→ Need for the second law of thermodynamics – Limitations of the first law of thermodynamics :→

1. The first law establishes definite relationship between the heat absorbed and the work performed by a system in a given process. But it puts no restriction on the direction of flow of heat.

   suppose the heat is flowing from a hot to cold body. First law simply reveals that the quantity of heat lost by the hot body is equal to the heat gained by the cold body. It never reveals that heat can only flow from the hot to the cold body and not in the reverse direction.

2. According to the first law, the energy of an isolated system remains constant during a specified change of state. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously, i.e., whether it is feasible.

3. The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for second law.

The second law helps us to determine the direction in which energy can be transferred. It also help us to predict whether a given process or chemical reaction can occur spontaneously It introduce a new concept of entropy. It also help us to know the equilibrium conditions.

Varius forms of energy can be completely transformed into one another, yet heat is a typical form of energy which cannot be completely transformed into work. The second law helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

→ Second law of thermodynamics - different statements of the law :→

1. Kelvin - Planck statement :→

- It is impossible to construct an engine which, operating in a complete cycle, will absorb heat from a single body, and convert it completely to work, without leaving changes in the working system.

2. Clausius statement :→

- It is impossible to transfer for a self acting machine, unaided by an external agency to convert heat continuously, from one body at lower temperature to a body at a higher temperature.

3. Planck statement :→

- It is impossible to construct a device that will work in a complete cycle and convert heat into work without making any change in the surroundings.

4. Thomson statement :→

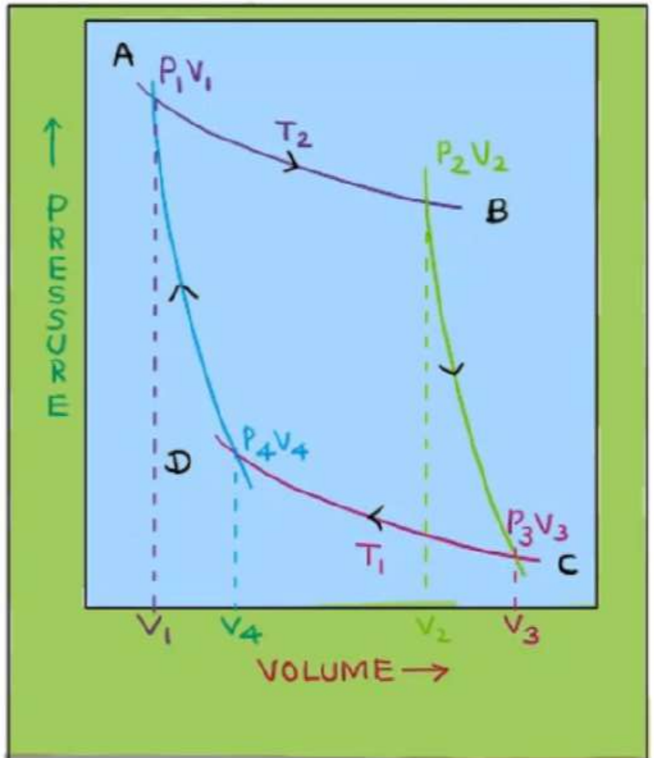
- It is impossible to obtain a continuous supply of work by cooling a body to a temp. lower than that of coldest of its surroundigs.

5. Diffusion of a gas always takes place from a region of higher to one at lower pressure, until the pressure becomes uniform.

From all above statements, it reveals that they are all modified forms of the same fundamental idea, " all forms of energy are convertible into heat but the heat so obtained cannot be converted into forms of energy by any process.

→ Carnot cycle:→

- This concept was given by a French engineer Sadi Carnot in 1824.
- Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work.
- The system consist of one mole of an ideal gas which is subjected to a series of four successive operations, commonly termed as four strokes, as given below-



The four operations in Carnot cycle

I. Stroke 1. Isothermal Expansion:→

- The gas is allowed to expand reversibly and isothermally at the temp T_2 so that volume increases from V_1 to V_2.
- Since in the isothermal expansion of an ideal gas

$$\Delta E = 0$$

From the first law of thermodynamics

$$\Delta E = q + w$$

$$\text{or} \quad q = -w$$

i.e. heat absorbed is equal to the work done by the system on surroundings.

Let q_2 be the heat absorbed by the system at temp T_2 and w_1 be the work done by the system on the surroundings. Then

$$q_2 = -w_1 = RT_2 \ln\left(\frac{V_2}{V_1}\right) \text{ — } ①$$

II. Stroke 2. Adiabatic expansion:→

- The gas is then allowed to expand reversibly and adiabatically from volume V_2 to V_3.
- Since work is done by the system adiabatically, it is not in position to absorb heat. The temperature of the system, therefore, falls from T_2 to T_1.
- For adiabatic process $q = 0$

From first law of thermodynamics

$$\Delta E = q + w$$

or $$\Delta E = W$$

Since the process involves expansion of the gas, therefore work is done by the system on the surroundings. Hence, by convention, w is negative so that

$$\Delta E = -W$$

Now, by definition,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\Delta E = C_V \Delta T = C_V(T_1 - T_2) = -W$$

or $$-W = C_V(T_1 - T_2)$$

or $$-W = -C_V(T_2 - T_1)$$

If the work done in this stage is denoted by W_2, then

$$-W_2 = -C_V(T_2 - T_1) \quad — ②$$

III. Stroke 3. Isothermal compression:→

- After this, the gas is subjected to a reversible and isothermal compression at the lower temperature T_1 so that the volume decreases from V_3 to V_4.
- In this case, work is done on the system. Hence, heat will produced and given up to the surroundings. Since compression takes place Isothermally and reversibly,

$$\Delta E = 0$$

Therefore, if q_1 is the heat given out to the surroundings at the temp T_1 and W_3 is the work done on the system in this process then

$$-q_1 = W_3 = RT_1 \ln\left(\frac{V_4}{V_3}\right) — ③$$

IV. Stroke 4. Adiabatic compression:→

- Finally, by an adiabatic and reversible compression, the gas is restored to its original volume V_1 and temp T_2.
- In this case, work is done on the system. Hence W is positive.
- According to first law

$$\Delta E = q + W$$

Since in adiabatic process, $q = 0$, hence

$$\Delta E = W = C_V \Delta T = C_V (T_2 - T_1)$$

Let W_4 be the work done in this stage. Then,

$$W_4 = C_V (T_2 - T_1) — ④$$

where $T_2 - T_1$ is the increase in temp produced by the adiabatic compression

– The net heat absorbed (q) by the ideal gas in the whole cycle is given by-

$$q = q_2 + (-q_1)$$

$$q = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$$

$$q = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \left(\frac{V_3}{V_4}\right) \text{ — } ⑤$$

– For adiabatic expansion of an ideal gas the following equations can be written as

$$C_V \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_3}{V_2}\right) \quad \text{(For stage II)}$$

$$C_V \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_4}{V_1}\right) \quad \text{(For stage IV)}$$

$$\text{or} \qquad \frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{OR} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Hence, the net heat absorbed, according to eq. ⑤, may be put as

$$q = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$q = q_2 - q_1 = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right) - ⑥$$

Similarly, the net work done by the gas is given by

$$W = -W_1 + (-W_2) + W_3 + W_4$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) - C_V(T_2 - T_1) + RT_1 \ln\left(\frac{V_4}{V_3}\right) + C_V(T_2 - T_1)$$

$$w = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$$

or $$w = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_3}{V_4}\right) \quad — ⑦$$

Since $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$w = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$w = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right) \quad — ⑧$$

It follows from equation ⑥ and ⑧ that $q = w$. Thus, the essential condition for a cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.

- The relationship between w, the net work done by the system and q_2, the quantity of heat absorbed at higher temperature T_2, in Carnot cycle, can be obtained by dividing eq. ⑧ by eq. ①

$$w = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right)$$

$$q_2 = RT_2 \ln\left(\frac{V_2}{V_1}\right)$$

$$\frac{w}{q_2} = \frac{(T_2 - T_1)}{T_2}$$

or $$w = q_2 \frac{(T_2 - T_1)}{T_2} \quad — ⑨$$

- Since $(T_2 - T_1)/T_2 < 1$, it follows that $w < q_2$, i.e. work done is less than heat absorbed. This means that only a part of the heat absorbed by the system at higher temperature T_2 is transformed into work. The rest of the heat q_1 is given out by the system to the surroundings which is at lower temperature T_1.

→ Efficiency of carnot cycle:→

- The fraction of the heat absorbed by an engine which it can convert into work gives the efficiency (η) of the engine.
- We know that

$$\eta = \frac{w}{q_2} = \frac{(T_2 - T_1)}{T_2} \quad — \quad ①$$

Since $\frac{(T_2 - T_1)}{T_2} < 1$, the efficiency of a heat engine is always less than 1. No heat engine has yet been constructed which has an efficiency equal unity. Mathematically, however, if $T_1 = 0$, efficency = 1.

It follows from eq. 1 that the efficiency depends upon the difference between T_2 and T_1. The greater the difference between the temperature of 'source' and 'sink', the greater is the efficiency. This explains why superheated steam is used in a steam engine.

- The net heat absorbed by the system, q, is equal to $q_2 - q_1$ and according to first law of thermodynamics, this must be equivalent to the net work done by the system. Thus.

$$w = q = q_2 - q_1 \quad - ②$$

From equation ① and ②

$$\eta = \frac{a_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad - ③$$

- From eq. ③ it is evident that, " the efficiency of an actual engine is always less than unity."

→ Carnot theorem:→

- This theorem consist of two parts:-

1. Carnot's first theorem:→

- All reversible heat engines operating between the same temperature limits have the same efficiency.
- In other words, the efficiency of a machine working reversibly depends only the temp of the source and the sink. It is independent of the nature of the substance or substance used for operation.

