THERMODYNAMICS

GIBBS ENERGY CHANGE AND EQUILIBRIUM

THE SECOND LAW OF THERMODYNAMICS

There are two types of processes reversible process or quasi static process in which system remains in equilibrium with surrounding throughout the process.

However reversible processes cannot take place on it's own – and are not natural process. Reversible process does not lead to production of disorder.

On the other hand, most of the processes taking place around us is example of irreversible process. Irreversible process also natural processes or spontaneous processes.

The second law of thermodynamics predict's direction of natural change. It does so with the help of state function 'S' - called entropy of system. But for predicting direction of natural change another quantity $S_{surrounding}$ is also needed. $S_{surrounding}$ which is called entropy of surrounding is a path dependent quantity.

$$egin{aligned} \mathrm{dS}_{\mathrm{system}} &= rac{\mathrm{dq}_{\mathrm{rev}}}{\mathrm{T}} \ \mathrm{dS}_{\mathrm{surr}} &= -rac{\mathrm{dq}}{\mathrm{T}} \end{aligned}$$

Since S_{system} is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible. ΔS_{AB} will be same irrespective of path (A direct consequence of S_{system} being a state function).

However, If same transition from A to B is done by different irreversible path's, $\Delta S_{surrounding}$ will be different in all processes. However, if transition from A \rightarrow B take place by many reversible path's, ΔS_{surer} along each path will be same because

$$-\sum_{A \circledast B}^{\text{path }1} \frac{dq_{\text{rev}}}{T} = -\Delta S_{\text{system}} = -\sum_{A \circledast B}^{\text{path }2} \frac{dq_{\text{rev}}}{T}$$

\Rightarrow	$\Delta S_{surr} (path)$	$() = -\Delta S_s$	$\sum_{B}^{\text{ystem}} = -\Delta S_{\text{surr}} (\text{path } 2)$	
		ΔS_{system}	$\Delta S_{ m surrounding}$	
	reversible	$\int^{B} dq_{rev}$	$-\int_{a}^{B} dq_{rev}$	
	process	A T	${f J}_{ m A}$ T	
	Irreversible	$\int^{B} dq_{rev}$	$\int_{a}^{B} \frac{dq_{irrev}}{dq_{irrev}} = -\left(\frac{q_{irrev}}{dq_{irrev}}\right)$	
	process	A T	$\begin{bmatrix} \mathbf{J} & \mathbf{T} \end{bmatrix}^{-} \begin{bmatrix} \mathbf{T} \end{bmatrix}_{\mathbf{A} \to \mathbf{B}}$	

Entropy changes of system and surrounding in reversible and irrversible process

Note that

t
$$\Delta$$

$$\Delta \mathbf{S}_{\mathrm{surr}} = -rac{\mathbf{q}_{\mathrm{actual}}}{\mathrm{T}}$$

The central concept of entropy is given briefly, because JEE syllabus deals with consequence of second law rather than it's derivation.

Prediction of Spontaneity of Process: If total entropy change in a process is positive the process must be spontaneous.

 $\Delta S_{system} + \Delta S_{surrounding} > 0$ for spontaneous change.

The second law of thermodynamics was developed during course of development of cyclic engines. Second law was discovered while studying efficiency of steam engines. In 1824 a French engineer Sodi Carnot pointed out that for a cyclic heat engine to produce continuous mechanical works, it must exchange heat with two bodies at different temperature without a cold body to discard heat, the engine can-not function continuously.

2nd Law Statement

It is impossible for a system to undergo cyclic process whose sole effects are the flow of heat from a heat reservoir and the performance of an equivalent amount of work by the system on surrounding.

The key term in above statement is cyclic engine. If the first part of it's operation when engine do work heat is absorbed and expansion on take place in second part, it must return to it's original state and to contract, it must loose heat to a cold object (sink).

In other words, energy taken from source in one cycle can not be completely converted into work.

Efficiency of Carnot Engine.

Carnot has devised an engine based on reversible steps. The efficiency of Carnot engine is maximum, because it is based on reversible cycle. A Carnot engine completes a cycle in four steps.



