## THE SECOND LAW

**Limitation of the first law:**

- The first law of Thermodynamics doesn't place any restriction on the conversion of energy from one form to another; it simply requires that the total quantity of energy be the same before and after the convention.
- The first law can't give any information regarding feasibility and direction of a process.
- The first law states that energy of one form can be converted into an equivalent amount of energy of another form. But heat can't be completely converted into an equivalent amount of work without producing some changes elsewhere.

**Spontaneous Processes:** Processes which do not require work to be done to bring it about are called spontaneous processes.

Example of such changes—

i) Expansion of a gas to fill the available volume.

ii) A hot body cools to the temperature of its surroundings.

However, opposite of these changes — i.e.

i) to confine a gas to a smaller volume,

ii) cooling of an object with a refrigerator, do not occur spontaneously; each one must be brought about by doing work.

All natural processes proceed spontaneously (i.e., without external aid) and are thermodynamically irreversible in nature.

Direction of a spontaneous change is related to the distribution of energy. Spontaneous changes are always accompanied by a dispersal of energy into a more disordered form. It is highly improbable that the chaotic distribution of energy will become organized into uniform motion. Therefore, the direction of spontaneous change will be one that leads to the greater chaotic dispersal of the total energy of an isolated system.

A gas does not spontaneously contract, because to do so the chaotic motion of its molecules would have to bring them all into the same region of the container. But the opposite change - the expansion is spontaneous because the molecules have natural tendency for increasing chaos.

**The second law of thermodynamics:**

**Kelvin - Planck statement:** "It is impossible for a system to undergo a cyclic process whose only effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings."

The second law tells us that it is impossible to have a cyclic machine that completely converts a certain amount of heat into mechanical work.

All other forms of energy can be completely converted into heat, but the complete conversion of heat into any other form of energy (e.g. work) can't take place without leaving some changes in the system or surroundings.

**Clausius Statement:** "It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a cold reservoir and the flow of an equal amount of heat out of the system into a hot reservoir."

**Heal Engine:** A heat engine is a machine that converts heat into work. e.g., steam engine. It works by withdrawing a quantity of heat $|q_H|$ from a hot reservoir, performs $|w|$ amount of work and $|q_C|$ amount of heat is delivered to the sink.

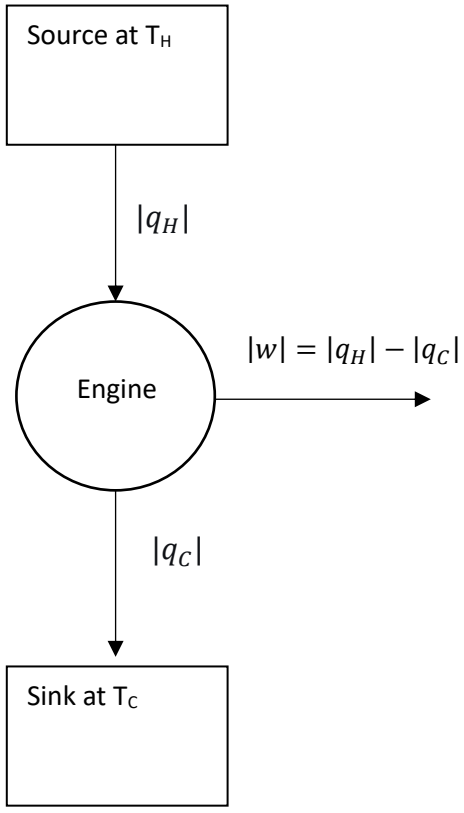
Efficiency of heat engine,

$$\in = \frac{work\ performed}{heat\ absorbed}$$

$$or, \in = \frac{|w|}{|q_H|}$$

$$\in = \frac{|q_H| - |q_C|}{|q_H|}$$

$$\in = 1 - \frac{|q_C|}{|q_H|} \ldots\ldots\ldots (1)$$



**Carnot Cycle**

A Carnot cycle is defined as a reversible cycle that consists of two isothermal steps at different temperatures and two adiabatic steps. The working material for a Carnot cycle is $n$ mol of a perfect gas. All stages are thermodynamically reversible.

**Stage 1: Reversible isothermal expansion at $T_H$**

The system is at equilibrium with the heat source at $T_H$ and expands from $p_1V_1$ to $p_2V_2$. In the process, it withdraws $q_H$, amount of heat from the source.

Here,

$$w_1 = -nRT_H \, ln \, \frac{V_2}{V_1}$$

Also, $\Delta U = 0$ (isothermal process, T=constant)

$$\therefore q_H = -w_1 = nRT_H \, ln \, \frac{V_2}{V_1}$$

**Stage 2: Reversible adiabatic expansion**

The system is removed from the contact of the hot source and is enclosed with thermal insulation. The gas is made to expand adiabatically from $p_2V_2$ to $p_3V_3$. The temperature of the system drops from $T_H$ to $T_C$, the temperature of the sink.

$$w_2 = C_V(T_C - T_H)$$

$$q = 0$$

**Stage 3: Reversible isothermal compression at $T_C$**

The system is brought to thermal equilibrium with the sink at $T_C$. The gas is compressed from $p_3V_3$ to $p_4V_4$ at $T_C$. During compression it delivers $q_C$ amount of heat to the sink.