2. Carnot's second theorem:→

- Of all heat engines working between the same two temperatures of source and sink, none can be more efficient than a reversible engine (Carnot engine).

→ Proof of Carnot's first theorem:→

- Suppose two reversible engines E_r and E_r' are operating between the same source and the sink.

- Assuming that E_r is less efficient than E_r' i.e. $\eta_{E_r} < \eta_{E_r'}$
- When engine E_r' absorb a certain quantity of heat (Q_2) from the source (T_2), it convert a part of into work (W') and rejects the remaining part $Q_2 - W'$ to sink (T_1). On the other hand, when engine E_r absorbs the same quantity of heat from the source but being less efficient than E_r', it converts a smaller portion into work (W) and thus rejects a large amount ($Q_2 - W$) to the sink.

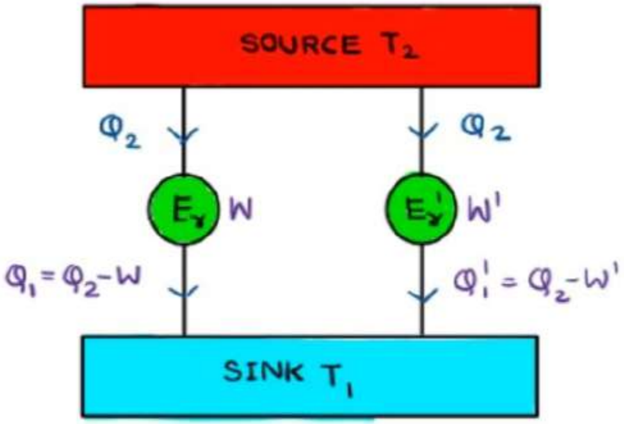


Fig:- Two engines operating between same temp. limits

- Suppose two engines E_r and E_r' are coupled to obtain a composite system in which E_r' operates in the direct manner while E_r in the opposite manner, i.e. it withdraws heat from the sink, some work is being done on it and gives up heat to the source. Thus, it means that E_r is acting as refrigerator.
- Heat transfer at source T_2 = $Q_2 - Q_2 = 0$
- Work produced = $W' - W$
- Heat transfer at sink T_2 = $Q_1 - Q_1'$

$$= (Q_2 - W) - (Q_2 - W')$$

$$= Q_2 - W - Q_2 + W'$$

$$Q_1 - Q_1' = W' - W \quad - ①$$

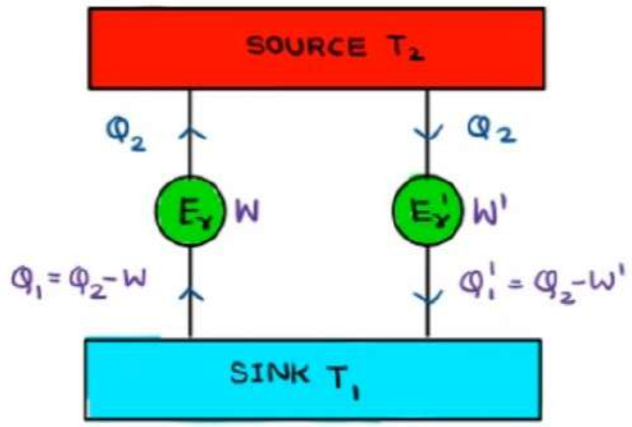


Fig. - Composite engine

Eq. ① shows that heat absorbed by the system is equal to work done. This goes against second law of thermodynamics.

As $W' > W$, it means that the composite system is able to convert heat absorbed $(Q_1 - Q_1')$ at the lower temperature completely into work. This, however, against the second law and therefore that engine E_r' is more efficient than E_r is wrong. Thus, it can be concluded that the efficiencies of both engines must be same.

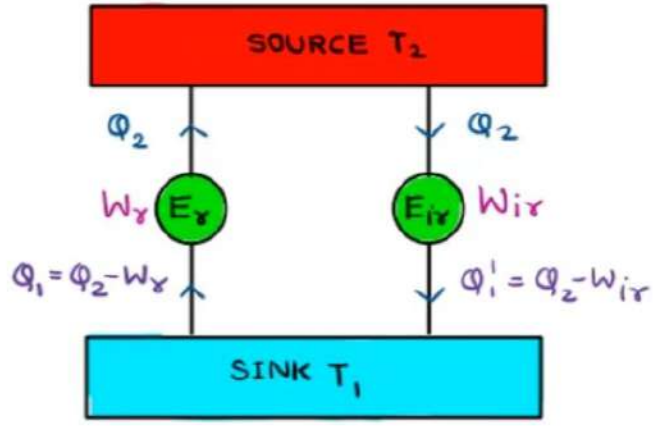


Fig.- Composite engine

→ Proof of Carnot's second theorem:→

- Suppose there are two engines, one is irreversible (E_{ir}) and other is reversible (E_r).
- Assuming that, the efficiency of E_{ir} is more than that of E_r i.e. $\eta_{E_{ir}} > \eta_{E_r}$.
- Suppose two engines are coupled. The irreversible engine operates in the direct manner because it cannot reversed whereas the reversible engine operates in the reverse direction and thus acts as a refrigerator.
- Heat transfer at source T_2 = $Q_2 - Q_2 = 0$
- Work produced = $W_{ir} - W_r$
- Heat transfer at sink T_2 = $Q_1 - Q_1'$

$$= (Q_2 - W_r) - (Q_2 - W_{ir})$$

$$= Q_2 - W_r - Q_2 + W_{ir}$$

$$Q_1 - Q_1' = W_{ir} - W_r \quad — ②$$

The composite engine is not withdrawing any heat from the source whereas the heat withdrawn from the sink is transformed completely into work. But this is contrary to the second law. Therefor, the reversible engine can not be less efficient than irrversible engine. Hence it can be concluded that the efficiency of a engine must be equal to or less than the efficiency of reversible engine when both are operating between same two heat reservoirs.

→ Thermodynamic scale of temperature:→

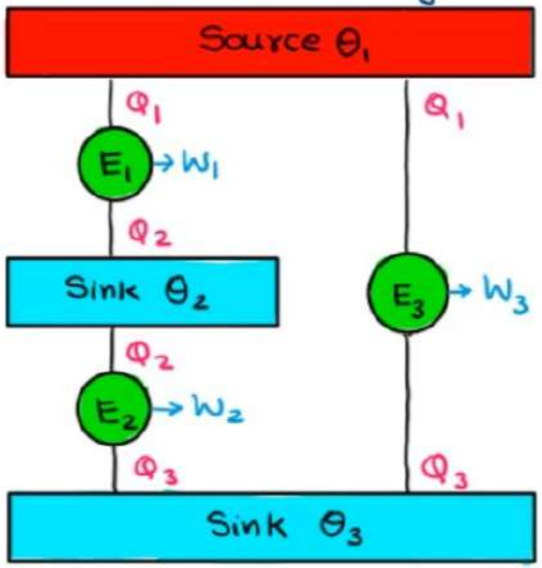
- The empirical temperature scales depends upon the nature and properties of working substances. e.g., expansion of mercury, the change in resistance of platinum etc., with rise of temperature. Such thermometers with different working substances do not agree in scales.
- The efficiency of Carnot's reversible engine does not depend upon the working substances. This property had been used by Lord Kelvin and he worked out a theory to produce a temperature scale which was not depending upon the nature of working substance. Since the basis of this is law of thermodynamics, it is also known as thermodynamic scale of temperature or sometimes Kelvin's work scale as the work done by a Carnot's engine is involved.
- The efficiency of all reversible Carnot engine working between the two temperatures is a function of those two temperatures only.
- Let the efficiency of reversible engine E_1 is

$$\eta_1 = \frac{Q_1 - Q_2}{Q_1} = f(\theta_1, \theta_2)$$

$$1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

or $$\frac{Q_2}{Q_1} = 1 - f(\theta_1, \theta_2)$$

$$\frac{Q_1}{Q_2} = \frac{1}{1-f(\theta_1,\theta_2)} \quad \text{OR} \quad \frac{Q_1}{Q_2} = F(\theta_1,\theta_2) \; — ① \quad \because F(\theta_1,\theta_2) = \frac{1}{1-f(\theta_1,\theta_2)}$$



θ = temp. $\theta_1 > \theta_2 > \theta_3$

— Similarly for reversible engine E_2

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3) \quad — ②$$

and for E_3

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3) \quad — ③$$

Now

$$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3} \quad — ④$$

OR

$$F(\theta_1, \theta_2) = \frac{F(\theta_1, \theta_3)}{F(\theta_2, \theta_3)} \quad — ⑥$$

In equation ⑥, θ_3 is not present on left hand side, while it present in both the factors on the right hand side. Therefore the form of $F(\theta_1, \theta_3)$ and $F(\theta_2, \theta_3)$ must be given by

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1) \cdot \phi(\theta_3)}{\phi(\theta_2) \cdot \phi(\theta_3)}$$

or $$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \quad — ⑦$$

or $$\frac{Q_1}{Q_2} = \frac{\phi(\theta_1)}{\phi(\theta_2)} \quad — ⑧$$

If $\phi(\theta)$ is represented by T the temperature on the thermodynamic scale, we get

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad - ⑨$$

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2} \quad \text{or} \quad \eta = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad - ⑩$$

Eq. 9 may be written as

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad - ⑪$$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \text{or} \quad \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad - ⑫$$

Eq. ⑨ gives the definition of the Kelvin's absolute thermodynamic scale of temperature, i.e. the ratio of any two temperatures measured on this scale is same as the ratio of quantities of heat taken in and given out by a reversible engine working between these temperatures.

