★ CONCEPT OF ENTROPY : 2.2 BSC

Definition of entropy from the efficiency of Carnot's engine:

Based on second law, we define a new thermodynamic property called entropy. We express the efficiency of a heat engine by the following expression.

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$

We know $W = Q_2 - Q_1$

Neglecting the signs of heat quantities it may be said that W is equal to the algebraic sum of Q_2 and Q_1. Therefore,

$$W = Q_2 + Q_1$$

$$\frac{Q_2 + Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \; ; \; 1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \; ; \; \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2}$$

This tells that in a reversible cycle sum of (Q/T) terms is equal to zero. This is stated as

$$\oint \frac{q_{rev}}{T} = 0$$

We know that the cyclic integral of an exact differential is zero

So $\frac{q_{rev}}{T}$ is an exact differential $\frac{q_{rev}}{T}$ is denoted as dS

$$\therefore dS = \frac{q_{rev}}{T}$$

S is called the entropy. It is a state property. If S_1 is the entropy of the system in its initial state and S_2, at the final state

$$S_2 - S_1 = \Delta S = \int_1^2 \frac{q_{rev}}{T}$$

ΔS is entropy change. It does not depend upon the path in which the system undergoes the change. It depends upon the initial and final states only. **Entropy is an extensive property similar to internal energy.**

Definition:

It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

Change of entropy (ΔS) of a system is defined as the integral of all the terms involving heat change (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly.

$$\text{Mathematically } \Delta S = \int_1^2 \frac{q_{rev}}{T}$$

For an engine working irreversibly the efficiency is less than one. Therefore in a irreversible cycle, the sum of (q_{rev}/T) terms is less than zero.

$$\oint \frac{q_{ir}}{T} < 0$$

Units of entropy :

CGS units Calories per degree i.e., Cal deg^{-1}

This is known as entropy unit i.e., eu

SI units Joules per degree kelvin i.e., JK^{-1}

Properties of Entropy

Relation of the Entropy Changes to Changes in the other properties of the system :

Consider a reversible expansion. According to first law of thermodynamics

$$q_{rev} = dE + P_{op}\, dV$$

Since the expansion is reversible

$$P_{op}\, dV = PdV \;\;\&\;\; q_{rev} = dE + PdV$$

Dividing throught out by T $\dfrac{q_{rev}}{T} = \dfrac{dE}{T} + \dfrac{P}{T} dV$

According to the definiton of entropy the equation becomes

$$dS = \frac{1}{T} dE + \frac{P}{T} dV$$

This expression incorporates both first law and second law. It is a general expression for all the changes in a system.

Entropy as a state function - Entropy as a functionof V and T

Let us consider the general expression for entropy change

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \qquad (4)$$

If we consider internal energy as a function of temperature and volume

$$E = f(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

Substituting this value of dE in equation (4)

$$dS = \frac{1}{T}\left[C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV\right] + \frac{P}{T} dV$$

$$dS = \frac{C_v}{T} dT + \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T dV + \frac{P}{T} dV$$

$$dS = \frac{C_v}{T} dT + \left[\frac{1}{T} P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV$$

At constant volume $dV = 0$

$$\therefore dS_V = \frac{C_V}{T} dT \; ; \; \Delta S_{V,} = \int_1^2 \frac{C_V}{T} dT$$

ln $\frac{T_2}{T_1}$

This relation gives the entropy change of the system at constant volume

At constant temperature $dT = 0$

$$dS_T = 0 + \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)\right] dV_T$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]$$

From this expression we can get the following equation

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$$

This relates entropy change with volume at constant temperature α is coefficient of expansion and β is coefficient of compressibility

Entropy as a Function of P and T

Consider the general expression for the change in entropy

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \qquad (4)$$

Consider also the definition of enthalpy $H = $ [illegible] PV

$$E = H - PV\,;\ dE = dH - PdV - VdP$$

Substituting this value of dE in equation (4)

$$dS = \frac{dH}{T} - \frac{V}{T}dP \qquad (5)$$

If we consider enthalpy as a function of temperature and pressure $H = f(P, T)$

$$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Substituting this value of dH in (5)

$$dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP$$

At constant pressure $dP = 0$

$$\therefore\ dS_V = \frac{C_P}{T}dT\,;\ \Delta S_V = \int_1^2 \frac{C_P}{T}dT$$

$$\Delta S = C_P \ln\frac{T_2}{T_1}$$

This equation relates entropy change with temperature, at constant pressure.

