Entropy (S)

Entropy is a measure of randomness or disorder of a system. It consider as a quantitative measure of increasing the probability of spontaneous process. If the change from initial to final results in an increase in randomness.

$$\Delta S = S_f - S_i$$

Carnot recognized that when Q_{rev} , a path-dependent property, is divided by *T*, a *new* path-independent property is generated, called Entropy . It is defined as

$$\Delta S = \frac{Q_{rev.}}{T} \tag{1}$$

We note that if Q_{hot} is the heat absorbed by an engine at T_{hot} , then $-Q_{hot}$ must be the heat lost by the surroundings (the hot reservoir) at T_{hot} , and the entropy of the surroundings is

$$\Delta S_{surr} = -\frac{Q_{hot.}}{T_{hot}} \tag{2}$$

Hence, for any system and its surroundings or universe,

in reversible process
$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = 0$$
 (3)

Therefore there are two cases in which $\Delta S = 0$,

(a) a system in a reversible cyclic process and

(b) a system and its surroundings undergoing any reversible process.

In irreversible process, the entropy change of the total system or universe (a system and its surroundings) is always positive because ΔS_{syst} in irreversible process. In mathematical symbols, we write

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} > 0 \tag{4}$$

EX.5/ What is entropy change for vaporization of 1 mole of water in equilibrium with its vapor at 25C, $\Delta H_{\nu} = 10500$ cal/mole ?

Sol/

At constant pressure , $Q_P = \Delta H_v$

 $\Delta S = \Delta H_v / T = 10500/298 = 35.2 \text{ cal/mole.deg.}$

Entropy and disorder

Thermodynamic systems describe by macroscopic properties such as T, P, or composition can also be described in terms of microscopic quantities such as molecular random motions.

Disorder can be seen as the number of ways the inside of a system can be arranged so that from the outside the system looks the same.

$$S = k \ln O$$

Where k is the Boltzmann constant.

 \boldsymbol{O} is the number of microscopic states or configuration. The probability \boldsymbol{P} for

$$P = (O_1/O_2) = (V_1/V_2)^N$$

$$\Delta S = S_2 - S_1 = k \ln(O_1/O_2) = k N_A \ln(V_1/V_2),$$

N=no. of particles.

The Third law of thermodynamics

The entropy of pure crystalline substance is Zero. A pure perfect crystal has only one possible configuration and according to eq. $[S =k \ln(1) =0]$ its entropy Zero.

The third law.

$$S_T = \sum \frac{dq_{rev.i}}{T_i} + S_0 \tag{1}$$

Where, S_0 is the molar entropy at absolute zero and ,

S_T is the molar entropy at any temperature.

Entropy changes during a phase change as the temperature rises from OK to T. The following equation shows S_T for a substance that undergoes two phase changes ,melting (*m*) and vaporization (**v**).

from eq.
$$\overline{C}_{P} = \frac{dq_{P}}{dT} \Rightarrow dq = C_{P} dT$$
 (3)

In substitute (3) in eq.(1) we obtain

$$S_{T} = \int_{0}^{T_{m}} \frac{C_{P} dT}{T} + \frac{\Delta H_{m}}{T_{m}} + \int_{T_{m}}^{T_{v}} \frac{C_{P} dT}{T} + \frac{\Delta H_{v}}{T_{v}} + \int_{T_{v}}^{T} \frac{C_{P} dT}{T}$$
(2)

Where, $S_0 = 0$ has been omitted.

Free energy functions and applications

Consider an isolated system composed of a closed container (i.e., the system) in equilibrium with a temperature bath (i.e., the surrounding) then according to equations:

$$\Delta S_{isolatedssystem} = \Delta S_{syst} + \Delta S_{surr} \ge 0 \tag{1}$$

Equilibrium is a condition where the transfer of heat occurs reversibly:

therefore at constant temperature $-\Delta S = \Delta S$ and

Now, renaming $-\Delta S_{syst} = \Delta S_{surr}$ and $Q_{rev} = Q$, we write equation as

$$\Delta S - \frac{Q}{T} \ge 0 \tag{3}$$

which can also be written in the following way:

 $Q - T \Delta S \le 0$ (at T=const.) (4)

For a process at constant volume, $Q_v = \Delta E$, so eq.(4) become

$$\Delta E - T \Delta S \le 0 \qquad (at T=const, V=const) \qquad (5)$$

In the case of a process at constant pressure, $Q_P = \Delta H$, and

$$\Delta H - T \Delta S \le 0$$
 (at T=const, P=const) (6)

- The terms on the left of eq.5 and eq.6 define as:

Helmholtz free energy or work function A,

$$A = E - T S \tag{7}$$

And

Gibbs free energy ,G

$$G = H - T S \tag{8}$$

Thus equilibrium and spontaneity conditions are reduced to only.

$$\Delta A = 0$$
 (at $T = \text{constant.}$, $V = \text{constant}$) (9)

$$\Delta G = 0$$
 (at *T*=constant, *P*=constant) (10)

Maximum Net Work.

The system does maximum work (W_{max}) when it is working under Reversible W conditions.

$$\Delta A - W_{\text{max}} = 0 \quad or \quad \Delta A = W_{\text{max}}$$
(3)
$$\Delta G - W_a = 0 \quad or \quad \Delta G = W_a$$
(4)

The main eq. for Gibbs eq.

$$\Delta G = \Delta H - T \Delta S \qquad (5)$$
$$\Delta G = nRT \ln \frac{P_2}{P_1} \qquad (6)$$

 $\Delta G = nRT \ln \frac{a_2}{a_1}$ (7) a_1 and a_2 activities of solute.