→ zero of absolute scale:→

If in equation ⑩, $T_1 = 0$, then $Q_1 = 0$ and $\eta = 1$

If in equation ⑫, $T_2 = 0$, then $Q_2 = 0$ and $\eta = 1$

The zero of the absolute scale is temperature of the sink at which no heat is given out and all the heat taken from the source gets converted into work by a reversible engine. This zero is termed as the "absolute zero".

- At temperature lower than the absolute zero, the thermal energy will be negative which is not possible. It means that more heat is being converted into work than what is absorbed at higher temperature which is contrary to second law of thermodynamics. Hence the zero on the perfect gas scale and thermodynamic scale is the same.
- With the help of following equation we can obtain the value on any other temperature scale because

$$\frac{T}{T_0} = \frac{Q}{Q_0} \quad \text{or} \quad T = T_0 \times \frac{Q}{Q_0}$$

T = unknown temperature

Q = heat taken in

Q_0 = heat given out

T_0 = Ice point

→ Concept of entropy and entropy as a state function :→

- The efficiency of Carnot cycle is given by

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad — ①$$

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

or $$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

or $$\frac{q_1}{T_1} = \frac{q_2}{T_2} \quad — ②$$

or $$\frac{q_{rev}}{T} = \text{constant} \quad — ③$$

where q_{rev} is the quantity of heat exchanged in a process carried out reversibly at a temperature T.

Quantity q_{rev}/T represents a definite quantity or state function, viz., the entropy change of the system.

- Eq. ② has been derived by giving +ve sign to the heat absorbed (q_2) and negative sign to the heat lost (q_1) by the system. Describing q_1 and q_2 only as heat exchanged (may be evolved or absorbed), Eq. ② may be written as

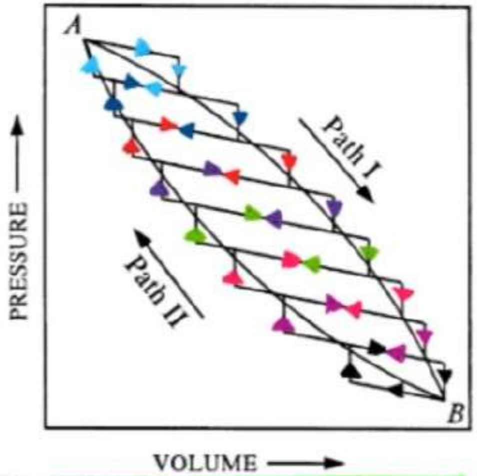
$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad — ④$$

Thus, when the isothermal and adiabatic processes in a Carnot cycle are carried out infintesimally slowly (i.e. reversibly), the summation of q/T terms is equal to zero.

- Any clyclic process, if carried out reversibly, can be shown to consist of a series of Carnot cycles.

Consider a cyclic process in which the change from the state A to state B and back to the state A is carried out reversibly.

The path ABA may be considered to consist of a number of small Carnot cycles, i.e, of a series of isothermals and adiabatics, as shown in figure.



Entropy change in a reversible cyclic process.

The lines slanting horizontally stand for adiabatics and those slanting vertically stand for isothermals of the small Carnot cycles.

If each isothermal and adiabatic change is made extremely minute, i.e. each Carnot cycle is made extremelly small by increasing their number, the path inside the loop cancel one another and the cycle corresponds to the continuous isothermal curve ABA. Thus, any reversible cycle can be regarded as being made up of infinite number of small Carnot cycles.

- Knowing that for each Carnot cycle $q_1/T_1 + q_2/T_2 = 0$, it follows that in the case of the reversible cycle ABA, consisting of a series of Carnot cycle, the summation takes the form.

$$\Sigma \frac{q}{T} = 0 \quad \text{——} \quad ⑤$$

i.e. the sum of all the q/T terms of the Carnot cycle involved is zero.

- When the change are infinitesimal, the eq. ⑤ may be written as.

$$\sum \frac{dq}{T} = 0 \quad — ⑥$$

- Since the cycle is performed in two steps, viz., from A to B and back from B to A, it follows that

$$\sum \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \quad — ⑦$$

Where

$\int_A^B \frac{dq}{T}$ = summation of all the $\frac{dq}{T}$ terms when system changes from A to B along path I.

$\int_B^A \frac{dq}{T}$ = summation of all the $\frac{dq}{T}$ terms when system changes from B to A along path II.

From eq. ⑦

$$\int_A^B \frac{dq}{T} = -\int_B^A \frac{dq}{T}$$

or

$$\int_A^B \frac{dq}{T}(\text{path I}) = \int_A^B \frac{dq}{T}(\text{path II}) \quad — ⑧$$

- It follows from eq. ⑧ that $\int_A^B dq/T$ is a definite quantity independent of the path followed for the change and depends only upon the initial and final state of the system.

This quantity, i.e., $\int_A^B dq/T$, like ΔE and ΔH, should represent the change in some single valued function of the state A and B of the system. This function is called **entropy** and is denoted by S.

If S_A = Entropy in the initial state A
and S_B = Entropy in the final state B
then the change in entropy, ΔS

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \quad \text{—} \quad ⑨$$

For each infinitesimally small change

$$dS = \frac{dq}{T} \quad \text{—} \quad ⑩$$

At constant temperature, for a finite change, dS becomes ΔS and dq becomes q.

$$\Delta S = \frac{q}{T} \quad \text{—} \quad ⑪$$

- Since entropy is a state function, the change in entropy (ΔS) from A and B will invariably be the same whether the change is reversible or not. However, mathematically, it will be given by the equation ⑫ when only the change has been brought about reversibly. This is because the above equation has been derived from Carnot cycle which works reversibly.

$$\Delta S = \int_A^B \frac{dq}{T} \quad — ⑫$$

Thus, the entropy change for a finite change of state of system at constant temperature is given by.

$$\Delta S = \frac{q_{rev}}{T} \quad — ⑬$$

→ Unit of entropy:→

$$\Delta S = \frac{q_{rev}}{T} = \frac{\text{Joule}}{\text{Kelvin}} = \frac{J}{K} = JK^{-1}$$ (known as entropy unit, e.u.)

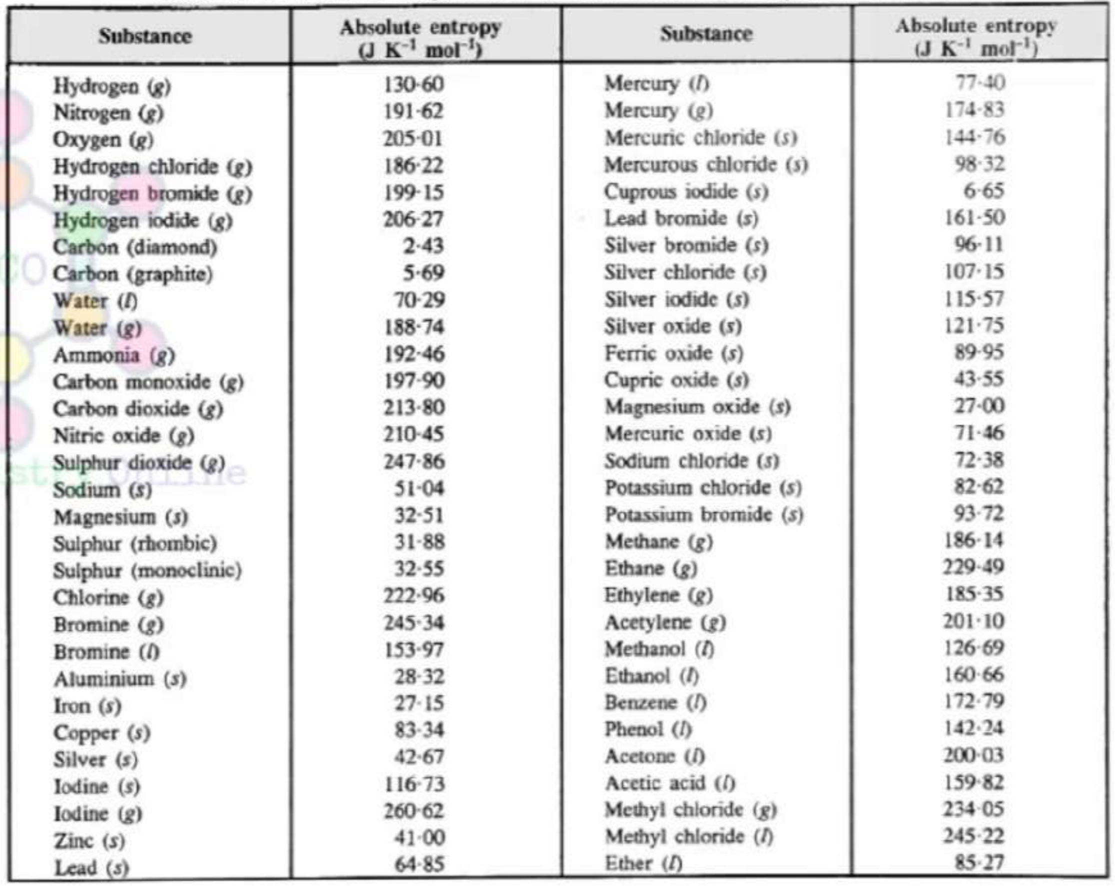
→ Standard entropy:→

- Entropy of one mole of a substance in pure state at one atmospheric pressure and 25°c, is termed as standard entropy of that substance and is denoted by S°.
- When a reaction involves each reactant and each product in its standard state, the entropy change is said to be standard entropy change. This is denoted by ΔS°. The general equation is then written as -

$$\boxed{\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}}$$

- Entropies of various substances at any given temperature and pressure can be calculated by applying the third law of thermodynamics.

