# Thermodynamics: Classical to Statistical
Prof. Sandip Paul
Department of Chemistry
Indian Institute of Technology Guwahati
## Lecture - 05
## Gibbs and Helmholtz free energy

So, we will discuss Entropy change for mixing of two ideal gases. Suppose, initially we have a system having two containers and in one container bromine gas is there and in another container nitrogen gas is there.

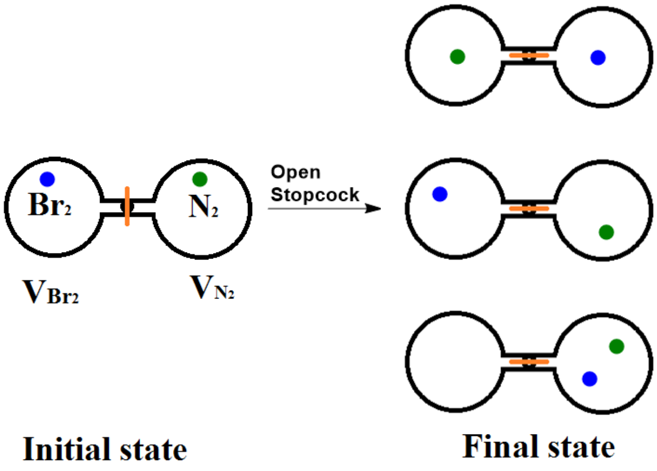

**Figure 1**

This is our initial state. There is stop cock between them. If we remove the stop cock, they will mix. Here we have bromine plus nitrogen and this is our final state.

We are assuming here that both bromine and nitrogen, they behave ideally. And our goal is to calculate the entropy of mixing of bromine and nitrogen. What is entropy change for nitrogen gas molecule?

$$\Delta S_{N2} = n_{N2}\, R\ln (V_{N2} + V_{Br2})/ V_{N2}$$

Where, $n_{N2}$= number of moles of $N_2$ gas

As we know , $\Delta S_{N2} = nR\ln(V_{final} / V_{initial})$

So, this is entropy change for nitrogen gas. What about entropy change for bromine gas? We say this is delta SBr2 in similar manner we can write this,

$$\Delta S_{Br2} = n_{Br2} R\ln(V_{N2} + V_{Br2})/V_{Br2}$$

So, what is total entropy change? That is nothing but entropy change for mixing.

$$\Delta S_{mix} = \Delta S_{N2} + \Delta S_{Br2}$$

$$= n_{N2}R\ln(V_{N2}+V_{Br2})/V_{N2} + n_{Br2}R\ln(V_{N2}+V_{Br2})/V_{Br2}$$

$$= - n_{N2}R\ln V_{N2} /(V_{N2}+V_{Br2}) - n_{Br2}R\ln V_{Br2} /(V_{N2}+V_{Br2})$$

At constant T & P , for ideal gas $V \alpha n$

$$\Delta S_{mix} = - n_{N2}R\ln n_{N2} /(n_{N2}+n_{Br2}) - n_{Br2}R\ln n_{Br2} /(n_{N2}+n_{Br2})$$

$$= (n_2/n)nR\ln(n_{N2}/n) – n_{Br2}\times n/n \ R\ln n_{Br2}/n \quad ,\text{where } n= n_{N2} +n_{Br2}$$

where n is nothing but nN2 plus nBR2 or total number of moles in the system.

$$\Delta S_{mix} = -nX_{N2}R\ln X_{N2} – n X_{Br2}R\ln X_{Br2}$$

$$X_{N2} = \text{mole fraction of } N_2 = n_{N2} /n$$

$$X_{Br2} = \text{mole fraction of } Br_2 = n_{Br2}/n$$

So, we can simplify this expression or in general we can write,

$$\Delta S_{mix} = -nR\sum x_i + \ln x_i \quad ,x_i = \text{mole fraction of i-th species } 0\leq x_i\leq 1 \ ,x_i \text{ fraction}$$

$$\Delta S_{mix} > 0 \text{ , entropy of mixing is positive}$$

It says that entropy of mixing is positive or in other words, the mixing is entropically favourable.

The entropy change Arising from a phase transition :

Next we discuss, the entropy change arising from a phase transition. Now all phase transitions, suppose we have solid ice, while it melts it gives liquid water, and from there we get water vapour. So, from solid to liquid, liquid to vapour. So, while phase transition takes place, this phase transitions are accomplish by change of entropy. Because solid ice, the system not that much cavity, but when it melts and it forms liquid water molecules are more cavity. When it further boils this water vapour this furthermore, more cavity water molecules are. Under the condition of constant pressure , the latent heat of a phase transition is its enthalpy of transition($\Delta H_{trans}$). At the temperature of transition ,$T_{trans}$ the system is in equilibrium. So the heat is transferred reversibly from the surroundings. So the entropy of transition ,

$$\Delta S_{trans}=\Delta H_{trans}/T_{trans}$$

We know , $dS_{sys} > 0$ for spontenious process(applicable for isolated system only)

$$\text{In general , } dS_{total} = dS_{universe} = dS_{sys} + dS_{sur} > 0$$

$\Rightarrow$for spontaneous process.

