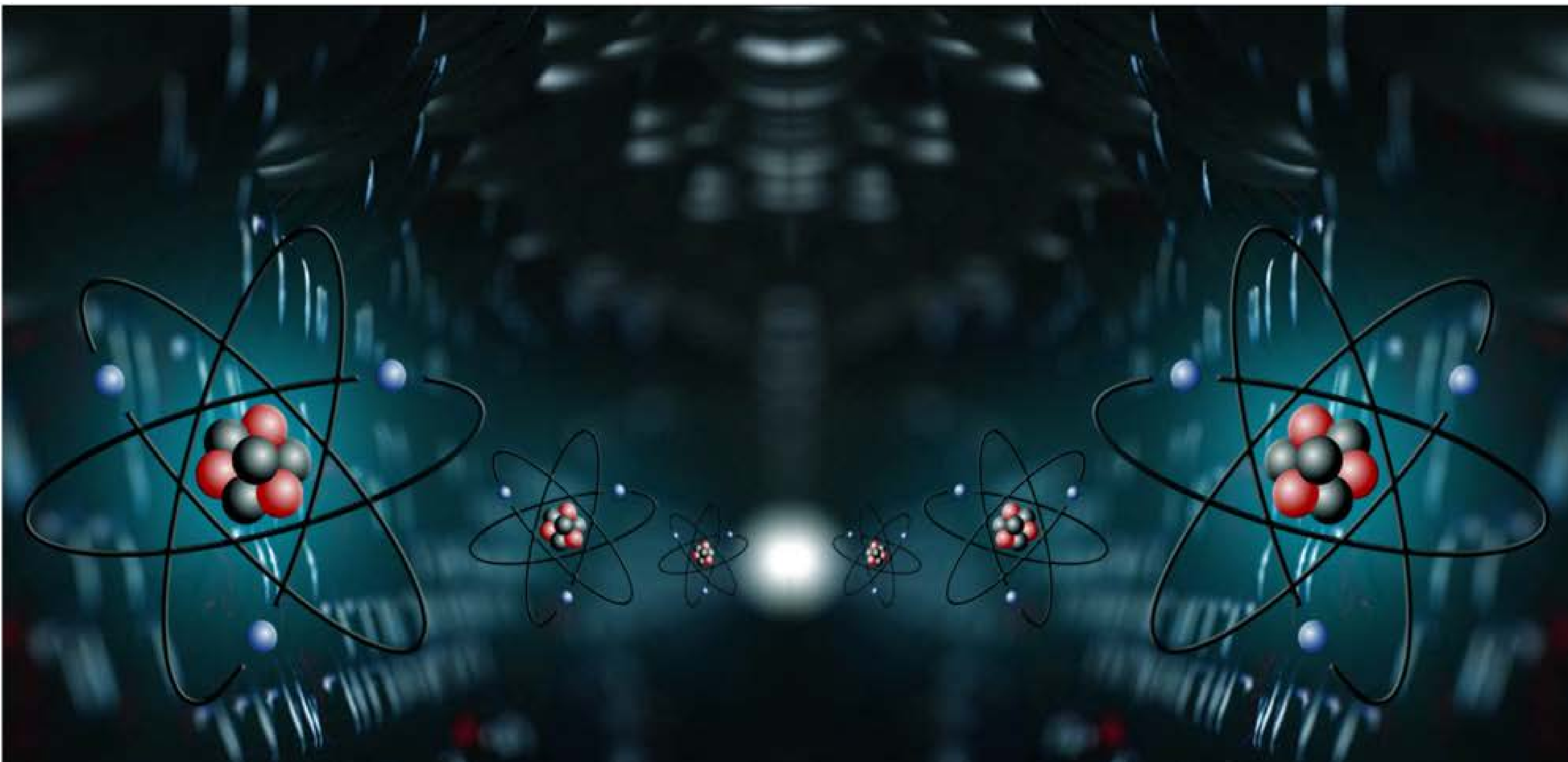

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