$$w_3 = -nRT_C \, ln \, \frac{V_4}{V_3}$$

$$q_C = +nRT_C \, ln \, \frac{V_4}{V_3}$$

**Stage 4: Reversible adiabatic compression**

The system is removed from the sink, surrounded by thermal insulation and compressed adiabatically from $p_4V_4$ to $p_1V_1$. Temperature increases from $T_C \rightarrow T_H$.

$$w_4 = C_V(T_H - T_C)$$

$$q = 0$$

Total work performed,

$$w_{rev} = w_1 + w_2 + w_3 + w_4$$
$$= -nRT_H \, ln \, \frac{V_2}{V_1} + C_V(T_C - T_H) - nRT_C \, ln \, \frac{V_4}{V_3} + C_V(T_H - T_C)$$
$$= -nRT_H \, ln \, \frac{V_2}{V_1} - nRT_C \, ln \, \frac{V_4}{V_3}$$

Again, for adiabatic changes BC and DA,

$$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$$
$$T_C V_4^{\gamma-1} = T_H V_1^{\gamma-1}$$

Dividing,

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$
$$or, \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Using this, we get,

$$w_{rev} = -nRT_H \ln\frac{V_2}{V_1} - nRT_C \ln\frac{V_1}{V_2}$$
$$= -nRT_H \ln\frac{V_2}{V_1} + nRT_C \ln\frac{V_2}{V_1}$$
$$= -nR \ln\frac{V_2}{V_1}(T_H - T_C)$$

Carnot efficiency,

$$\in_{rev} = \left(\frac{|w|}{|q_H|}\right)_{rev}$$
$$= \frac{nR \ln\frac{V_2}{V_1}(T_H - T_C)}{nRT_H \, ln \, \frac{V_2}{V_1}}$$
$$= \frac{T_H - T_C}{T_H}$$
$$\in_{rev} = 1 - \frac{T_C}{T_H} \ldots\ldots\ldots (2)$$

Equation (2) gives the efficiency of any reversible engine working between the temperature of the source and the sink. Efficiency depends only on the temperature difference $(T_H - T_C)$ and is independent of the nature of the working substance.

For $\in = 1$,

either $T_H \rightarrow \infty$

or $T_C \rightarrow 0$,

both can't be realized in practice.

Therefore, heat can't be transformed completely into work.

From equations (1) and (2),

$$1 - \frac{|q_C|}{|q_H|} = 1 - \frac{T_C}{T_H}$$

$$or, \frac{|q_C|}{|q_H|} = \frac{T_C}{T_H}$$

$$or, \frac{|q_C|}{T_C} = \frac{|q_H|}{T_H}$$

**Concept of Entropy, S**

The first law led to the introduction of the internal energy U. The second law uses another state function entropy S to identify the direction of a spontaneous change.

We know that in a Carnot cycle,

$$\frac{q_H}{T_H} = \frac{-q_C}{T_H}$$

$$\Rightarrow \frac{q_H}{T_H} + \frac{q_C}{T_H} = 0$$

where $q_H$ is the heat received from the source at temperature $T_{\mathrm{H}}$ and $q_C$ is the heat delivered to the sink at temperature $T_{\mathrm{C}}$.

In a reversible Carnot cycle,

$$\oint \frac{dq_{rev}}{T} = \frac{q_H}{T_H} + \frac{q_C}{T_H} = 0$$

Now, any reversible cycle can be approximated as a collection of Carnot cycles (Figure 1).

As shown in the figure 1, a reversible cyclic process represented by $pbcra$ consists of large numbers of infinitesimal isothermals followed by adiabates. Let us consider the Carnot cycle $pqrs$, where $pq$ and $rs$ are the isotherms with heat changes $dq'_H$ at $T'_H$ and $dq'_C$ at $T'_C$ respectively.

Heat changes along the adiabats $qr$ and $ps$ are zero:

$$\frac{dq'_H}{T'_H} + \frac{dq'_C}{T'_C} = 0$$

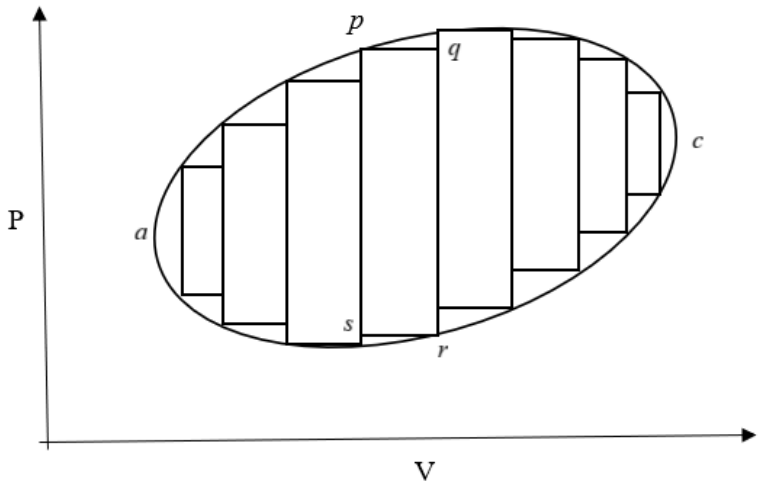



**Figure 1**

For other Carnot cycle, similarly,

$$\frac{dq_H''}{T_H''} + \frac{dq_C''}{T_C''} = 0$$

and so on. Hence, for the complete reversible cycle,

$$\sum \frac{dq_{rev}}{T} = 0$$

The collection of Carnot cycles considered in the reversible cycle $pbcra$ can not cover the complete cycle, but if we consider infinite number of cycles, the isothermals of the Carnot cycles match the overall cycle exactly, and the sum becomes an integral