Standard Absolute Entropies (S°) of Elements and Compounds at 25°C



Substance	Absolute entropy (J K^{-1} mol^{-1})	Substance	Absolute entropy (J K^{-1} mol^{-1})
Hydrogen (*g*)	130·60	Mercury (*l*)	77·40
Nitrogen (*g*)	191·62	Mercury (*g*)	174·83
Oxygen (*g*)	205·01	Mercuric chloride (*s*)	144·76
Hydrogen chloride (*g*)	186·22	Mercurous chloride (*s*)	98·32
Hydrogen bromide (*g*)	199·15	Cuprous iodide (*s*)	6·65
Hydrogen iodide (*g*)	206·27	Lead bromide (*s*)	161·50
Carbon (diamond)	2·43	Silver bromide (*s*)	96·11
Carbon (graphite)	5·69	Silver chloride (*s*)	107·15
Water (*l*)	70·29	Silver iodide (*s*)	115·57
Water (*g*)	188·74	Silver oxide (*s*)	121·75
Ammonia (*g*)	192·46	Ferric oxide (*s*)	89·95
Carbon monoxide (*g*)	197·90	Cupric oxide (*s*)	43·55
Carbon dioxide (*g*)	213·80	Magnesium oxide (*s*)	27·00
Nitric oxide (*g*)	210·45	Mercuric oxide (*s*)	71·46
Sulphur dioxide (*g*)	247·86	Sodium chloride (*s*)	72·38
Sodium (*s*)	51·04	Potassium chloride (*s*)	82·62
Magnesium (*s*)	32·51	Potassium bromide (*s*)	93·72
Sulphur (rhombic)	31·88	Methane (*g*)	186·14
Sulphur (monoclinic)	32·55	Ethane (*g*)	229·49
Chlorine (*g*)	222·96	Ethylene (*g*)	185·35
Bromine (*g*)	245·34	Acetylene (*g*)	201·10
Bromine (*l*)	153·97	Methanol (*l*)	126·69
Aluminium (*s*)	28·32	Ethanol (*l*)	160·66
Iron (*s*)	27·15	Benzene (*l*)	172·79
Copper (*s*)	83·34	Phenol (*l*)	142·24
Silver (*s*)	42·67	Acetone (*l*)	200·03
Iodine (*s*)	116·73	Acetic acid (*l*)	159·82
Iodine (*g*)	260·62	Methyl chloride (*g*)	234·05
Zinc (*s*)	41·00	Methyl chloride (*l*)	245·22
Lead (*s*)	64·85	Ether (*l*)	85·27

→ Entropy as a criteria of spontaneity and equilibrium: →

- Consider isothermal expansion of an ideal gas at constant temperature into vacuum. This will, evidently, proceed spontaneously, i.e., irreversibly. Since there is no opposing force, the work done (w) by the system will be zero.

Further, since there is no change in temperature during the process, there will be no change in the internal energy of the system, i.e., $\Delta E = 0$

Hence from the first law equation, $q = 0$, i.e. no heat is absorbed or evolved in the process. In other words, no heat is supplied to or removed from the surroundings. The entropy of the surroundigs, therefore, remains unchanged.

- Entropy of the system is a state function i.e. its temp and pressure (or volume) and is independent of the previous history of the system.

In the above process, the volume of the gas increases from V_1 to V_2 at constant temperature T. Hence, increase in entropy of one mole gas is given by

$$\Delta S = R \ln \frac{V_2}{V_1} \quad \text{—} \quad ①$$

- The total increase in entropy of the system and its surroundigs during the spontaneous process of expansion considerd above is, thus

$$R \ln \frac{V_2}{V_1} + 0 = R \ln \frac{V_2}{V_1}$$

Since $V_2 > V_1$, it is obvious that the spontaneous (irreversible) isothermal expansion of gas is accompanied by increase in the entropy of the system and its surroundings considered together.

- Now consider isothermal expansion of the ideal gas from volume V_1 to V_2 carried out reversibly at the same temp T.

The expansion is now carried out infinitesimally slowly, i.e. the pressure of frictionless piston is so adjusted that it remain always less than that of the gas by an infinitesimally small amount. In this case gas does some external work given by

$$W = -P\Delta V \quad — ②$$

Consequently, an equivalent amount of heat (q_{rev}) is absorbed revesibly by the system from the surroundings at temperature T. Hence, increase in the entropy of the system is q_{rev}/T.

The heat lost reversibly at temperature T by the surroundings is also q_{rev}. Hence, derease in the entropy of the surroundings is q_{rev}/T.

Giving appropriate sign, +ve for increase and -ve for decrease of entropy, the net entropy change of the system and its surroundigs is given by

$$\frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \quad — ③$$

Thus, in the reversible isothermal expansion of a gas, the total entropy change of the system and its surroundings considered together is zero.

→ Conclusion :→

- A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundigs taken together while in thermodynamically reversible process, the entropy of the system and its surroundings taken together remains unaltered. Thus, we can write :

$$(\Delta S_{sys} + \Delta S_{sur}) = 0 \qquad \text{For reversible (equilibrium) process}$$

$$(\Delta S_{sys} + \Delta S_{sur}) > 0 \qquad \text{For irreversible (spontaneous) process}$$

Combining the two, we have

$$\Delta S_{sys} + \Delta S_{sur} \geq 0 \text{ — ④} \begin{cases} \text{Equal to sign (=) reversible process} \\ \text{Greater than sign (>) irreversible process} \end{cases}$$

Eq. ④ may be stated as follows :

In a reversible process, the entropy of the system and the surroundings taken together remains constant while in an irreversible process, the entropy of the system and the surroundings taken together increases.

- This conclusion helps us to predict whether a given process can take place spontaneously or not, i.e, whether it is thermodynamically feasible or not.

since all processes in nature occur spontaneously, i.e. irreversibly, it follows that entropy of the universe is increasing continously. This is another statement of the second law.

- The essentials of First law and the Second law of thermodynamics were thus summed up by the German physicist Rudolf Clausius (1822-1888) as follows:

"The energy of the universe remains constant ; the entropy of the universe tends towards maximum."

→ Physical significance of entropy :→

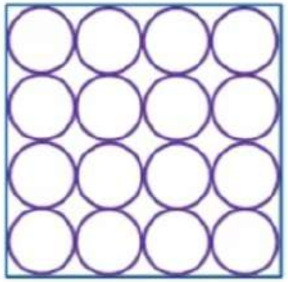
1. Entropy as a measure of the disorder of the system:→

- All spontaneous processes, such as flow of heat a hot end to cold end of a conductor, flow of electricty from a point at a higher potential to a point at a lower potential, expansion of a gas in vacuum, diffusion of a solute from a concentrated to a dilute solution, are accompained by increase in the 'disorder' of the system.

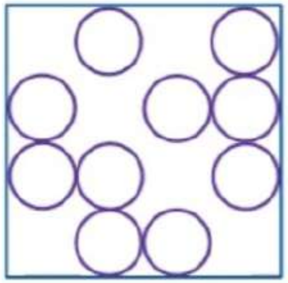
  spontaneous processes are accompained by increase in entropy as well as increase in the disorder of the system.

- The melting of a solid or evaporation of a liquid is accompanied by increase of entropy. Solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in a liquid and least in a gas. Thus, increase of entropy implies increase in order.

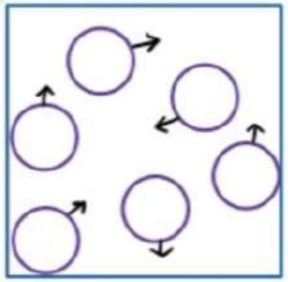
Entropy $\propto$ disorderness of the system



Solid



Liquid



Gas

disorderness → Gas > Liquid > Solid

Entropy → Gas > Liquid > Solid

- Thus, entropy is regarded as a measure of the disorder of a system. The great thermodynamicist Gibbs described entropy as a measure of the "mixed-up-ness" of a system.

2. Entropy as a measure of probability:→

- All spontaneous processes lead to increase in entropy and also to increase in disorder. When a process is spontaneous it means that it is proceeding from a less probable to a more probable state.

It appears, therefore, that there is a close relation between entropy S and the thermodynamic probability W of the state of the system both of which increase at the same time. This relationship was expressed by Boltzmann as

$$S = k \ln W + \text{Constant} \quad -①$$

Where k = Boltzmann constant, i.e., gas constant per single molecule $\left(=\frac{R}{N_A}\right)$

Boltzmann defined thermodynamic probability of a system as the ratio of the probability of the actual state to the probability of the state in which there is complete order for the same energy and volume

According to Planck, the constant in eq. ① is zero, Hence,

$$S = k \ln W \quad -②$$

Eq. ② is called the Boltzmann entropy equation. A solid at absolute zero temperature is considered to be in a most ordered state. In this case, evidently, W is unity and hence $S_0 = 0$. The entropy of crystalline solid at absolute zero, is therefore, taken as zero.

3. Entropy and Unavailable energy:→

- The internal energy of any substance is composed of various forms of energy. According to second law of thermodynamics all forms of energy are not equally convertible into useful work. The remaining part of energy which is not converted into work is alwayas unavailable and entropy is the measure of this unavailable energy.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temp.}}$$

$$\text{or} \quad \text{Unavailable energy} = \text{Entropy} \times \text{Temp.}$$

→ Entropy change in physical change:→

A. From solid phase to liquid phase :→

- When a solid changes into liquid state at its fusion point, the process requires absorption of heat (heat of fusion).
- Suppose one mole of a substance changes from solid to liquid reversibly at its fusion point T_{fus}, under a constant pressure. If ΔH_{fus} is the molar heat of fusion, then the entropy change of the process is given by

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}}$$

B. From liquid phase to vapour phase:→

- Suppose one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b, under a constant pressure. If ΔH_{vap} is the molar heat of vaporisation, the entropy change of the process is given by

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

- Since ΔH_{fus} and ΔH_{vap} are both positive, the processes of fusion and vaporisation are both accompained by increase of entropy.
- If we consider the change of state from vapour to liquid or liquid to solid, then ΔH_{fus} and ΔH_{vap} will both be negative and hence the process of condenation of vapour or freezing of a liquid would be accompained by decrease of entropy.