Reversible isothermal expansion from P_1 , V_1 to P_2 , V_2 at temp T_H

Reversible adiabatic expansion from P_2 , V_2 at temp T_H to P_3 , V_3 at temp T_c

Reversible isothermal compression from P₃, V₃ to P₄, V₄ at temp T_H

Reversible isothermal compression from P_4 , V_4 to P_1 , V_1 at temp T_c

A car not engine rejects minimum heat to the surrounding in its operation and maximum part of heat taken form source is converted into work. Hence efficiency of car not engine is given by

$$\eta = \frac{\text{Net work done by engine in one cycle}}{\text{Net heat ab sorbed from source}}$$

 $\eta = \frac{-W_{net}}{Q_H}$ where w_{net} is net work done on the engine(system) in one cycle.

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It can be easily shown that – $w_{net} = q_H + q_C = w_{net}$

$$q_{H} + q_{C} = nRT_{H} \ln \frac{V_{2}}{V_{1}} + nRT_{C} \ln \frac{V_{4}}{V_{3}} \text{ also}$$

$$\begin{cases} T_{C}V_{4}^{\gamma-1} = T_{h}V_{1}^{\gamma-1} \\ T_{C}V_{3}^{\gamma-1} = T_{h}V_{2}^{\gamma-1} \end{cases} \Longrightarrow \begin{cases} \frac{V_{4}}{V_{3}} = \frac{V_{1}}{V_{2}} \end{cases}$$

because of reversible adiabatic process substituting these result's

$$\eta = \frac{T_{\rm H} - T_{\rm C}}{T_{\rm H}} = \frac{q_{\rm H} + q_{\rm C}}{q_{\rm H}}$$

Efficiency of Carnot engine only depends upon temperature of source and sink and independent of choice of working substance.

Sum of the $\frac{q_{rev}}{T}$ in a cyclic process is zero. For the Carnot cycle \Rightarrow for car not cycle

$$\frac{q_{\rm H}}{T_{\rm H}} + \frac{q_{\rm C}}{T_{\rm C}} = 0$$
$$\sum \frac{q_{\rm rev}}{T} = 0$$

The result in previous article is valid for any reversible cyclic process. It can be very easily verified.

Hence $\iint \frac{dq_{rev}}{T} = 0 \implies \text{Sum of } \frac{dq_{rev}}{T}$ the over a cyclic path is zero. now $\iint dX = 0$ If $\Rightarrow dX$

is firetail of a state function and X is state function.

$$\Rightarrow dS = \frac{dq_{rev}}{T} = definite quantity$$

$$\Rightarrow S_{system} \qquad is \qquad a \qquad state \qquad function.$$

Clausius Inequality

From our experience we known if any one step in carnot engine is consciously made irreversible the efficiency of carnot engine will decrease from theoretical value

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$$\eta = \frac{q_{\rm H} + q_{\rm C}}{q_{\rm H}} = \frac{T_{\rm H} - T_{\rm C}}{T_{\rm H}}$$
$$\frac{q_{\rm H}}{T_{\rm H}} + \frac{q_{\rm C}}{T_{\rm C}} < 0 \implies$$
$$\sum \frac{q_{\rm irr}}{T} < 0 \implies$$

this mathematical statement is called Clasius inequality.

THIRD LAW OF THERMODYNAMICS

Third law of thermodynamics helps in determining absolute entropy of substances. It is based on an assumption that entropy of every perfectly crystalline substance is zero at zero Kelvin. This is justified because, at absolute zero every substance is in state of lowest energy and position of every atom or molecule is defined in solid. Hence at T=0 S(T=0)=0 Third law

If we have sufficient heat capacity data (and the data on phase changes) we could write

$$S(T) = S(T = 0) + \int_0^r \frac{C_p}{T} dT$$
(i)

(If there is a phase change between 0 K and T, we would have to add the entropy of the phase change.) If C_p were constant near T = 0, we would have,

$$S(T) = S(T = 0) + C_p \quad \frac{T}{0} \quad \ln$$

Which is undefined. Fortunately, experimentally $C_p \rightarrow 0$ as $T \rightarrow 0$. For nonmetals C_p is proportional to T^3 at low temperature. For metals C_p is proportional to T^3 at low temperatures but shifts over to being proportional to T at extremely low temperatures. (The latter happens when the atomic motion "freezes out" and the heat capacity is due to the motion of the conduction electrons in the metal.)

equation (i) could be used to calculate absolute entropies for substances if we know what the entropy is at absolute zero. Experimentally it appears that the entropy at absolute zero

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is the same for all substances. The third law of thermodynamics modifies this observation and sets

$$S(T = 0) = 0$$

for all elements and compounds in their most stable and perfect crystalline state at absolute zero and one atmosphere pressure. (All except for helium, which is a liquid at the lowest observable temperatures at one atmosphere.)