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

Since the integral of $\frac{dq_{rev}}{T}$ in a thermodynamic cycle is zero, it indicates that $\frac{dq_{rev}}{T}$ is the differential of a state function. This state function is called entropy $S$. So, its differential is given by

$$dS = \frac{dq_{rev}}{T}$$

So,

$$\oint dS = 0$$

**The thermodynamic definition of entropy**

The defining equation of entropy is

$$dS = \frac{dq_{rev}}{T}$$

This equation is applicable only for a reversible process in a closed system.

The entropy change on going from state 1 to state 2 during a process equals to

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

Entropy is an extensive state function and $dS$ is an exact differential. The unit is $JK^{-1}$.

**Entropy change in reversible (non-cyclic) processes**

Reversible processes are finely balanced changes in which the system is in equilibrium with its surroundings at every stage. Each infinitesimal step along a reversible path occurs without dispersing energy chaotically and hence without increasing the entropy. Therefore, reversible processes don't generate entropy. This is justified in the following discussions.

In a reversible process, any heat flow between system and surroundings must occur with no finite temperature difference. Let $dq_{rev}$ be the heat flow into the system from the surroundings during an infinitesimal change of the reversible process. In a reversible process, heat absorbed by the process is exactly equal to that lost by the surroundings. So, the corresponding heat flow into the surroundings is $-dq_{rev}$.

$$\therefore dS_{sys} = \frac{dq_{rev}}{T_{sys}}$$

And entropy change in the surroundings is given by

$$dS_{surr} = -\frac{dq_{rev}}{T_{surr}}$$

Therefore, total entropy change is

$$\begin{aligned} dS_{total} &= dS_{sys} + dS_{surr} \\ &= \frac{dq_{rev}}{T_{sys}} - \frac{dq_{rev}}{T_{surr}} \\ &= 0 \quad [as\ T_{sys} = T_{surr}] \end{aligned}$$

(i) **Entropy change in a reversible isothermal expansion of a perfect gas:**

Let us consider $n$ mol of an ideal gas undergoing reversible and isothermal expansion from $V_1$ to $V_2$. Entropy change is given by,

$$\Delta S_{sys} = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T}\int_1^2 dq_{rev} = \frac{q_{rev}}{T}$$

For isothermal change, $\Delta U = 0$

From 1st law,

$$\Delta U = 0 = q_{rev} + w_{rev}$$

$$\Rightarrow q_{rev} = -w_{rev}$$

Now,

$$w_{rev} = -nRTln\frac{V_2}{V_1}$$

$$\therefore q_{rev} = +nRTln\frac{V_2}{V_1}$$

$$\therefore \Delta S_{sys} = \frac{q_{rev}}{T} = nRln\frac{V_2}{V_1}$$

Now, $p_1V_1 = p_2V_2$

$$\therefore \Delta S_{sys} = nRln\frac{V_2}{V_1} = nRln\frac{p_1}{p_2}$$

Since the surroundings loses exactly equivalent amount of heat, the corresponding heat flow into the surroundings is $-q_{rev}$ and its entropy change is

$$\Delta S_{surr} = -\frac{q_{rev}}{T} = -nRln\frac{V_2}{V_1}$$

Therefore, total entropy change is

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = nRln\frac{V_2}{V_1} - nRln\frac{V_2}{V_1} = 0$$

**Prob**: Calculate the entropy change of a system containing a perfect gas when 1.00 mol of the gas doubles its volume at any temperature.

Sol$^n$: Here, $V_2 = 2V_1 \Rightarrow \frac{V_2}{V_1} = 2$

$$\therefore \Delta S_{sys} = 2.303nR\ log\frac{V_2}{V_1} = 2.303 \times 1\ mol\ \times 8.314\ JK^{-1}mol^{-1} \times log2 = 5.67\ JK^{-1}$$

**Prob**: Calculate the change in entropy of the system when the pressure of a perfect gas is changed isothermally from 5 $atm$ to 10 $atm$.

**Prob:** Calculate the entropy change when Ar at 298 K, 100 atm in a container of volume 500 $cm^3$ is allowed to expand to 1000 $cm^3$.

(ii) **Entropy change of phase transition at the transition temperature**

When a substance changes its phase, a change in the degree of molecular order occurs. Therefore, a phase transition always occurs with a change in entropy. e.g. when a substance vaporizes, a compact condensed phase changes into a widely dispersed gas, as a result the entropy of the substance increases considerably. The entropy of a solid substance increases when it melts to liquid.