C. From one crystalline form to another :→

- The change in entropy when one mole of a solid substance undergoes change of state from one crystalline form to another crystalline form at the transition temp T, is given by

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T}$$

where ΔH_{tr} is the molar heat of transition of the substance.

→ Entropy as a function of V & T :→

- The dependence of entropy on volume and temperature can be represented as

$$S = f(T,V) \quad — ①$$

Differential of eq. ① is given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad — ②$$

From the First law of thermodynamic

$$dE = dq - dw$$

or $$dq = dE + dw$$

or $$TdS = dE + PdV \qquad (\because dS = \frac{dq}{T} \text{ or } dq = TdS \text{ and } dw = pdV)$$

or $$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad — ③$$

Eq. ③ is called fundamental equation of thermodynamics.

we know that internal energy is a function of T and V

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

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad — ④$$

Substitute value of dE into eq. ③

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

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

or $$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV \quad — ⑤$$

Comparing equation ② and ⑤

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V = \frac{C_V}{T} \quad — ⑥ \quad \because \left(\frac{\partial E}{\partial T}\right)_V = C_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \quad — ⑦$$

Eq. ⑥ gives variation in entropy of the system with temperature at constant volume. Since C_V has positive value, it follows that $(\partial S/\partial T)_V$ has positive value. This shows that the entropy of a system increases on increasing its temperature at constant volume. For a finite change of temperature at constant volume, we have,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T}\,dT \quad — ⑧$$

Eq. ⑦ gives the variation in entropy with volume at constant temperature, i.e. isothermal volume dependence of entropy. This expression can be simplified using the following procedure.

Differentiating eq. ⑥ with respect to volume at constant temperature, we get

$$\frac{\partial}{\partial V}\left\{\left(\frac{\partial S}{\partial T}\right)_V\right\}_T = \frac{1}{T}\frac{\partial}{\partial V}\left\{\left(\frac{\partial E}{\partial T}\right)_V\right\}_T$$

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 E}{\partial V \partial T} \quad — ⑨$$

Differentiation of eq. ⑦ with temperature at constant volume gives

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

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\left[\frac{\partial^2 E}{\partial T \partial V} + \left(\frac{\partial P}{\partial T}\right)_V\right] - \frac{1}{T^2}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

or

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\frac{\partial^2 E}{\partial T \partial V} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T^2}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \quad — ⑩$$

Since S is a state function, we have

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

Thus from eq. ⑨ and ⑩

$$\frac{1}{T}\frac{\partial^2 E}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 E}{\partial T \partial V} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T^2}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

Since E is also a state function, the above expression is reduces to

or $$0 = \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T^2}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

or $$\frac{1}{T^2}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = \left(\frac{\partial P}{\partial T}\right)_V \quad — ⑪$$

This is an important expression, known as the thermodynamic equation of state, as it relates various variables of the states.

Comparing eq. ⑦ with eq. ⑪, we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad — ⑫$$

Substituting eq. ⑥ and eq. ⑫ in eq. ②, we get

$$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad — ⑬$$

Eq. ⑬ describes the variation in entropy with temperature and volume.

→ Entropy as a function of P & T :→

– The dependence of entropy on pressure and temperature can be represented as

$$S = f(T,P) \quad — \quad ①$$

Differential of eq. ① is given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad — ②$$

From the first law of thermodynamics

$$dE = dq - dW$$

or $dq = dE + dW$

or $TdS = dE + PdV$ $\left(\because dS = \frac{dq}{T} \text{ or } dq = TdS \text{ and } dw = pdv\right)$

or $dS = \frac{1}{T}dE + \frac{P}{T}dV \quad — ③$

Eq. ③ is called fundamental equation of thermodynamics.

Enthalpy is given by

$$H = E + PV$$

or $E = H - PV$

Differentiate above equation

$$dE = dH - PdV - VdP \quad — ④$$

we know that enthalpy is a function of T and P

$$H = f(T,P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad — ⑤$$

Substitute value of dH into eq. ④

$$dE = \left\{\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP\right\} - PdV - VdP$$

Substitute value of dE into eq. ③

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

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

or $$dS = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP \quad — ⑥$$

comparing equation ② and ⑥, we get

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_P}{T} \quad — ⑦ \qquad \because \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad — ⑧$$

Eq. ⑦ gives variation in entropy of the system with temperature at constant pressure. Since C_p has positive value, it follows that $(\partial S/\partial T)_p$ has positive value. This shows that the entropy of a system increases on increasing its temperature at constant pressure. For a finite change of temperature at constant pressure, we have,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT \quad — ⑨$$

Eq. ⑧ gives the variation in entropy with pressure at constant temperature, i.e. isothermal pressure dependence of entropy. This expression can be simplified using the following procedure.

Differentiating eq. ⑦ with respect to pressure at constant temperature, we get

$$\frac{\partial}{\partial P}\left\{\left(\frac{\partial S}{\partial T}\right)_P\right\}_T = \frac{1}{T}\frac{\partial}{\partial P}\left\{\left(\frac{\partial H}{\partial T}\right)_P\right\}_T$$

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial P \partial T} \quad — ⑩$$

Differentiation of eq. ⑧ with temperature at constant pressure gives

$$\frac{\partial}{\partial T}\left\{\left(\frac{\partial S}{\partial P}\right)_T\right\}_P = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\right\}_P$$

$$\frac{\partial^2 S}{\partial T \partial P} = \frac{1}{T}\left[\frac{\partial^2 H}{\partial T \partial P} - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

or $$\frac{\partial^2 S}{\partial T \partial P} = \frac{1}{T}\frac{\partial^2 H}{\partial T \partial P} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \quad \text{— ⑪}$$

Since S is a state function, we have

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{\partial^2 S}{\partial T \partial P}$$

Thus from eq. ⑩ and ⑪

$$\frac{1}{T}\frac{\partial^2 H}{\partial P \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial T \partial P} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

Since H is also a state function, the above expression is reduces to

or $$0 = -\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] = -\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{— ⑫}$$

This is an another important expression, known as the thermodynamic equation of state, as it relates various variables of the states.

Comparing eq. ⑧ with eq. ⑫, we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{— ⑬}$$

Substituting eq. ⑦ and eq. ⑬ in eq. ②, we get

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{— ⑭}$$

Eq. ⑭ describes the variation in entropy with temperature and pressure.

→ Entropy change in ideal gases :→

- Since entropy of a system varies with the state of the system, its value for a pure gaseous substance will depends upon any two of the three variables T, P and V. Since T is taken generally as one of the variables, the second variable to be considered may be V or P. Thus, the two variables to be considered are either T and V or T and P.

– When T and V are the two variables :→

– The increase in entropy of the gas for an infinitesimally small change is given by the expression

$$dS = \frac{dq_{rev}}{T} \quad \text{—} \quad ①$$

Where dq_{rev} is small amount of heat absorbed by the system (gas) reversibly from surroundigs at temperature T.

According to first law of thermodynamics

$$\Delta E = q + w$$

$$\text{or} \quad dq_{rev} = dE - dw \quad \text{—} \quad ②$$

If the work involved is due to expansion of the gas, then, for an infinitesimal increase in volume dV against a pressure P,

$$-dw = PdV \quad \text{—} \quad ③$$

Eq. ② can be written as

$$dq_{rev} = C_V dT + PdV \quad \text{—} \quad ④ \qquad C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad dE = C_V dT$$

For one mole of an ideal gas $PV = RT$ or $P = \frac{RT}{V}$ ⑤

Substitute value of p in eq. ④

$$dq_{rev} = C_V dT + RT\frac{dV}{V} \quad — ⑥$$

divide equation ⑥ by T on both sides

$$\frac{dq_{rev}}{T} = \frac{C_V dT}{T} + \frac{RT}{T}\frac{dV}{V}$$

$$dS = C_V\frac{dT}{T} + R\frac{dV}{V} \quad — ⑦$$

For a finite change of state of a system, the entropy change (ΔS) is obtained by integrating the eq. ⑦ between the limits of the initial state 1 and final state 2. Assuming C_V to be constant within the temperature range T_1 and T_2, for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_V\int_{T_1}^{T_2}\frac{dT}{T} + R\int_{V_1}^{V_2}\frac{dV}{V}$$

Thus $$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \quad — ⑧$$

For n moles of the ideal gas, the above equation may be written as

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} \quad — ⑨$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the intial and final volumes as well as on the initial and final temperatures.

— When T and P are two variables :→

— If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$P_1V_1 = RT_1$ for one mole of gas in the initial state

or $$V_1 = \frac{RT_1}{P_1} \quad — ⑩$$

$P_2V_2 = RT_2$ for one mole of gas in the final state

or $$V_2 = \frac{RT_2}{P_2} \quad — ⑪$$

Divide eq. ⑪ by eq. ⑩

$$\frac{V_2}{V_1} = \frac{RT_2/P_2}{RT_1/P_1}$$

or $$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1} \quad — ⑫$$

Substituting this value in eq. ⑧

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{P_1T_2}{P_2T_1}$$

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

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln P_1 + R \ln T_2 - (R \ln P_2 + R \ln T_1)$$

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

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

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

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

$$\Delta S = (C_V + R) \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \text{—⑬}$$

$$\because C_P - C_V = R$$
$$C_P = C_V + R$$

For n moles of the ideal gas,

$$\Delta S = n C_P \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} \quad \text{—⑭}$$

It is evident from the above equations that the entropy change for the change of state of an ideal gas depends on the initial and final pressure as well as on the initial and final temperature.

