# VIVEKANANDA COLLEGE
# THAKURPUKUR
# KOLKATA-700063

NAAC ACCREDITED ‘A’ GRADE

Topic: Thermodynamics
Course Title: General Physical Chemistry
Paper: BCMA CC3
Unit: Principles of Thermodynamics
Semester: 2
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Name of the Department: Biochemistry

## Second law of thermodynamics:

→ The energy function (U) and enthalpy function (H) cannot predict the spontaneity of a process.

→ Any given chemical change tries to attain a minimum energy state. But this does not mean any exothermic reaction is spontaneous.

e.g. vaporization of water at low pressure causes a positive change in $\Delta_r U$.

e.g. polymorphic transformation of quartz is spontaneous but has a positive $\Delta_r H$.

→ Thus, thermodynamics needs a new law and a new physical quantity to define spontaneity of a process, since the first law and its energy functions (H and U) are not sufficient to define spontaneity.

→ A new function (entropy) was established from the work of Carnot.

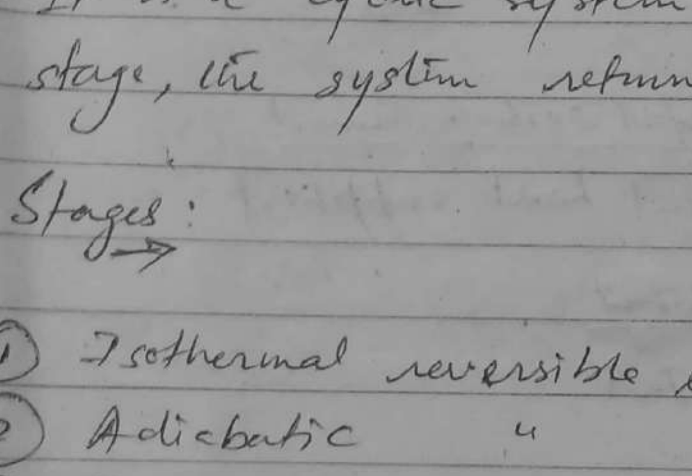
## → Carnot cycle :

→ Idealized reversible cycle between two thermal reservoirs, one at a higher temperature $T_2$ (source) and one at a lower temperature $T_1$ (sink).

→ It has 4 stages.
→ It is a cyclic system i.e. after the fourth stage, the system returns to its starting point.

Stages :

① Isothermal reversible expansion ($\Delta T = 0$)
② Adiabatic " " ($dq = 0$, $T$ decreases)
③ Isothermal " compression ($\Delta T = 0$)
④ Adiabatic " " ($dq = 0$, $T$ increases)



→ For expansions ① and ②, the sign of work is negative.

→ For compressions ③ and ④ the sign of work is positive.

→ Total work = area under the curve ABCD.
→ Since it is a cyclic process, $\Delta U = 0$.
∵ ~~dq~~ $dU = dq + dw$ and $dU = 0$.
$\Rightarrow dq = -dw$ i.e. $\underline{q_{total} = -w_{total}}$

Now, $q_{total}$ = total heat involved in all the 4 stages

[Note that in adiabatic stages 2 and 4, $dq = 0$ i.e. $q = 0$]

$\therefore$ $q_{total}$ = heat involved in steps ① and ③ only

$$= q_2 + q_1$$

$\therefore$ Efficiency $(\eta) = \dfrac{\text{Total work obtained}}{\text{Total heat supplied}}$

$$= \frac{-w_{total}}{q_{total}}$$

$$= \frac{-w_{total}}{q_2}$$

But, $-w_{total} = q_2 + q_1$

$$\therefore \boxed{\eta = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2}}$$

$$\Rightarrow \eta = 1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \quad \text{where } T_2 > T_1$$

This can be easily proved if we consider all the 4 stages of the cycle seperately.