At the transition temperature, any transfer of heat between the system and its surrounding is reversible because the two phases in the system are in equilibrium.

At constant temperature, $T_{trs}$,

$$\Delta S_{sys} = \int_1^2 \frac{dq_{rev}}{T_{trs}} = \frac{1}{T_{trs}} \int_1^2 dq_{rev} = \frac{q_{rev}}{T_{trs}}$$

where, $q_{rev}$ is the heat of transition.

At constant pressure $p$,

$$q_{rev} = q_p = \Delta_{trs} H$$

$$\therefore \Delta S_{sys} = \frac{\Delta_{trs} H}{T_{trs}}$$

If the transition is exothermic ($\Delta_{trs} H < 0$), as in freezing or condensation, the entropy change is negative. It is consistent with the system becoming more ordered when a solid is formed from a liquid. If the transition is endothermic ($\Delta_{trs} H > 0$), as in melting, then the entropy change is positive, which is consistent with the system becoming more disordered.

**Trouton's Rule**: For a wide range of liquids, standard molar entropy of vaporization is about 85 $JK^{-1}mol^{-1}$. This empirical observation is called Trouton's Rule.

The explanation for this rule is that a comparable amount of disorder is generated when any liquid evaporates and becomes a gas.

Water is an exception to Trouton's rule. Standard molar entropy of vaporization of water is 109.1 $JK^{-1}mol^{-1}$. Due to the presence of hydrogen bonding, molecules of liquid water are less

random than other liquids. As a result, entropy of the liquid water is less than other liquid. Therefore, vaporization entropy (= entropy of vapour phase - entropy of liquid phase) is higher.

**Prob:** Predict the standard molar enthalpy of vaporisation of bromine given that it boils at 59.2° C.

Sol$^{n}$: Here, transition temperature, $T_{trs} = T_b = 59.2 + 273.15 = 332.4K$

There is no hydrogen bonding in liquid bromine. So, it is safe to use Trouton's rule.

$$\Delta S_{sys} = \frac{\Delta_{trs}H}{T_{trs}} = 85\, JK^{-1}mol^{-1}$$

$$\Rightarrow \frac{\Delta_{vap}H}{T_b} = 85\, JK^{-1}mol^{-1}$$

$$\Rightarrow \Delta_{vap}H = 85\, JK^{-1}mol^{-1} \times T_b$$

$$\Rightarrow \Delta_{vap}H = 85\, JK^{-1}mol^{-1} \times 332.4\, K$$

$$\Rightarrow \Delta_{vap}H = 28249.75\, Jmol^{-1}$$

**Entropy change in irreversible processes**

Let us consider an infinitesimally small stage of an irreversible process taking place in a system. For this infinitesimal change, the application of the first law of thermodynamics gives

$$dU_{irr} = dq_{irr} + dw_{irr}$$

If the same change occurs reversibly, then

$$dU_{rev} = dq_{rev} + dw_{rev}$$

Since, internal energy is a state function, for a given change in the state of the system

$$dU_{irr} = dU_{rev}$$

Hence, we have

$$dq_{rev} + dw_{rev} = dq_{irr} + dw_{irr}$$

We know that $|dw_{rev}| > |dw_{irr}|$ which means the amount of heat absorbed in a reversible process is greater than that in an irreversible process for the same change of state of the system:

$$dq_{rev} > dq_{irr}$$

Again,

$$dS_{sys} = \frac{dq_{rev}}{T}$$

$$\Rightarrow \mathrm{T}dS_{sys} = dq_{rev}$$

Therefore,

$$T\mathrm{d}S_{sys} > dq_{irr}$$

$$\Rightarrow \mathrm{d}S_{sys} > \frac{dq_{irr}}{T}$$

This inequality is known as Clausius inequality.

For the complete process,

$$\Delta S_{sys} > \frac{q_{irr}}{T}$$

Surroundings are like a reservoir of constant volume. At constant volume, heat lost by the surroundings $q_{surr}$ can be equated to internal energy change $\Delta U_{surr}$.Now, $\Delta U_{surr}$ is a state function, so $q_{surr}$ is same whether the heat lost is reversible or irreversible. So, we can use the formula of entropy change in a reversible process to calculate entropy change in the surroundings:

$$\Delta S_{surr} = \frac{q_{surr}}{T}$$

Now, $q_{surr} = -q_{irr}$

Therefore,

$$\Delta S_{surr} = -\frac{q_{irr}}{T}$$

So, the total entropy change

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = \left(> \frac{q_{irr}}{T}\right) - \frac{q_{irr}}{T} > 0$$

Thus, a thermodynamically irreversible process is always accompanied by an increase in entropy of the universe, i.e. system and the surroundings.

**Entropy change in irreversible isothermal expansion of a perfect gas**

Let us consider isothermal expansion of a perfect gas from $V_1$ to $V_2$ against zero opposing pressure (i.e. free expansion).