→ Entropy change in mixing of gases:→

– For one mole of an ideal gas

$$dS = C_v \frac{dT}{T} + R\frac{dV}{V} \quad — ①$$

Integrating equation ①, assuming that C_v remains constant for an ideal gas, we have

$$S = C_v \ln T + R \ln V + S_0 \; - ②$$

Where S_0 = Integration constant

We know that $C_p - C_v = R$

or $C_v = C_p - R$

For one mole of an ideal gas

$$PV = RT$$

or $V = \frac{RT}{P}$

Substitute value of C_v and V in eq. ②

$$S = (C_p - R)\ln T + R \ln \frac{RT}{P} + S_0$$

or $S = C_p \ln T - R\ln T + R\ln R + R\ln T - R\ln P + S_0$

or $S = C_p \ln T - R\ln P + R\ln R + S_0$

or $S = C_p \ln T - R\ln p + S_0' \; - ③$ where $S_0' = R\ln R + S_0$ (another constant)

- Entropy of a system consisting of a mixture would evidently be given by the sum of individual entropies of the constituents at pressure (or concentrations) existing in the mixture. If n_1, n_2, n_3 etc. are the number of moles of the various gases present in the mixture and p_1, p_2, p_3 etc. are their partial pressure, then, the entropy of the mixture is given by

$$S = n_1(C_p \ln T - R\ln p_1 + S_0') + n_2(C_p \ln T - R\ln p_2 + S_0') + n_3(C_p \ln T - R\ln p_3 + S_0') + \text{------}$$

$$S = \Sigma n\,(C_p \ln T - R\ln p + S_0') \quad - \text{④}$$

The partial pressure (p) of an ideal gas is given by the expression

$$p = \varkappa P$$

where $\varkappa$ = mole fraction of particular gas in the mixture.

P = total pressure

substituting value of p in eq. ④

$$S = \Sigma n\,(C_p \ln T - R\ln \varkappa p + S_0')$$

or $$S = \Sigma n\,(C_p \ln T - R\ln \varkappa - R\ln P + S_0') \quad - \text{⑤}$$

Eq. ⑤ gives the entropy of mixture of ideal gases.

→ Entropy of mixing :→

- Entropy of mixing is defined as the difference between the entropy of the mixture of gases and the sum of the entropies of the separate gases, each at pressure P. Thus,

$$\Delta S_{mix} = \sum n \left(C_p \ln T - R \ln x - R \ln P + S_0' \right) - \sum n \left(C_p \ln T - R \ln P + S_0' \right) \quad \text{— ⑥}$$

$$\Delta S_{mix} = \sum n (-R \ln x)$$

$$\text{or} \quad \Delta S_{mix} = -R \sum n \ln x$$

$$\text{or} \quad \Delta S_{mix} = -R \left(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3 + \dots \right) \quad \text{— ⑦}$$

$$\text{or} \quad \Delta S_{mix} = -R \sum n_i \ln x_i \quad \text{— ⑧}$$

where n_i = number of moles of each constituent of the mixture.
x_i = mole fraction of each constituent of the mixture.

If n is the total number of moles, then, evidently,

$$n = n_1 + n_2 + n_3 + \dots$$

Dividing both sides by n, we have

$$1 = \frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} + \dots = x_1 + x_2 + x_3 + \dots = \sum x_i$$

Thus, for a total of 1 mole of the gaseous mixture ($\sum n_i = \sum x_i$), the entropy of mixing is given by

$$\Delta S_{mix} = -R \sum x_i \ln x_i \quad \text{— ⑨}$$

Since x_i is a fraction, the entropy of mixing is always positive.

→ Clausius inequality :→

- The Clausius inequality shows that the definition of entropy is consistent with the second law.
- We know that work done by the reversible engine (carnot engine) is always more than or equal to a irreversible engine, Thus

$$-dw_{rev} \geq -dw$$

or $$dw - dw_{rev} \geq 0$$

Because internal energy is a state function, its change is the same for reversible and irreversible paths between the same two states, So

$$dE = dq + dw = dq_{rev} + dw_{rev}$$

$$dw - dw_{rev} = dq_{rev} - dq$$

$$dq_{rev} - dq \geq 0$$

or $$dq_{rev} \geq dq$$

or $$\frac{dq_{rev}}{T} \geq \frac{dq}{T}$$

or $$dS \geq \frac{dq}{T} \quad - ① \qquad \because dS = \frac{dq_{rev}}{T}$$

- Eq. ① is called Clausius inequality. This expression has a great importance for discussion of the spontaneity of chemical reactions.
- If the system is isolated from its surroundings, so that $dq = 0$. The Clausius inequality implies that

$$dS \geq 0$$

So it is concluded that for a irreversible process (spontaneous process) entropy is greater than or equal to zero i.e. The entropy of universe is always increasing. The statement proved the second law of thermodynamics.

→ Gibbs and Helmholtz functions: Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities:→

- The values total entropy for reversible (equilibrium) and irreversible (spontaneous) processes are as follows-

$$(\Delta S_{sys} + \Delta S_{sur}) = 0 \quad \text{(For reversible process)}$$

$$(\Delta S_{sys} + \Delta S_{sur}) > 0 \quad \text{(For irreversible process)}$$

- If the total entropy change is positive, the process is feasible. If it is zero, the system remains in a state of equilibrium.

  However, in order to decide about the feasibility of a process, the knowledge about entropy change of the system as well as that of surroundings is required. This is not always convenient.

  Therefore, entropy change is considered in terms of other state functions which depend on state of the system only and can be determined more conveniently.

- Two such functions are the work function (A) and the free energy function (G). These are defined by the equations.

$$A = E - TS \quad - ①$$

$$G = H - TS \quad - ②$$

- Since, E, H and S depend only upon the state of a system, it is evident that the functions A and G also depend upon the state of the system.

Let the three functions in eq. ① at constant T, be A_1, E_1 and S_1 so that

$$A_1 = E_1 - TS_1 \quad - ③$$

At the same temp T the three functions in another state of the system becomes A_2, E_2 and S_2. Then,

$$A_2 = E_2 - TS_2 \quad - ④$$

Substracting eq. ③ from eq. ④

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \quad - ⑤$$

where ΔA = Change in the function A

ΔE = change in internal energy

ΔS = change in entropy of the system

- Suppose the change under reference is brought about reversibly at constant temperature T and that heat absorbed is equal to q_{rev}. Since

$\Delta S = \frac{q_{rev}}{T}$, hence, substituting in eq. ⑤

$$\Delta A = \Delta E - q_{rev} \quad - ⑥$$

From the equation of first law of thermodynamics, viz., $\Delta E = q + W$, it follows that

$W_{rev} = \Delta E - q_{rev}$ — ⑦

If work done by the system, it is negative so that

$-W_{rev} = \Delta E - q_{rev}$ — ⑧

Comparing eq. ⑥ and ⑧

$\Delta A = -W_{rev}$ — ⑨

or $-\Delta A = W_{rev}$ — ⑩

Since the process is carried out reversibly, w represents the maximum work. It is thus clear that decrease in the function A (i.e. $-\Delta A$) gives the maximum work that can be done by the system during the given change. The function A (from the German Arbeit which means work) is, therefore, termed as the work function. This is also referred to as Helmholtz free energy or Helmholtz function.

The German physicist Hermann von Helmholtz (1821-1894) was a versatile scientist who made contribution to optics, thermodynamics, acoustics and physiology.

- If G_1; H_1 and S_1 represent the thermodynamic functions in the intial state and G_2, H_2 and S_2 in the final state, at constant temp, then from eq. ②

$G_1 = H_1 - TS_1$ — ⑪

and $G_2 = H_2 - TS_2$ — ⑫

Substracting eq. ⑪ from eq. ⑫

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $$\Delta G = \Delta H - T\Delta S \quad — ⑬$$

We know that enthalpy change at constant pressure is given by

$$\Delta H = \Delta E - P\Delta V$$

$$\Delta G = \Delta E - P\Delta V - T\Delta S \quad — ⑭$$

OR $$\Delta G = \Delta A - P\Delta V \quad — ⑮ \qquad (\because \Delta A = \Delta E - T\Delta S)$$

Eq. ⑮ represents relationship between G and A

since $\Delta A = -W$ (From eq. 9)

hence $\Delta G = -W - P\Delta V$

or $$-\Delta G = W - P\Delta V \quad — ⑯$$

The quantity PΔV is the work done by the gas on expansion against the constant external pressure P. Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the net work. Thus,

$$\text{Net work} = W - P\Delta V = -\Delta G \quad — ⑰$$

- Hence, $-\Delta G$ is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called Gibbs function or Gibbs free energy or simply free energy. Thus, $-\Delta G$ is the measure of the decrease in free energy. The net work that is measure may be electrical work or chemical work. This quantity is of great importance in physical chemistry; it is named in honour of the great American physicist, J.W. Gibbs(1839-1903)

→ Variation of G and A with P, V and T :→

① Variation of G with T and P :→

– The Gibbs free energy is given by

$$G = H - TS$$ — ①

Since $H = E + PV$

hence $G = E + PV - TS$ — ②

Differentiate eq. ②

$$dG = dE + PdV + VdP - TdS - SdT$$ — ③

The first law equation for an infintesimal change is

$$dq = dE - dW$$ — ④

If the work done is only due to expansion, then,

$$-dW = PdV$$

$$\therefore \quad dq = dE + PdV$$ — ⑤

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad TdS = dq$$ — ⑥

From equation ③, ⑤ and ⑥

$$dG = dq + VdP - dq - SdT$$

or $dG = VdP - SdT$ — ⑦

Eq. ⑦ gives change of free energy when a system undergoes, reversibly, a change of pressure as well as change of temperature.