① Isothermal reversible expansion ~~compression~~:

$$\Delta T = 0 \ , \ \Delta U_1 = 0$$

$$q_2 = -w_2 = RT_2 \ln \frac{V_2}{V_1}$$

② Adiabatic reversible expansion:

$$q = 0 \qquad w' = \Delta U_2 = \int_{T_2}^{T_1} C_{v,m}\, dT$$

$$= C_{v,m}(T_1 - T_2)$$

③ Isothermal reversible compression:

$$\Delta U = 0 \ , \ \Delta T = 0 \qquad q_1 = -w_1 = RT_1 \ln \frac{V_4}{V_3}$$

④ Adiabatic reversible compression:

$$q = 0 \qquad w'' = \Delta U_4 = \int_{T_1}^{T_2} C_{v,m}\, dT = C_{v,m}(T_2 - T_1)$$

$$\therefore w_{total} = w_2 + w' + w_1 + w''$$

$$= -RT_2 \ln\frac{V_2}{V_1} + C_{v,m}(T_1 - T_2)$$

$$- RT_1 \ln\frac{V_4}{V_3} + C_{v,m}(T_2 - T_1)$$

$$\therefore \boxed{w_{total} = -RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_4}{V_3}}$$

Also, $q_{total} = -w_{total}$

or, $\boxed{q_{total} = RT_2 \ln\frac{V_2}{V_1} + RT_1 \ln\frac{V_4}{V_3}}$

⇒ For step ② : adiabatic rev. exp.

$dq = 0$ and $TV^{\gamma-1}$ = constant

i.e. $T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

⇒ For step ④ : adiabatic rev. comp.

$dq = 0$ and $TV^{\gamma-1}$ = constant

i.e. $T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1}$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

Thus, $\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$

i.e. $\frac{V_3}{V_2} = \frac{V_4}{V_1}$ or, $\frac{V_1}{V_2} = \frac{V_4}{V_3}$.

$$\therefore W_{total} = -RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_4}{V_3}$$

$$= -RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_1}{V_2}$$

$$= -RT_2 \ln\frac{V_2}{V_1} + RT_1 \ln\frac{V_2}{V_1}$$

$$= -R \ln\frac{V_2}{V_1}\left[T_2 - T_1\right]$$

$$\therefore \text{Efficiency } (\eta) = \frac{-W_{total}}{q_2} = \frac{R\ln\frac{V_2}{V_1}(T_2 - T_1)}{RT_2 \ln\frac{V_2}{V_1}}$$

$$\Rightarrow \boxed{\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}}$$

$T_2$ = source temperature
$T_1$ = sink temperature

⇒ Implications:

ⓐ If $T_2 = T_1$, $\eta = 0$ i.e. no work can be done in the cycle. Thus an isothermal cycle causes no conversion of heat into work or vice versa.

ⓑ If $\eta = 1$, then either $T_1 = 0$ or $T_2 = \infty$.
None of which are physically possible.
So the efficiency is always less than one.

→ Second law of thermodynamics:

Kelvin Planck statement:

It is impossible for a system operating in a cycle and connected to a single reservoir, to produce any positive amount of work in the surroundings.

Clausius statement:

It is impossible for a cycle to convert heat into work without simultaneous transfer of heat from a body at a higher temperature to a body at a lower temperature.

⇒ What is entropy function?

We know, for a reversible Carnot cycle operating between two temperatures $T_2$ and $T_1$, its

efficiency can be written as $\eta = \frac{q_1 + q_2}{q_2}$

$$\eta = \frac{T_2 - T_1}{T_2} \quad \text{(shown earlier)}$$

$$\therefore \quad \frac{q_1 + q_2}{q_2} = \frac{T_2 - T_1}{T_2} = \eta$$

$$\Rightarrow \quad 1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\Rightarrow \quad \frac{q_1}{q_2} = -\frac{T_1}{T_2}$$

$$\Rightarrow \quad \frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

$$\Rightarrow \quad \boxed{\frac{q_1}{T_1} + \frac{q_2}{T_2}} = 0$$

i.e. the sum of the ratios of the heat involved and the corresponding temperature is zero for a Carnot cycle.