Since entropy is a state function, entropy change in reversible isothermal expansion is same as that in an irreversible process. For $n$ mole of gas in the system:

$$\Delta S_{sys} = nRln\frac{V_2}{V_1}$$

For, free expansion, there is no opposing force, the work done by the system is zero:

$$w = 0$$

Temperature being constant, $\Delta\, U = 0$

From 1st law,

$$\Delta U = 0 = q + w$$

$$\Rightarrow q = 0$$

No heat is exchanged between the system and surroundings, consequently:

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

Total change in entropy in the process:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = nRln\frac{V_2}{V_1}$$

Since, $V_2 > V_1$, $ln\frac{V_2}{V_1} > 0$ which means $\Delta S_{total} > 0$

Thus, irreversible isothermal expansion of an ideal gas is accompanied by an increase in entropy of the system and its surroundings.

**Second Law of Thermodynamics:** The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{total} > 0$$

where $\Delta S_{total}$ is the total entropy of the system and its surroundings.

$$\text{i.e. } \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

The second law in terms of entropy tells us that thermodynamically irreversible processes being spontaneous, must be accompanied by an increase in entropy. In other words, irreversible processes generated entropy. Since all processes in nature occur spontaneously, i.e. irreversibly, it follows that the entropy of the universe is increasing continuously.

**Entropy, spontaneity and equilibrium**

The second law of thermodynamics states that the total entropy of the universe — that is, the sum of the entropy changes of the system and the surroundings — always increases for a spontaneous process:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

Thus, a process is spontaneous if it results in an increase in the entropy of the universe. The system continues to change in this direction until equilibrium is attained. At equilibrium, the entropy of the universe becomes constant (maximum value), and hence:

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

**Combined form of the first and second law of thermodynamics:**

For an infinitesimally small change in the state of a system. The first law gives

$$dU = dq + dw$$

If the process is reversible and the system does only P-V work then

$$dw = -pdV$$

The first law becomes

$$dU = dq_{rev} - pdV$$

From the second law,

$$dS = \frac{dq_{rev}}{T}$$

$$\Rightarrow \mathrm{TdS} = dq_{rev}$$

Combining these relations

$$dU = TdS - pdV \ldots\ldots\ldots (1)$$

Equation (1) is the combined form of the first and second law of thermodynamics. This is a fundamental equation of thermodynamics.

Also, from the definition of enthalpy $H = U + pV$

We obtain

$$dH = dU + pdV + Vdp$$

Substituting the value of $dU$ from equation (1), we get

$$dH = TdS - pdV + pdV + Vdp \qquad (neglecting\ dVdp)$$

Or,

$$dH = TdS + Vdp \ldots\ldots\ldots\ldots (2)$$

This is another fundamental equation of thermodynamics.

**Molecular interpretation and statistical interpretation of entropy**

Entropy is a measure of molecular disorder of the system. The more the randomness in a system greater is the entropy. Of the three states of matter, molecules in the gaseous state are more disordered than those in the liquid state, while molecules in the solid state are the least disordered. Thus, the entropy in the three states is in the following order:

$$S_g \gg S_l > S_s$$

All spontaneous processes are accompanied by increase in entropy. In other words, "disorder" of the system increases in a spontaneous process. Therefore, increase of entropy implies increase in molecular disorder.

Disordered states naturally have higher probabilities than ordered states. For example, in the mixing of two gases, the disordered mixed states are far more probable than the ordered, unmixed states. A spontaneous change, therefore, invariably takes place from a less probable state to a more probable state. Thus, entropy is related to thermodynamic probability $W$ by the Boltzmann equation

$$S = klnW$$

where $k$ is the Boltzmann constant.

When a given quantity of energy stored at high temperature in a system, the system has a lower entropy than the same quantity of energy stored at a lower temperature. Mathematically,

$$dS = \frac{dq_{rev}}{T}$$

The molecules in a system at higher temperatures are highly disordered. A small additional transfer of energy as heat will result in a relatively small additional disorder. In contrast, molecules in a system at low temperature are highly ordered, and the transfer of the same quantity of energy as heat will increase disorderliness in the molecules to a great extent. Molecular interpretation, therefore suggests that change in entropy should be inversely proportional to the temp° at which the transformation takes place.

**Variation of Entropy with temperature**

For a reversible process in a closed system, the defining equation of entropy is

$$dS = \frac{dq_{rev}}{T}$$

Now, when the state of a system is changed by heating it from initial state at temperature $T_1$ to the final state at temperature $T_2$ , the entropy change in the system can be obtained by integrating:

$$\int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

$$\Rightarrow S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} \ldots\ldots\ldots\ldots (1)$$

When the process occurs at constant pressure

$$C_p = \left(\frac{dq_{rev}}{dT}\right)_p$$

$$\Rightarrow dq_{rev} = C_p dT$$

Equation (1) becomes,

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} C_p \frac{dT}{T} \ldots\ldots\ldots\ldots (2)$$

Similarly, when the process occurs at constant volume,

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} C_V \frac{dT}{T} \ldots\ldots\ldots\ldots (3)$$

When $C_p$ and $C_V$ are independent of temperature in the temperature range of interest, we obtain

$$S(T_2) = S(T_1) + C_p ln\frac{T_2}{T_1} \ldots\ldots\ldots\ldots (4)$$

$$or, \Delta S = C_p ln\frac{T_2}{T_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$S(T_2) = S(T_1) + C_V ln\frac{T_2}{T_1} \ldots\ldots\ldots\ldots (6)$$

$$or, \Delta S = C_V ln\frac{T_2}{T_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

**Prob:** One mole of an ideal gas is heated from 100 K to 300 K. Calculate $\Delta S$ if

(a) the volume is kept constant

(b) the pressure is kept constant

Assume that $C_V = 1.5\ R$.