At constant temperature the above equation(6) reduces to

$$dS = -V\alpha\, dP\,;\ \left(\frac{\partial S}{\partial P}\right)_T = -V\alpha$$

V is molar volume and α is coefficient of expansion.

Temperature Dependence of Entropy : If we keep the pressure and volume as constants, the entropy of the system changes with temperatūre. At constant volume.

$$dS = \frac{C_V}{T}dT$$

P

and at constant $dS_p = \frac{C_p}{T} dT$

Therefore $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$; $C_p = T\left(\frac{\partial S}{\partial T}\right)_P$

Entropy change in ideal gases

Entropy change in isothermal expansion of an ideal gas

From First law $\Delta E = Q - W$

In an isothermal reversible expansion of an ideal gas $\Delta E = 0$

$$\therefore Q_{rev} - W = 0 \text{ ; i.e., } Q_{rev} = W$$

We know work done in such a case

$$W = nRT \ln \frac{V_2}{V_1} \text{ ; } \therefore Q_{rev} = nRT \ln \frac{V_2}{V_1}$$

Dividing through out by T $\frac{Q_{rev}}{T} = nR \ln \frac{V_2}{V_1}$

But by definition $\frac{Q_{rev}}{T} = \Delta S$; $\Delta S = nR \ln \frac{V_2}{V_1}$

Entropy change when V and T are the variables :

The general expression for the entropy change of any system is give below.

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \qquad (4)$$

For an ideal gas $dE = C_V dT$

$$\therefore \quad dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

For one mole of an ideal gas $P = RT/V$.

Substituting this value of P in the above equation

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

Integrating this equation between limites.

$$\int_1^2 dS = \int_{T_1}^{T_2} \frac{C_V}{T} dT + R \int_{V_1}^{V} \frac{dV}{V}$$

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

Entropy change when P and T are the variables

We know, from definition E = H – PV

$$dE = dH - PdV - VdP$$

Substituting this value of dE in equation (4)

$$dS = \frac{1}{T}(dH - PdV - VdP), + \frac{P}{T} dV$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

For and ideal gas $dH = C_p dT$;

$$dS = \frac{1}{T} C_p dT - \frac{V}{T} dP$$

For one mole of an ideal gas $V = RT/P$

$$dS = \frac{1}{T} C_p dT - \frac{R}{P} dP$$

Intergrating between limits

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Summary : Entropy changes in isothermal (constant temperature) processes

$$\Delta S_T = R \ln \frac{V_2}{V_1} = 2.303\, R \log \frac{V_2}{V_1} \quad \text{(or)}$$

$$\Delta S_T = R \ln \frac{P_1}{P_2} = 2.303\, R \log \frac{P_1}{P_2}$$

Entropy changes in isobaric (constant pressure) processes

$$\Delta S_P = C_p \ln (T_2/T_1) = 2.303\, C_p \log (T_2/T_1)$$

Entropy changes in isochoric (constant volume) processes

$$\Delta S_V = C_v \ln (T_2/T_1) = 2.303\, C_v \log (T_2/T_1)$$

Entropy of mixing of ideal gases :

Consider the expression for the entropy change of an ideal gas

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

General integration of the above gives

$$S = C_v \ln T + R \ln V + S_0 \qquad (7)$$

S_0 is the integration constant

Now consider a number of ideal gases placed in a vessel separately using partitions. Let n_i be number of moles of the gas i and V_i be its volume. If the gases are at the same temperature, the total entropy is given as

$$S_1 = \Sigma n_i (C_v \ln T + R \ln V_i + S_i) \qquad (8)$$

If the partitions are removed, the gases mix together. Now the volume of each gas is the total volume. The total entropy after mixing, is given as

$$S_2 = \Sigma n_i (C_v \ln T + R \ln V + S_i) \qquad (9)$$

If the gases, before mixing were at the same pressure

$$\frac{V_i}{V} = \frac{n_i}{n} = X_i$$

n is the total number of moles. X_i is the mole fraction of i the gas, Rearranging

$$V_i = X_i V$$

Substituting this value of V_i in (8)