The advantage of this law is that it allows us to use experimental data to compute the absolute entropy of a substance. For example, suppose we want to calculate the absolute entropy of liquid water at 25°C. We would need to know the C_p of ice from 0 K to 273.15 K. We also need the heat of fusion of water at its normal melting point. With all of this data, which can be obtained partly from theory and partly from experiment, we find

S°_{H20} (25°C) = 0 +
$$\int_0^{273.15} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{273.15} + \int_{273.15}^{298.15} \frac{C_p(l)}{T} dT$$

Some substances may undergo several phase changes.

GIBB'S FUNCTION

Entropy is a universal criterion of spontaneity. This means for any process if $\Delta S_{Total} > 0$ the process is spontaneous. Most of the chemical process take place at constant temperature and pressure. A very useful criteria of spontaneity of process at constant temperature and pressure is Gibb's function:

Gibb's function (G) is defined as

 $G = H - TS \qquad \dots \dots \dots (i)$

Gibb's function and spontaneous process:

from 2nd law we known:

 $dq = dV + PdV \qquad \dots \dots \dots \dots (iii)$

substituting value of dq from equation (iii) to equation (ii)

$$\mathrm{dV} + \mathrm{PdV} - \mathrm{TdS} \le 0$$

$$\Rightarrow$$
 d(H – TS)_{P,T} \leq 0

 $d(H - TS)_{P,T}^{-} = (dH - TdS - SdT)_{P,T}$ $= (dU + PdV + VdP - TdS - SdT)_{P,T} \le 0$ $\Rightarrow d(H - TS)_{P,T} \le 0$ $\Rightarrow d(dG)_{P,T} \le 0$

Statement

During course of every spontaneous process, Gibb's function decreases. If a process is allowed to run spontaneously, eventually it attain equilibrium. At equilibrium, the Gibb's function attains minimum value. No further decrease to the value of Gibb's function is possible at equilibrium.

Hence at equilibrium. (dG)T, P = 0.

 \Rightarrow Entropy changes in spontaneous process:

 $\Delta S_{system} + \Delta S_{surrounding} \ge 0$

The sign > is for spontaneous process. A state of equilibrium in a close system is attained spontaneously. As system approaches equilibrium from non-equilibrium state – $S_{Total keeps}$ on increasing and at equilibrium S_{Total} attains its maximum value.

 $\Rightarrow \Delta S_{Total} = 0$ at equilibrium at this point

 $S_{Total} = maximum value at equilibrium in a close system$

spontaneous and non spontaneous									
Sign of ∆H	Sign of ∆S	Comment	Example	$\Delta \mathrm{H}^{\circ}_{298}$	ΔS°_{298}				
_	+	spontaneous at all temperature	$\begin{array}{l} H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \\ C(s) + O_2(g) \longrightarrow CO_2(g) \end{array}$	-185 -394	14.1 3				
_	_	spontaneous at low temperature	$\begin{split} H_2(g) + 1/2 & O_2(g) \longrightarrow H_2O(^{\ell}) \\ 2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \end{split}$	-44 -198	-119 -187				
+	+	spontaneous at high temperature	$\begin{array}{c} NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g) \\ N_2(g) + O_2(g) \longrightarrow 2NO(g) \end{array}$	176 180	284 25				
+	_	non spontaneous at all temperature	$3O_2 \longrightarrow 2O3$ $2H_2O(^{\ell}) + O_2(g) \longrightarrow 2H_2O_2(^{\ell})$	286 196	-137 -126				

Spontaneous and Non-Spontaneous

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SIGNIFICANCE OF GIBB'S FUNCTION

(a) Decrease in Gibb's function at constant temperature and pressure is related to $\Delta S_{\mbox{total}}$

(total entropy change of system and surrounding).