**Entropy change in an ideal gas when T and V are the two variables**

From thermodynamic definition, if an ideal gas absorbs a small amount of heat $dq_{rev}$ reversibly from the surroundings at $T$, then entropy change is

$$dS = \frac{dq_{rev}}{T}$$

From 1st law,

$$dU = dq_{rev} + dw$$

where $dw$ is the p-V work of expansion given by

$$dw = -pdV$$

And, from the definition of heat capacity,

$$C_V = \left(\frac{dU}{dT}\right)_V$$

$$\Rightarrow dU = C_V dT$$

Therefore, the first law becomes,

$$dq_{rev} = dU - dw$$

$$\Rightarrow dq_{rev} = C_V dT + pdV$$

$$\Rightarrow \frac{dq_{rev}}{T} = C_V \frac{dT}{T} + \frac{p}{T} dV$$

$$\Rightarrow dS = C_V \frac{dT}{T} + nR \frac{dV}{V} \quad \Big| \quad [pV = nRT, \therefore \frac{p}{T} = \frac{nR}{V}]$$

For a finite change of state of the system, integrating the above equation between the limits of the initial state 1 and the final state 2 assuming $C_V$ to be constant within the temperature $T_1$ and $T_2$, we have,

$$\int_1^2 dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \mathrm{S_2 - S_1} = C_V ln \frac{T_2}{T_1} + nRln \frac{V_2}{V_1}$$

$$\Rightarrow \Delta S = C_V ln \frac{T_2}{T_1} + nRln \frac{V_2}{V_1}$$

**Prob:** Calculate the entropy change, when 1 mol Ar at 25°C and 100 atm in a container of volume 500 $cm^3$ is allowed to expand to 1000 $cm^3$ and is simultaneously heated to 100°C ($C_{v,m}$ = 12.47 $JK^{-1}mol^{-1}$).

**Entropy change in an ideal gas when *p* and *T* are the two variables**

From thermodynamic definition, if an ideal gas absorbs a small amount of heat $dq_{rev}$ reversibly from the surroundings at $T$, then entropy change is

$$dS = \frac{dq_{rev}}{T}$$

From 1st law,

$$dU = dq_{rev} + dw$$

where $dw$ is the p-V work of expansion given by

$$dw = -pdV$$

Therefore, the first law becomes,

$$dq_{rev} = dU - dw$$
$$\Rightarrow dq_{rev} = dU + pdV \ldots\ldots\ldots\ldots (1)$$

From the definition of enthalpy,

$$H = U + pV$$
$$\Rightarrow \mathrm{U} = \mathrm{H} - \mathrm{pV}$$

Now, differentiating, we get

$$dU = dH - pdV - Vdp \ldots\ldots\ldots\ldots (2)$$

From equations (1) and (2),

$$dq_{rev} = dH - pdV - Vdp + pdV$$
$$\Rightarrow dq_{rev} = dH - Vdp \ldots\ldots\ldots\ldots\ldots (3)$$

And, from the definition of heat capacity,

$$C_p = \left(\frac{dH}{dT}\right)_p$$
$$\Rightarrow dH = C_p dT$$

Putting this equation (3) becomes,

$$dq_{rev} = C_p dT - Vdp$$
$$\Rightarrow \frac{dq_{rev}}{T} = C_p \frac{dT}{T} - \frac{V}{T} dp$$
$$\Rightarrow dS = C_p \frac{dT}{T} - nR \frac{dp}{p} \quad \Big| \quad [pV = nRT, \therefore \frac{V}{T} = \frac{nR}{p}]$$

For a finite change of state of the system, integrating the above equation between the limits of the initial state 1 and the final state 2 assuming $C_p$ to be constant within the temperature $T_1$ and $T_2$, we have,

$$\int_1^2 dS = C_p \int_{T_1}^{T_2} \frac{dT}{T} - nR \int_{p_1}^{p_2} \frac{dp}{p}$$
$$\Rightarrow \mathrm{S}_2 - \mathrm{S}_1 = C_p ln \frac{T_2}{T_1} - nRln \frac{p_2}{p_1}$$
$$\Rightarrow \Delta S = C_p ln \frac{T_2}{T_1} - nRln \frac{p_2}{p_1}$$

## Third Law of Thermodynamics

### Nernst Heat Theorem

Nernst heat theorem is stated as:

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \to 0$ as $T \to 0$ provided all the substances involved are perfectly ordered.