⇒ In fact, for any reversible cycle, involving 'n' no. of steps (where $n \to \infty$), the amount of heat transferred in each step to the temperature and their corresponding sum for all the steps combined is zero.

i.e. $$\sum_i \frac{q_i}{T_i} = 0,$$

where $q_i$ = amount of heat transferred at temperature $T_i$

⇒ For a reversible cycle with infinite steps, the amount of heat transferred is infinitesimally small and can be written as $dq_{i(rev)}$ and if the no. of steps involved 'n' is very large, the summation can be replaced by an integral and we can write

for a cyclic reversible engine with infinite steps

$$\oint \frac{dq_{i\,(rev)}}{T_i} = 0$$

i.e. it is an exact differential.

$\therefore$ $\frac{q_{rev}}{T}$ is a state function.

⇒ this is defined as 'entropy' (s).

$$\therefore dS = d\left(\frac{q_{rev}}{T}\right) \quad \text{i.e.} \quad \left[S = \frac{q_{rev}}{T}\right]$$

Entropy is a state function since its cyclic integral is zero and it is extensive.

$$\left[\oint dS = 0\right]$$

⇒ Remember that entropy is always calculated using a reversible path connecting the initial and final states.

⇒ Unit : $JK^{-1}$ or $cal\,K^{-1}$
(1 eu → entropy unit)

⇒ If there is any irreversibility at any stage in a cycle, the net work obtained $|W_{net}|$ is always less than the net work obtained in a reversible cycle operating between the same temperatures.

$$\therefore \eta_{irr} < \eta_{rev}$$

$$\text{i.e.} \quad \frac{|W_{net}|}{q_2} < \frac{T_2 - T_1}{T_2}$$

$$\text{i.e.} \quad \frac{q_2 + q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

$$\Rightarrow \frac{q_1}{q_2} < -\frac{T_1}{T_2}$$

$$\Rightarrow \frac{q_1}{T_1} + \frac{q_2}{T_2} < 0$$

i.e. $$\boxed{\oint \frac{dq_{irr}}{T} < 0}$$

[Previously we found $\oint \frac{dq_{rev}}{T} = 0$]

⇒ Since entropy is a state function, between two states A and B, we can write

$$\oint dS = 0 \Rightarrow \int_A^B dS + \int_B^A dS = 0$$

$$\Rightarrow \int_A^B dS = -\int_B^A dS$$

i.e. entropy change from A → B is equal and opposite from B → A.

⇒ Thus for reversible heat exchanges between system and surroundings, we can write

$$\Delta S_{system} = -\Delta S_{surroundings}$$

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

⇒ Thus, in a reversible process, the entropy is merely exchanged between system and surroundings and the total entropy change is always zero.

⇒ What about an irreversible process?

This can be shown by Clausius Inequality.

Let us consider a change from A → B irreversibly and let us assume the reverse pathway (B → A) is carried out reversibly.

$$\begin{tikzcd} A \arrow[r, "irr"] & B \arrow[l, bend left, "rev"] \end{tikzcd}$$

The total entropy change for this cycle can be written as

$$\oint \frac{dq_{irr}}{T} = \int_A^B \frac{dq_{irr}}{T} + \int_B^A \frac{dq_{rev}}{T}$$

$$\Rightarrow \oint \frac{dq_{irr}}{T} = \int_A^B \frac{dq_{irr}}{T} - \int_A^B \frac{dq_{rev}}{T}$$

Again, we have seen before, $\oint \frac{dq_{irr}}{T} < 0$.

$$\therefore \int_A^B \frac{dq_{irr}}{T} < \int_A^B \frac{dq_{rev}}{T}$$

$$\Rightarrow \int_A^B \frac{dq_{irr}}{T} < \int_A^B dS \quad \left[\because S = \frac{q_{rev}}{T}\right]$$

$$\therefore \boxed{\int_A^B \frac{dq_{irr}}{T} < \Delta S_{AB}}$$ Clausius Inequality

⇒ For any change in an <u>isolated</u> system,

$$dq(irr) = 0$$

$$\text{ie. } 0 < \Delta S_{AB}$$

$$\text{ie. } \Delta S_{AB} > 0.$$

This is the requirement for a real transformation in an isolated system i.e. the entropy of a system increases whenever a natural change is occurring.