$$S_1 = \Sigma n_i (C_v \ln T + R \ln X_i + R \ln V + S_i) \qquad (10)$$

The increase in entropy due to mixing of gases is obtained as

$$\Delta S_m = S_2 - S_1 = (9) - (10)$$

$$\text{i.e., } \Delta S_m = - R\Sigma n_i \ln X_i$$

For one mole of the gases

$\Sigma n_i [C_v \ln T + R \ln V + S_i -$
$C_v \ln T + R \ln x_1 + R \ln V +$

$$\Delta S_m = -R \Sigma \frac{n_i}{n} \ln X_i = -R \Sigma X_i \ln X_i$$

For two gases the above equation becomes

$$\Delta S_m = - R(X_1 \ln X_1 + X_2 \ln X_2)$$

This relation gives the entropy of mixing of ideal gases for one mole. The mole fraction of a gas in a mixture is always less than one. So In X_i is negative and ***entropy of mixing is positive***. The mixing of two or more gases is accompanied by an increase in entropy. The above equation is also valid for mixing of ideal liquids and solid solutions.

Entropy changes and reversible process :

Let us take isothermal expansion of an ideal gas at constant teperature is vacuum from a volume V_1 to a volume V_2 This process will be ***spontaneous*** (irreversible). Since there is no opposing force the work done by the system (W) will be zero. Since the process

is isothermal $\Delta E = 0$

According to first law $\Delta E = Q - W$

Since ΔE and W are zero $Q = 0$

This means that in this process no heat is absorbed or evolved i.e., no heat is removed from or supplied to the surroundings i.e.,

$$\Delta S_{sur} = 0$$

For the above process, ΔS_{sys} is given by $\Delta S_{sys} = R \ln \frac{V_2}{V_1}$

$$\therefore \text{Total } \Delta S = \Delta S_{sys} + \Delta S_{sur} = R \ln \frac{V_2}{V_1}$$

Since the process is an expansion process $V_2 > V_1$

$$\therefore \Delta S_{Total} > 0$$

i.e, During the spontaneous (irreversible) isothermal expansion of an ideal gas results in an increase in the total entropy of the system and its surroundings taken together.

Now let us take the isothermal reversible expansion of an ideal gas at constant temperature from a volume of V_1 to a volume of V_2.

Here $W = P\Delta V$. In this case also $\Delta E = 0$ According to first law $\Delta E = Q - W = 0$. So $Q = W$. So $\Delta S_{sys} = Q_{rev}/T$

i.e., the entropy of the system will increase.

The surroundings will lose an amount of heat equivalent to - Q

$$\text{So } \Delta S_{sur} = -Q_{rev}/T$$

i.e.. the entropy of the sorroundings will decrease

Therefore the total change in entropy of both the system and surroundings

$$\Delta S_{Total} = \Delta S_{sys} + \Delta S_{sur}$$
$$= (Q_{rev} / T) + (-Q_{rev} / T) = 0$$

i.e. During a reversible isothermal expansion of an ideal gas there is no change in the total entropy of the system and its surroundings taken together. To sum up for an irreversible process

$$\Delta S_{Total} = \Delta S_{sys} + \Delta S_{sur} > 0$$

For a reversible process

$$\Delta S_{Total} = \Delta S_{sys} + \Delta S_{sur} = 0$$

Entropy changes in physical state

When there is a change in a system, the entropy change is given by the following expression

$$\Delta S = \int_1^2 \frac{q_{rev}}{T}$$

For an isothermal transformation T is constant

$$\Delta S = \frac{1}{T} \int_1^2 q_{rev} \qquad \text{i.e.} \quad \Delta S = \frac{Q_{rev}}{T}$$

If we know the reversible heat change in any isothermal transformation, ΔS can be calculated by the above expression.

Evaporation of a liquid at its normal boiling point is an example of isothermal transformation. This phase change is nearly a reversible transformation. Further it takes place at constant pressure. So the heat absorbed is equal to enthalpy change

$$Q_p = \Delta H_v$$

Since we consider the process is reversible, the entropy change for evaporation of one mole of the liquid is given as

$$\Delta S_v = \frac{Q_p}{T_b} \qquad \Delta S_v = \frac{\Delta H_v}{T_b}$$

Here ΔH_v is the heat of vapourisation and T_b is the normal boiling point of the liquid.

Another example of isothermal transformation is ***fusion*** of a ***solid***. By similar arguments we can show the entropy change of fusion of a solid is given as.

$$\Delta S_f = \frac{\Delta H_f}{T_m}$$

ΔH_f is heat of fusion and T_m is the melting point.