### Third Law of Thermodynamics

Let us consider a process involving conversion of solid substance. For example,

$$\text{Sulphur}(\beta) \rightarrow \text{Sulphur}(\alpha).$$

According to Nernst heat theorem, the entropy change $\Delta S$ for this conversion is zero at absolute zero.

$$\therefore \Delta S = S(\alpha) - S(\beta) = 0$$

$$\Rightarrow S(\alpha) = S(\beta)$$

Thus, absolute entropies of the product element and the reactant element in the solid state are same. If we arbitrarily assign zero values to the entropies of elements in their perfect crystalline form, then all compounds with perfectly crystalline structure will also have zero entropy at $T$=0. Because, the entropy change associated with the formation of the compounds and entropies of elements in their perfect crystalline form are zero at $T$=0. Thus. Planck stated the third law as:

"*All perfect crystals have zero entropy at absolute zero temperature* ($T$=0)."

### Determination of Absolute Entropies

Variation of entropy of a substance with temperature at constant pressure is given by

$$dS = \frac{C_P}{T} dT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

By integration of the entropy term from $T = 0\ K$ to some temperature $T$, we get

$$\int_{S_0}^{S_T} dS = \int_0^T \frac{C_P}{T} dT$$

$$\Rightarrow S_T - S_0 = \int_0^T \frac{C_P}{T} dT \ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

where $S_T$ and $S_o$ are entropy of the system at $T$ K and 0 K, respectively.

According to third law, $S_o = 0$, so

$$S_T = \int_0^T \frac{C_P}{T} dT = \int_0^T C_P \, dlnT \ldots\ldots\ldots (iii)$$

where $S_T$ is called the Third-law entropy or absolute entropy at temperature T.

Thus, entropies reported on the basis that $S(0) = 0$ are called Third-law entropies. When the substance is in its standard state at the temperature of interest *T*, entropy is called the 'standard Third-law entropy' denoted by $S_T°$.

**Third-law entropy or Absolute Entropy of a Solid**

From equation (iii), it is clear that the absolute entropy $S_T$ of a solid can be determined graphically by plotting $C_P/T$ against *T* or $C_P$ against *lnT*. Area under the curve between *T* = o and the temperature of interest *T* (**Figure 1**) gives an estimate of $S_T$. For generation of the plot, $C_P$ of the solid at various temperatures between *T* = o and the temperature of interest *T* need to be measured. Since it is impossible to attain absolute zero temperature, heat capacities are measured up to a minimum temperature ($T_{min}$) as low as 10 K to 15 K. Below this temperature ($T_{min}$), $C_P$ is calculated using the Debye T-cubed law: $C_P = aT^3$ where *a* is an empirical constant. Thus, absolute entropy of a solid can be determined using the integrals:

$$S_T = \int_{0K}^{T_{min}} \frac{C_P}{T} dT + \int_{T_{min}}^{T} \frac{C_P}{T} dT \ldots\ldots\ldots\ldots\ldots (iv)$$

Here, the first integral is evaluated using Debye T-cubed law and the second integral is evaluated from experimental determination of heat capacities.

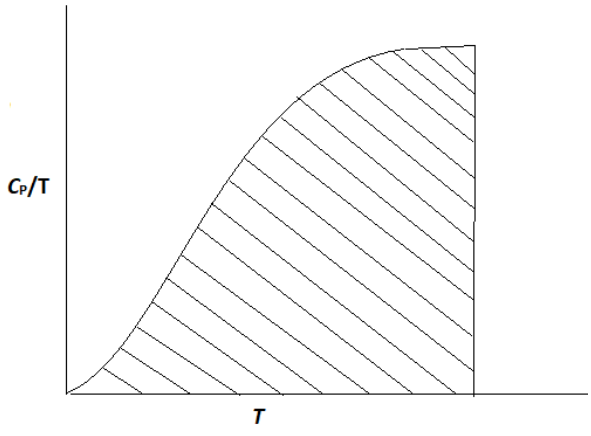



**Figure 1:** Schematic presentation of plot of $C_P/T$ versus *T*

**Third-law entropy or Absolute Entropy of a liquid**

For the determination of absolute entropy $S_T$ of a substance at a temperature of interest, one must take into account all the entropy changes that the substance has to undergo to reach the state at the temperature of interest from the absolute zero. Absolute entropy of a liquid at the temperature $T$, can be determined by the summation of entropy changes in the following three stages:

(1) Heating of the solid substance from absolute zero (0 K) up to its melting point $T_m$.

(2) Fusion of the solid to liquid at its melting point $T_m$.

(3) Heating of the liquid from its melting point $T_m$ up to the temperature of interest $T$.

Considering the three stages, integrals can be framed as

$$S_T = \int_{0K}^{T_m} \frac{C_P(s)}{T} dT + \frac{\Delta_{fus}H}{T_m} + \int_{T_m}^{T} \frac{C_P(l)}{T} dT \ldots\ldots\ldots (vii)$$

where $\Delta_{fus}H$ is the enthalpy of fusion of the solid state of the substance. Thus, determination of absolute entropy of a liquid necessitates evaluation of three integrals.

**Third-law entropy or Absolute Entropy of a gas at 25°C**

Absolute entropy of a gas at 25°C can be determined by adding up all the entropy changes associated with the substance while bringing it from absolute zero to its gaseous state at 298 K. ntropy changes in the following processes are considered:

(1) Heating of the crystalline solid from absolute zero to a minimum temperature $T_{min}$, where $0 < T_{min} < 15$ K. In this temperature range, entropy change $\Delta S_1$ is evaluated using Debye T-cubed law:

$$\Delta S_1 = \int_0^{T_{min}} aT^3 \frac{dT}{T} = \frac{1}{3} aT_{min}^3$$

(2) Fusion of the solid into its liquid form at its melting point $T_m$ brings an entropy change of $\Delta S_2$ given by

$$\Delta S_2 = \frac{\Delta_{fus}H}{T_m}$$

$\Delta_{fus}H$ is the enthalpy of fusion of the substance.