If pressure remains constant, i.e. $dp = 0$, then, from eq. ⑦

$$dG = -SdT$$

$$\text{or} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad — ⑧$$

If temperature remains constant, i.e. $dT = 0$, then, from eq. ⑦

$$dG = VdP$$

$$\text{or} \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad — ⑨$$

- If the free energy of a system be G_1 in initial state and G_2 in the final state when a change in pressure has taken place, at constant temp. Then integrating, eq. $dG = VdP$, the free energy change, ΔG is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP \quad — ⑩$$

where P_1 and P_2 are the initial and final pressures.

For one mole of an ideal gas $PV = RT$

$$\text{or} \quad V = \frac{RT}{P}$$

Substitute value of V in eq. ⑩

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

or $$\Delta G = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \quad — ⑪$$

$\left[\because \right.$ For an isothermal process
$P_1V_1 = P_2V_2$
or $\left. \frac{P_2}{P_1} = \frac{V_1}{V_2} \right]$

Where V_1 and V_2 are initial and final volumes

For n moles of the gas

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} \quad — ⑫$$

→ Variation of G and A with P, V and T :→

② Variation of A with T and V :→

– The Helmholtz work function is given by

$$A = E - TS \quad — ①$$

Differentiate eq. ①

$$dA = dE - TdS - SdT \quad — ②$$

The first law equation for an infintesimal change is

$$dE = dq - dw$$

$$\text{or} \quad dE = dq - PdV \quad — ③ \qquad \because dw = PdV$$

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad dq = TdS \quad — ④$$

From equation ③ and ④

$$dE = TdS - PdV \quad — ⑤$$

Substitute value of dE in equation ②

$$dA = TdS - PdV - TdS - SdT$$

$$\text{or} \quad dA = -PdV - SdT \quad — ⑥$$

Eq. ⑥ gives change of Helmholtz function when a system undergoes, reversibly, a change of volume as well as of temperature.

If volume remains constant, i.e., $dV = 0$, then, from eq. ⑥

$$dA = -SdT$$

$$\text{or} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad — ⑦$$

on the other hand, if temperature remains constant, i.e., $dT = 0$, then, from eq. ⑥

$$dA = -PdV$$

$$\text{or} \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad — ⑧$$

→ The Gibbs - Helmholtz equation: →

– The change in the free energy with temperature and pressure is given by following equation.

$$dG = VdP - SdT \quad - ①$$

At constant pressure $dP = 0$

$$dG = -SdT \quad - ②$$

Let G_1 = Free energy of system in its initial state at temperature T

and G_2 = Free energy of system in its final state at temperature T

Then

$$dG_1 = -S_1 dT \quad - ③$$

$$dG_2 = -S_1 dT \quad - ④$$

subtracting eq. ③ from eq. ④, we have

$$d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$d(\Delta G) = -\Delta S dT \quad - ⑤$$

As the pressure is constant

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S \quad - ⑥$$

we know that

$$\Delta G = \Delta H - T\Delta S$$

or

$$\frac{(\Delta G - \Delta H)}{T} = -\Delta S \quad - ⑦$$

From eq. ⑥ and ⑦

$$\frac{(\Delta G - \Delta H)}{T} = \left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

OR $$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \quad — ⑧$$

Eq. ⑧ is known as the Gibbs – Helmholtz equation. It is applicable to all processes occuring at constant pressure. It has been used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy change at two different temperatures are known.

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta E + T\left(\frac{\partial(\Delta A)}{\partial T}\right)_V \quad — ⑨$$

→ A and G as criteria for thermodynamic equilibrium and spontaneity :→

- The change of entropy for a given change of state is a definite quantity, independent of fact whether the change is brought about reversibly or irreversible. But, mathematically, it is given for a small change by the equation, only if the change (involving expansion of an ideal gas) is brought about reversibly.

$$dS = \frac{dq_{rev}}{T} = \frac{dE + PdV}{T} \quad - ① \qquad \left\{ \begin{array}{l} \because \ dq = dE - dW \\ -dW = PdV \end{array} \right.$$

$$\text{or} \quad TdS = dq_{rev} = dE + PdV \quad - ②$$

Suppose the small change of state is brought about irreversily. Now the heat absorbed by the system will be less ($\because q_{irr} < q_{rev}$). But the entropy change dS will have the same value. Hence, for an irreversible process.

$$TdS > q_{rev}$$

we may thus write

$TdS = dE + PdV$ (For a reversible process)

$TdS > dE + PdV$ (For an irreversible process)

combining the two, we have

$$TdS \geq dE + PdV \quad — ③$$

Equal to sign (=) for a reversible process

and Greater than sign (>) for an irreversible process

(A) Criteria in terms of change of work function :→

- Work function is given by

$$dA = dE - TdS \quad - \quad ④$$

Eq. ③ can be writtes as

$$dE - TdS \leq -PdV \quad - \quad ⑤$$

From eq. ④ and ⑤

$$dA \leq -PdV \quad - \quad ⑥$$

At constant volume

$$dA \leq 0$$

Equal to sign (=) for a reversible process
and less than sign (<) for an irreversible process

(B) Criteria in terms of change of Free energy :→

- Gibbs free energy is given by

$$G = H - TS$$

or $$G = E + PV - TS \quad - \quad ⑦ \quad (\because H = E + PV)$$

differentiate eq. ⑦

$$dG = dE + PdV + VdP - TdS - SdT \quad - \quad ⑧$$

From eq. ③ and ⑧

$$dG \leq TdS + VdP - TdS - SdT$$

or $dG \leq VdP - SdT$

At constant temperature and pressure

$$dG \leq 0$$

Equal to sign (=) for a reversible process
and less than sign (<) for an irreversible process

- The criteria in terms of free energy change viz. $(\partial G)_{T,P} \leq 0$, is most useful criteria to decide between reversibility and irreversibility of a process.

If, $\Delta G < 0$, −ve, process is irreversible or spontaneous

If, $\Delta G = 0$, process is reversible or equilibrium

If, $\Delta G > 0$, +ve, process will not proceed

→ Work function and free energy change advantage over entropy change :→

- The sum total of entropy change of the system and surroundings (i.e. $\Delta S_{sys} + \Delta S_{surr}$) serves as a criteria of spontaneity or feasibility of a process. Thus, we have to compute the entropy change of the system as well as that of the surroundigs in order to decide the feasibility of a process. This is not always convenient.

In case of work function or free energy change, feasibility of a process can be determined by computing only work function or free energy change of the system only and this is always convenient.

→ Nernst heat theorem :→

- This is an old generalisation but still has relevance as the forerunner of the third law of thermodynamics.

From Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \quad — ①$$

or

$$\Delta G - \Delta H = T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \quad — ②$$

where ΔG = Change in free energy

ΔH = Change in enthalpy

At absolute zero (i.e. $T=0$), $\Delta G = \Delta H$

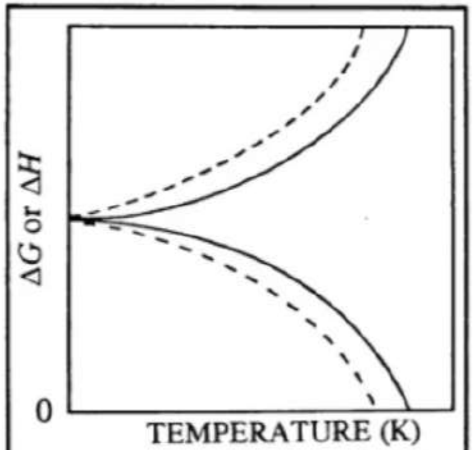


Fig. Variation of ΔG and ΔH with temperature.

- Richards, by measuring EMFs of cells at different temperatures, found that the value $\partial(\Delta G)/\partial T$ decreases with decrease in temperature and, therefore, concluded that ΔG and ΔH tend to approach each other more and more closely as temperature is lowered.
- Nernst, relying on this data, made an important suggestion that the value of $\partial(\Delta G)/\partial T$ approaches zero gradually as the temperature is lowerd towards the absolute zero. This is known as Nernst heat theorem.
- According to this theorem, ΔG and ΔH not only become equal to each to each other at absolute zero but also approaches each other asymptotically, that is, gradually at temperature close to absolute zero.

Thus, the approach of ΔG and ΔH towards each other is represented by the full lines and not represented by the dotted lines.

- Mathematically, the theorem may be expressed as

$$\underset{T\to 0}{Lt}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \underset{T\to 0}{Lt}\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = 0 \quad — ③$$

Lt = Limiting value

From the second law of thermodynamics

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S \quad — ④$$

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P$$

(Kirchhoff equation) — ⑤

where ΔS = Entropy change of the reaction

ΔC_p = Difference in the heat capacities of the products and reactants.

From eq. ③, ④ and ⑤

$$\underset{T\to 0}{Lt}\,\Delta S = 0 \quad — ⑥$$

and $$\underset{T\to 0}{Lt}\,\Delta C_p = 0 \quad — ⑦$$

The significance of these equations is that the entropy change of reaction tends to approach zero and that the difference between the heat capacities of products and reactants also tends to apprach zero as the temperature is lowered towards the absolute zero.

The Nernst theorem holds good only in the case of pure solids.