★ TROUTON'S RULE :

Trouton's rule states that the entropy of vapourisation of many liquids at their normal boiling point has approximately the same value.

$$\Delta S_v \approx 21 \text{ e.u. / mole } (1\text{Cal / degree } = 1\text{e.u})$$

$$\frac{\Delta H_v}{T_b} \approx 21 \text{ e.u. / mole}$$

Associated liquids like water, alcohols and amines do not obey Trouton's rule. Also liquids with low boiling points do no obey this rule.

Trouton's rule is useful to calculate the approximate heat of vapourisation from the boiling points.

Physical significace of entropy :

i) **Entropy - a measure of unavailabel energy :**

According to second law heat can not be completely converted into work. That means 'a certain amount of heat is not available for converting into work. Entropy is a measure of that unavailable energy.

ii) **Entropy - a measure of disorderliness in a system :**

Let us consider some spontaneous processes like diffusion of one gas into another or flow of heat from a hot end to a cold of a metal bar etc. In all these spontaneous processes there in an ***increase*** in disorderliness or randomness of the molecules constituting the system. We also know that for spontaneous processes the entropy increases. Thus entropy is a measure of disorderliness of the system.

For example the entropy of water will be more than that of ices. The entropy of steam at 100^{0}C will be more than water at 100^{0}C. The entropy of closely packed metals will be more than that of covale crystals Because randomness or disorderliness increases as go from ice to water or from water at 100^{0}C to steam at 100^{0}C from covalent crystals to close packed metals

iii) **Entropy - a measure of probability** :

A spontaneous process always proceeds from a less probab state to a more probable state This is quite natural We have alread seen that spontaneous process is always accompanied by increases in entropy Thus entropy may be taken as a measure probability of a thermodynamic state

CLAUSIUS INEQUALITY

In a reversible cycle $\oint \frac{dq_{rev}}{T} = 0$

But in an irreversible cycle $\oint \frac{dq_{irr}}{T} < 0$

Let a system go from state I to state II irreversibly and returns back to initial state reversibly The this cycle is known an irreversible cycle For such an irreversible cycle

$$\oint \frac{dq_{irr}}{T} = \int_1^2 \frac{dq_{irr}}{T} + \int_2^1 \frac{dq_{rev}}{T}$$

But $\oint \frac{dq_{irr}}{T} < 0$; $\therefore \int_1^2 \frac{dq_{irr}}{T} + \int_2^1 \frac{dq_{rev}}{T} < 0$

or $\int_1^2 \frac{dq_{irr}}{T} - \int_1^2 \frac{dq_{rev}}{T} < 0$

or $\int_1^2 \frac{dq_{irr}}{T} - \int_1^2 dS < 0$

The first term is the sum of dq/T terms for an irreversible change The second term is the change in entropy for the same change but in eversible fashion

or an infinitesimally small change $\frac{dq_{irr}}{T} - dS < 0$

$$\text{or} \qquad dS > \frac{dq_{irr}}{T}$$

This statement is known as clausius inequality. The entropy change in an irreversible change is greater than the sum of dq/T terms.

The Clausius inequality can be directly applied to changes in isolated system. For a change in isolates system $dq_{irr} = 0$.

$$\therefore ds > 0$$

So, entropy increases during change in an isolated system.

When equillibrium is established it reaches a maximum value. Suppose we consider the universe as an isolated system, according to clausius inequality the entropy of the unversse is increasing. This is another statement of second law of Thermodynamics.

ENTROPY AS A CRITERION OF SPONTANEOUS AND EQUILIBRIUM PROCESS IN ISOLATLED SYSTEMS - Q7

(Criteria / condition for a reversible and spontaneous process in terms of entropy) : Reversible change should take place under equilibrium conditions. Since present equilibrium in a change cannot be realised reversible changes are ideal. The condition for a reversible change is taken as the condition for equilibrium.

$$dS = \frac{q_{rev}}{T} ;$$

$$TdS = q_{rev}$$

This is the conditions for equilibrium in a state. In a irreversible change, there is no equilibrium. It takes place spontaneously. Therfore the condition for an irreversible change is taken as the condition for spontaneity.

$$dS > \frac{q_{irr}}{T} ; \quad TdS > q_{irr}$$

The above two conditions for equilibrium and spontaneity are stated as

$$TdS \geq q$$

According to first law, $q = dE + w$; $TdS \geq dE + W$

$$-dE - w + TdS \geq 0 ; -dE - P_{OP}\, dV - du + TdS \geq 0$$

dE is the work done other than work of expansion. These are the conditions for equilibrium and spontaniety in a system in terms of entropy

— x — x

Third law of thermodynamics