(3) Heating of the liquid from its melting point $T_m$ to its boiling point $T_b$. Associated entropy change is

$$\Delta S_3 = \int_{T_m}^{T_b} \frac{C_P(l)}{T} dT$$

$C_P(l)$ is the heat capacity of the substance in the liquid state.

(4) Vaporisation of the liquid at $T_b$ leads to an entropy change of

$$\Delta S_4 = \frac{\Delta_{vap}H}{T_b}$$

$\Delta_{vap}H$ is the enthalpy of vaporization of the liquid.

(5) Heating the gas from $T_b$ to 298 K. Entropy change involved in this process

$$\Delta S_5 = \int_{T_b}^{298K} \frac{C_P(g)}{T}\, dT$$

where $C_P(g)$ is the heat capacity of the substance in the gaseous state.

So, absolute entropy of the gas at 298K is given by

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

**Residual entropy**

Absolute entropies or Third-law entropies are determined assuming $S(0) = 0$. Entropies are also calculated using Boltzmann equation

$$S = klnW$$

where $k$ is the Boltzmann constant. In many cases, calculated entropies and Third law entropies are found to be same, but in some cases, Third-law entropies are less than the calculated entropies. One reason cited for this discrepancy is that some disorder is present in the solid state even at absolute zero.

Entropy of a substance at T=0 is greater than zero. The value of entropy of a substance at absolute zero is called residual entropy.

The origin of residual entropy in a crystal at 0 K is due to alternative arrangements of molecules possible in the solid. Let us consider a crystal composed of AB molecules, where A and B are similar atoms (such as CO). There may be so little energy difference between …AB AB AB AB…., …AB BA BA AB…., and other arrangements that the molecules adopt the orientations AB and BA at random in the solid.

We can calculate the entropy arising from residual disorder by using the Boltzmann equation

$$S = klnW$$

We suppose that the two orientations are equally probable, and that the sample consists of $N$ molecules. Because the same energy can be achieved in $2^N$ different ways,

$$W = 2^N$$

$$\therefore S = klnW = kln2^N = Nkln2 = nRln2$$

Residual molar entropy of solids composed of molecules that can adopt either of two orientations is given by $S_m = Rln2$. If $s$ orientations are possible, the residual molar entropy will be

$$S_m = Rlns$$

**Prob 1:** Heat capacity at constant volume for uranium metal is 3.04 J $K^{-1}$ $mol^{-1}$. Calculate the absolute entropy of the metal at 20 K.

Sol$^n$: At $T$= 20 K, $C_p = C_v$ = 3.04 J $K^{-1}$ $mol^{-1}$.

At low temperatures (0 K < T < 20 K), applying Debye T-cubed law, $C_P = aT^3$.

$$a = \frac{C_P}{T^3} = \frac{3.04\ \text{J}\ K^{-1}mol^{-1}}{(20K)^3} = 38.03 \times 10^{-5} J\ K^{-4}\ mol^{-1}$$

Absolute entropy is given by

$$S_T = \int_0^T \frac{C_P}{T} dT = \int_0^T \frac{aT^3}{T} dT = a\int_0^T T^2 dT = \frac{a}{3}T^3$$

$$= \frac{38.04\ \text{J}\ K^{-4}mol^{-1}}{3}(20\ K)^3 = 1.01\ JK^{-1}mol^{-1}$$

**Prob 2:** How did Planck state the third law of thermodynamics?

Sol$^n$ : Planck stated the third law as: "All perfect crystals have zero entropy at absolute zero temperature (T=0)."

**Prob 3:** Heat capacity of a gas at 1 atm pressure is 50.0 J $K^{-1}$ $mol^{-1}$. Calculate the entropy change for heating the gas from its boiling point (300 K) to 350 K.

Sol$^n$: Here we use the integral

$$\Delta S = \int_{T_b}^T \frac{C_P(g)}{T} dT$$

$$= \int_{300}^{350} \frac{50.0}{T} dT$$

$$= 50.0\ ln\frac{350}{300}$$

$$= 50 \times 2.303 \log\frac{7}{6}$$

$$= 7.71\ JK^{-1}mol^{-1}$$

**Prob 4**: Calculate residual molar entropy for the solids (i) CO and (ii) $FClO_3$

**MODEL QUESTIONS**

1. State the Nernst heat theorem. How does it lead to the proposal of third law of thermodynamics?
2. State and explain the third law of thermodynamics.
3. Discuss how the absolute entropy of a solid can be determined with the help of third law of thermodynamics?
4. Discuss how entropy of a pure liquid can be determined with the help of third law.
5. Evaluate theoretically the absolute entropy of a gas above its boiling point using third law. Write all the steps involved precisely.
6. Mention one limitation of third law.