We known:

$$\Delta G = \Delta H - T\Delta S \qquad \dots \dots (i)$$

at constant T and pressure

also $\Delta H = q_p$ at constant pressure

 $q_{\rm P}$ = heat absorbed by system at constant pressure.

$$\Rightarrow \qquad \Delta G = q_P - T\Delta S \qquad \dots \dots (ii)$$

this gives

$$\frac{\Delta G}{T} = -\frac{q_{\rm P}}{T} + \Delta S$$

 $-\frac{q_{\rm P}}{T} + \Delta S_{\rm surrounding}$

$$\Rightarrow -\frac{\Delta G}{T} = (\Delta S_{surrounding} + \Delta S_{system})$$

Student might get confused in

Ex:

 \Rightarrow

 $-\frac{q}{T} = \Delta S_{surr.}$

Ex: q = Heat absorbed by system

-q = Heat absorbed by surrounding

$$-\Delta G = T(\Delta S_{Total})$$

Note equation (ii) can be written as $\Delta G = q - q_{rev}$.

for spontaneous process $(\Delta G)_{T,P} < 0$

$$\Rightarrow$$
 q-q_{rev} < 0 \Rightarrow q_{rev} > q

Gibbs Function And Non PV Work

Decrease in Gibb's function at constant temperature and pressure in a process gives an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electrical work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

 $dU = dq - PdV = dw_{non-PV}$ - dw_{non-PV} = non-PV work done by the system. dG = d (H - TS)= dH - TdS - SdT dG = dU + PdV + VdP - TdS - SdT

 $dG = dq - PdV - w_{non,PV} + PdV + VdP - TdS - SdT$

for a reversible change at cont. T and P

 $dG = dq_{rev.} - dw_{non} + VdP - TdS - SdT$

since $dq_{rev} = TdS$

 \Rightarrow -(dG)_{T,P} = dw_{non-PV}

Non-PV work is work done due to chemical energy transformation or due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

Gibbs Free Energy Change at Constant Temperature

In order to derive an equation which will enable us to calculate the Gibbs free energy change of an isothermal process but with varying pressure, we may conveniently start with the equation,

$$G = E + PV - TS$$

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Differentiating the above equation, we get

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

According to first law of thermodynamics,

dQ = dE + PdV

$$\therefore \qquad dG = dQ + VdP - TdS - SdT$$

Further since $\frac{dQ}{T} = dS$, we can replace dQ by TdS.

 $\therefore \qquad dG = VdP - SdT$

At constant temperature, dT = 0

$$\therefore \qquad dG = VdP$$

$$\left(\frac{dG}{dP}\right)_{r} = V$$
or

Thus, Gibb's function of every substance increases on increasing pressure, but this increase is maximum for gases, compared to solids or liquids since gases have maximum molar volume. On integrating equation dG = VdP for very minute changes from state 1 to 2, we have

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

In case of one mole of a perfect gas,

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

∴ ΔG = RT $\int_{1}^{2} \frac{dP}{P} = RT \ln \frac{P_{2}}{P_{1}}$

For n moles of a perfect gas, the free energy change is

$$\Delta G = nRT \ln \frac{\frac{P_2}{P_1}}{P_1}$$

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Gibbs Free Energy Change at Constant Pressure

From equation which is

dG = VdP - SdT (Only for pure substances)

when pressure is constant, dP = 0

$$\therefore$$
 dG = - SdT

$$\left(\frac{dG}{dT}\right)_{p}=-S$$
 or

thus, Gibb's function of every substance decreases with temperature, but this decrease is maximum for gases

since they have maximum state of disorder. Hence on increasing temperature, gas phase gain maximum stability compared to solid or liquid phase.