→ Third law of thermodynamics :→

- According to Nernst heat theorem

$$\underset{T\to 0}{\mathrm{Lt}}\ \Delta S = 0 \quad — \quad ①$$

$$\underset{T\to 0}{\mathrm{Lt}}\ \Delta C_p = 0 \quad — \quad ②$$

According to eq. ②, at absolute zero, the heat capacities of products and reactants in solid state are identical. This leads to the suggestion that at absolute zero, all substances have the same heat capacity.

The quantum theory, as applied to heat capacities of solids, has shown that heat capacities of solids tends to become zero at 0 K.

The Nernst heat theorem may, therefore, be written as

$$\underset{T\to 0}{\mathrm{Lt}}\ C_p = 0 \quad — \quad ③$$

According to eq. ①, ΔS becomes zero at absolute zero, i.e. the entropy change of a process involving solids becomes zero at 0 K. In other words, the absolute entropies of products and reactants in the solid state are identical.

Planck, therefore, suggested that entropies of all pure solids approaches zero at 0 K, i.e.,

$$\underset{T\to 0}{\mathrm{Lt}}\ S = 0 \quad — \quad ④$$

- This statement was the basis of Third law of thermodynamics :

"At the absolute zero of temperature, the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline solid."

In a perfect crystal, at absolute zero temperature, there is a state of perfect order, i.e., zero disorder and hence of zero entropy.

Walther Nernst (1864-1941), the German chemist, was awarded the 1920 Chemistry Nobel Prize for his work in thermochemistry. He also did pioneering work in electrochemistry.

→ Evaluation of absolute entropy from heat capacity data :→

– For an infinitesimal small change of state of the system, the entropy change is given by.

$$dS = \frac{dq}{T} \quad — ①$$

At constant pressure

$$(\partial S)_p = \frac{(\partial q)_p}{T} \quad - ②$$

or $$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial q}{\partial T}\right)_p \times \frac{1}{T}$$

By definition

$$\left(\frac{\partial q}{\partial T}\right)_p = C_p$$

∴ $$\left(\frac{\partial S}{\partial T}\right)_p = C_p \times \frac{1}{T}$$

or at constant pressure $$dS = \left(\frac{C_p}{T}\right)_p dT \quad — ③$$

For a perfectly crystalline substance, the absolute entropy S=0 at T=0, Therefore

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} \left(\frac{C_p}{T}\right) dT$$

or $$S_T = \int_0^T C_p \frac{dT}{T} = \int_0^T C_p \, d\ln T \quad — ④$$

- The integral in eq. ④ can be evaluated by measuring C_p at various temperatures between $T=0$ and temperature T and then ploting C_p against $\ln T$ and determining the area under the curve between $T=0$ and the required temp T. This area gives directly the value of S_T.

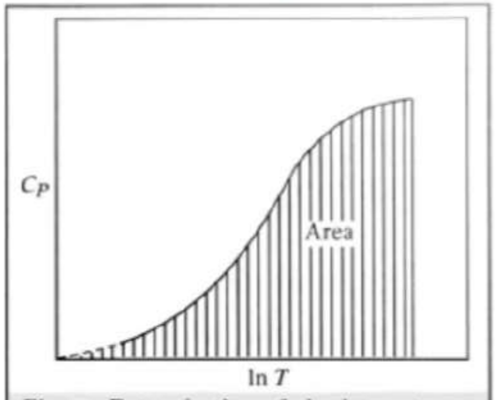


Fig. Determination of absolute entropy.

- Since it is not possible to obtain the value of C_p at absolute zero, heat capacities are measured up as to low a temperature as possible, usually up to 15 K and the value at the absolute zero is obtained by extrapolation.
- Eq. ④ Can be written as

$$S_T = \int_0^{T^*} C_p \frac{dT}{T} + \int_{T^*}^{T} C_p \frac{dT}{T} \quad - ⑤ \qquad \text{where } 0 < T^* < 15\,K.$$

The first integral of eq. ⑤ is evaluated with the help of the Debye theory of heat capacities of crystalline substances according to which, at very low temperatures ($0 < T^* < 15\,K$)

$$C_p \simeq C_v \simeq aT^3 \quad - ⑥$$

where a is an empirical constant. Eq. ⑥ is called Debye T^3 law or Debye third power law.

Eq. ⑤ may be written as

$$S_T = \int_0^{T^*} aT^3 \frac{dT}{T} + \int_{T^*}^{T} C_p \frac{dT}{T} = \frac{1}{3} a (T^*)^3 + \int_{T^*}^{T} C_p \frac{dT}{T} \quad - ⑦$$

The second integral in eq. ⑦ is evaluated from experimental measurement of heat capacities.

– Suppose, it is required to determine absolute entropy of a gas at 25°c under atmospheric pressure. This would be equal to the sum of the entropy changes involved in the following reversible processes. It is assumed that substance in solid state exists in two allotropic forms α and β.

1. Heating the crystalline solid from absolute zero to temp T^*, where $0 < T^* < 15K$ and evaluating the entropy change with the aid of the Debye theory. Let the entropy change be ΔS_1

$$\Delta S_1 = \int_0^{T^*} aT^3 \frac{dT}{T} = \frac{1}{3} a(T^*)^3 \quad — ⑧$$

2. Heating the crystalline solid from T^* to T_{tr}. (T_{tr} = transistion temp at which the crystalline solid changes from one allotropic form α to allotropic form β. The entropy change in this process is given by

$$\Delta S_2 = \int_{T^*}^{T_{tr}} C_{p,s}(\alpha)\, d\ln T \quad — ⑨$$

where $C_{p,s}(\alpha)$ = the heat capacity of solid in allotropic form α.

3. Transition of the solid from allotropic form α to allotropic form β at the transition temp T_{tr}. The entropy change in this process is given by

$$\Delta S_3 = \frac{\Delta H_{tr}}{T_{tr}} \quad — ⑩$$

where ΔH_{tr} = the molar enthalpy of transition.

4. Heating the solid in allotropic form β up to its fusion point T_{fus}. The entropy change in this process is given by

$$\Delta S_4 = \int_{T_{tr}}^{T_{fus}} C_{p,s}(\beta)\, d\ln T \quad — ⑪$$

Where $C_{p,s}(\beta)$ = heat capacity of substance in allotropic form β

5. Changing the solid in allotropic form β into the liquid state at fusion temperature T_{fus}. The entropy change of this process is given by

$$\Delta S_5 = \frac{\Delta H_{fus}}{T_{fus}} \quad — ⑫$$

where ΔH_{fus} = molar enthalpy of fusion of the substance.

6. Heating the liquid from its freezing point (T_{fus}) to its boiling point (T_b). The entropy change involved in this case is given by

$$\Delta S_6 = \int_{T_{fus}}^{T_b} C_{p,l}\, d\ln T \quad — ⑬$$

where $C_{p,l}$ = heat capacity of substance in liquid state.

7. Changing the liquid into the gaseous state at the temperature T_b. The entropy change is given by

$$\Delta S_7 = \frac{\Delta H_{vap}}{T_b} \quad — ⑭$$

where ΔH_{vap} = molar enthalpy of vaporisation of the substance.

8. Heating the gas from T_b to the required temperature, i.e. 25°c (298·15 K). The entropy change involved in this process is given by

$$\Delta S_8 = \int_{T_b}^{298 \cdot 15} C_{p,g} \, d\ln T \quad - ⑮$$

wher $C_{p,g}$ = heat capacity of the gaseous state at constant pressure.

- The absolute entropy of the gas at 298·15 K (25°c), S_T, is equal to the sum of all the entropy changes listed above. Thus,

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$$

- Absolute entropy of HCl at 25°c determined by above process is given in following table.

Contribution	J K^{-1} mol^{-1}
1. Extrapolation from 0 to 15 K [using the Debye T^3 law]	1·3
2. $\int C_P \, d\ln T$ for solid α from 15 to 98·36 K	29·5
3. Transition, solid α ⟶ solid β, 1190/98·36	12·1
4. $\int C_P \, d\ln T$ for solid β from 98·36 to 158·91 K	21·1
5. Fusion, 1992/158·91	12·6
6. $\int C_P \, d\ln T$ for liquid from 158·91 to 188·07 K	9·9
7. Vaporization, 16150/188·07	85·9
8. $\int C_P \, d\ln T$ from 188·07 to 298·15 K	13·5
	∴ $S^{\circ}_{298 \cdot 15}$ = **185·9**

→ Statement and concept of residual entropy:→

- Entropies calculated by using the Third law are called thermal entropies and entropies calculated by using the method of statistical mechanics (for example, by using the Boltzmann entropy equation at 0 K) are called statistical entropies. The results of statistical mechanics are more accurate, i.e., values of statistical entropies are more accurate than thermal entropies.
- It is found that the thermal entropies are somewhat smaller than the statistical entropies and the deviation ranging from 3·1 to 4·8 J K^{-1} mol^{-1}.

  Thus, entropies of substance (such as H_2, D_2, CO, NO, N_2O, H_2O, etc.) are not zero at 0 K, as the Third law formulates, but are finite. These entropies are called residual entropies.
- The existance of residual entropy in a crystal at 0 K is probably due to the alternative arrangement of molecule in the solid. Such arrangements are shown in fig.

CO CO CO CO

CO CO CO CO

Perfect crystal CO

CO CO OC OC

CO OC OC CO

Actual crystal CO

NNO NNO NNO NNO

NNO NNO NNO NNO

Perfect crystal of N_2O

NNO NNO ONN ONN

NNO ONN ONN NNO

Actual crystal of N_2O

- It is evident from experimental values of residual entropies of CO and N_2O, that the two alternative orientations of the CO and N_2O molecules in the solid state at 0 K are not completely random.