→ This entropy continues to increases till it reaches a maximum at equilibrium.

→ If the entire universe is considered to be an isolated system in which all the natural processes are spontaneous or irreversible, then we can gather that the entropy always tends to a maximum value.

⇒ Entropy change for an ideal gas:→

$$dU = dq + dw \quad (1^{st}\ law)$$

$$\Rightarrow dq = dU - dw$$

$$\Rightarrow dq_{rev} = dU + p\,dV \quad (\text{reversible process})$$

$$\Rightarrow \frac{dq_{rev}}{T} = \frac{1}{T}\,dU + \frac{p}{T}\,dV$$

Now, $U = f(T, V)$

$$\text{i.e. } dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\therefore \frac{dq_{rev}}{T} = dS = \frac{1}{T}\left\{\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right\} + \frac{p}{T}\,dV$$

⇒ For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $\frac{p}{T} = \frac{nR}{V}$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = n\,C_{V,m}$$

$$\therefore dS = \frac{C_V}{T}\,dT + nR\,\frac{dV}{V}$$

⇒ for a finite change,

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

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

Also, $C_V = n\,C_{V,m}$,

where $C_{V,m} \rightarrow$ molar heat capacity at const. volume,

$$\boxed{\Delta S = n\left[C_{V,m} \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}\right]}$$

This is the variation of $S$ with $T$ and $V$ (considering $C_V$ is temp. independent)

ⓐ For an isothermal change, $dT = 0$.

$$\therefore \boxed{\Delta S = nR\ln\frac{V_2}{V_1}}$$

ⓑ For an isochoric process, $dV = 0$.

$$\therefore \boxed{\Delta S = n\,C_{V,m} \ln\frac{T_2}{T_1}}$$

($C_{V,m}$ is temp. independent)

$\Rightarrow$ If $C_{V,m}$ is temperature dependent,

$$C_{V,m} = a + bT + cT^2 + \cdots - R$$

$$\left[\because C_{P,m} - C_{V,m} = R\right]$$

$$\therefore \Delta S = n\int_{T_1}^{T_2} \frac{a + bT + cT^2 + \cdots - R}{T}\, dT$$

$$= n\left[\int_{T_1}^{T_2} \frac{a-R}{T}\, dT + \int_{T_1}^{T_2} (b + cT + dT^2 + \cdots)\, dT\right]$$

$$\Rightarrow \Delta S = n\left[(a-R)\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \cdots\right]$$

$\Rightarrow$ Dependence on $p$:

We know, $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$

$$\Rightarrow \frac{V_2}{V_1} = \frac{p_1 T_2}{p_2 T_1}$$

$$\because \Delta S = n C_{v,m} \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

$$\Rightarrow \Delta S = n\left[C_{v,m}\ln\frac{T_2}{T_1} + R\ln\frac{p_1 T_2}{p_2 T_1}\right]$$

$$\Rightarrow \Delta S = n\left[(C_{v,m} + R)\ln\frac{T_2}{T_1} + R\ln\frac{p_1}{p_2}\right]$$

$$\Rightarrow \boxed{\Delta S = n\left[C_{p,m}\ln\frac{T_2}{T_1} + R\ln\frac{p_1}{p_2}\right]}$$

This is the variation of entropy for an ideal gas with both $T$ and $p$.

ⓐ For isothermal process, $dT = 0$

$$\therefore \boxed{\Delta S = nR \ln \frac{p_1}{p_2}}$$

ⓑ For isobaric condition, $dp = 0$

$$\therefore \boxed{\Delta S = n C_{p,m} \ln \frac{T_2}{T_1}}$$

(when $C_{p,m}$ is temp. independent)

and $$\Delta S = n\left[a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + c(T_2^2 - T_1^2) + \dots\right]$$

(when $C_{p,m}$ is dependent on $T$).