For Chemical Reaction

$$d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)$$

at constant temperature, If $\Delta_r V \, \underline{\sim} \, constant$

$$\begin{split} & \int_{1}^{2} d(\Delta_{r}C_{p}) = \Delta_{r}V_{1}^{2}dp \quad \Rightarrow \\ & \boxed{\Delta_{r}C_{p_{2}} - \Delta_{r}C_{p_{1}} = \Delta_{r}V(P_{2} - P_{1})} \quad \Rightarrow \\ & \text{only for condensed phase: equilibrium like} \end{split}$$

$$H_2O(s)$$

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GIBBS FREE ENERGY CHANGE IN CHEMICAL REACTIONS

Gibbs free energy changes have a direct relationship with the tendency of the system to proceed to a state of equilibrium. In view of this fact, it is desirable to have a knowledge of the free energy of chemical compounds so that the Gibbs free energy change of a possible reaction could be easily calculated. Standard free energies have been used for this case. A zero value of the Gibbs free energy is assigned to the free energies of the stable form of the elements at 25°C and 1 atm. pressure.

With this as reference point, free energies of compounds have been calculated which are called standard Gibbs free energies of formation. The difference in the Gibbs free energy of products and reactants in their standard states (at 25°C and 1 bar pressure) is denoted as ΔG° .

In standard enthalpy and entropy values are available, G° can be written from equation as,

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

GIBB'S FREE ENERGY IN CHEMICAL REACTIONS FROM GIBB'S FREE ENERGY OFFORMATION OF COMPOUNDS

Consider a chemical reaction,

 $aA + bB \rightarrow cC + dD$

The standard Gibb's free energy change ΔG° can be computed on the basis discussed above (i.e., by assigning zero value to the Gibbs free energy of the stable form of elements at 25°C and 1 bar pressure). With this as reference, the standard Gibbs free energy of the products and reactants can be determined. The standard Gibbs free energy change for the overall reaction can be evaluated as:

$$\Delta G^{\circ} = \sum G_{f(\text{products})}^{\circ} - \sum G_{f(\text{reactants})}^{\circ}$$

$$= \left(c G_{c}^{\circ} + d G_{D}^{\circ} \right) - \left(a G_{A}^{\circ} + b G_{B}^{\circ} \right)$$

A negative sign of ΔG° will show that the reaction will proceed spontaneously. note that ΔG° can be defined at any temperature, at standard pressure of 1 bar

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Reversible Phase Transitions and Gibb's Free Energy Change

During reversible phase transition which occurs at transition temperatures, Gibb's function change become zero, implying the fact that these processes are reversible processes.

at 373K and 1 atm pressure $\Delta G = 0$ for $H_2O(l) \rightarrow H_2O(g)$

at 273K and 1atm pressure $\Delta G = 0$ for $H_2O(s) \rightarrow H_2O(l)$

Gibb's energy and equilibrium constant, an important topic taken up in chemical equilibrium.

Application of Gibb's function in describing variation of vapour pressure, boiling and melting point with temperature is taken up in chemical equilibrium and liquid solutions variation of G/T with temperature, has important implication in predicting feasibility of process at different temperatures. This gives Famous Gibb's Helmholtz equation taken up in electrochemistry.

Topics of Thermodynamics taken up in Later Chapters Application of

- ➢ Gibb's function and non-PV work is taken in electrochemistry.
- ➢ Gibb's free energy and phase equilibrium taken in liquid solution.
- > Gibb's function and position of equilibrium and relationship between ΔG° and K_{eq} taken up in chemical equilibrium.
- > Variation of $\frac{G}{T}$ with temperature also called Gibb's Helmholtz equation taken in electrochemistry.
- **Ex.** K_a for CH₃COOH at 25°C is 1.754×10^{-5} . At 50°C, K_a is 1.633×10^{-5} What are ΔH° and ΔS° for the ionisation of CH₃COOH?

Sol. $(\Delta G^{\circ})_{298} = -2.303$ RT log K = $-2.303 \times 8.314 \times 298 \times \log(1.754 \times 10^{-5})$

= 27194 J.

 $(\Delta G^{\circ})_{323} = 2.303 \times 8.314 \times 323 \times \log(1.633 \times 10^{-5})$

= 29605 J.

 $\Delta G^{\underline{o}} = \Delta H^{\underline{o}} - T \Delta S^{\underline{o}}$

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 $27194 = \Delta H^{\circ} - 298 \Delta S^{\circ}$ $29605 = \Delta H^{\circ} - 323 \Delta S^{\circ}$ $\Delta H^{\circ} = -1.55 \text{ kJ/mol}$

 $\Delta S^{o} = -96.44 \text{J/mol. K}$