In general we need to calculate two quantities, $dS_{sys}$ and $dS_{surr}$ to examine whether the process is spontaneous or not. So it would be better if we can identify the spontaneity of any process by calculating only one parameter. Lets see, whether we can have one single parameter that can tell us whether the process is spontaneous or not.

From the Frist law of thermodynamics,

$$dU = \partial q + \partial W$$

At constant volume (no P-V work)

$$dU = \partial q = dq \quad \text{,as } \partial W = 0$$

we know , $dS \geq \partial q/Td$

$TdS \geq \partial q$

$dU \leq TdS$

$dU - TdS \leq 0$ at constant volume

$d(U-TS) \leq 0$ at constant volume and temperature

$\Rightarrow dA_{T,V} \leq 0$....(1) '<' sign represents spontaneous process and '=' sign equilibrium

$A = U - TS$ A⇒Helmhotz free energy(state function)

Figure 2 is plot of $A_{mix}$ versus Time.

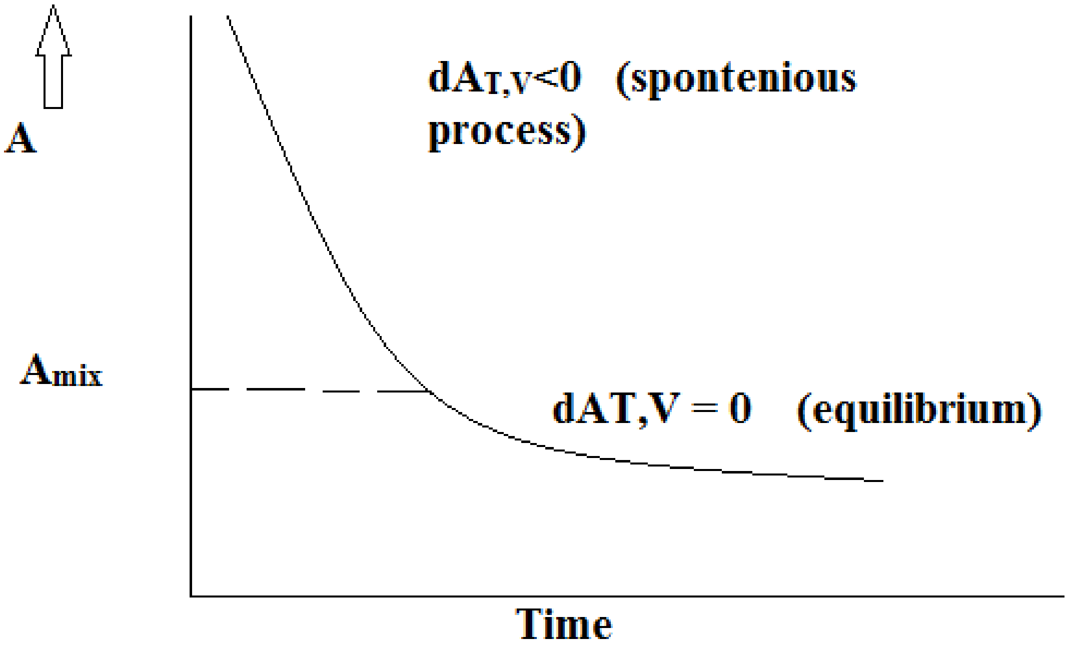

**Figure 2**

$A = U - TS \Rightarrow \Delta A = \Delta U - T\Delta S$ .... (2) at constant T and V

When $\Delta U < 0$ and $\Delta S > 0 \Rightarrow \Delta A_{T,V} < 0$

$\Delta U < 0$ and $\Delta S > 0 \Rightarrow$ we need to examine $\Delta U$ and $T\Delta S$

If $\Delta U > 0$ and $\Delta S > 0$ we also need to examine $\Delta U$ and $T\Delta S$

For the mixing of $Br2$ And $N2$ gas

$$\Delta Smix = -nR\sum x_i \ln x_i$$

$$\Delta U = 0$$

$$\Delta A_{mix} = nRT\sum x_i \ln x_i$$

since $x_i$ is fraction, $\Delta Amix \leq 0$.

Gibbs free energy(G) : since most of the reactions occur at constant T and P ,we know

$$dU = \partial q + \partial W$$

$$dS \geq \partial q/T \rightarrow TdS \geq \partial q$$

$$dU \leq TdS - PdV$$

$$d(V-TS +PV) \leq 0 \text{ at constant T and P}$$

$$d(H-TS) \leq 0$$

$$dG_{T,P} \leq 0$$

So that how the Gibbs free energy or Gibbs energy terms being point. So, Gibbs free energy sometimes we called Gibbs energy is termed as G and why we need to have G why Helmholtz energy is not sufficient? Because most of the, or since most of the reactions occur at constant T and P.

$G = H-TS$ , variation of Gibbs free energy with tempareture and pressure

$$G = H-TS$$

$$dG = dH-TdS-SdT$$

$$dG =(dU+PdV)/\partial q +VdP-TdS/\partial q-SdT$$

$$dG = \partial q +VdP - \partial q-SdT$$

$$dG = Vdp - SdT \qquad . \qquad . \quad . \quad . \quad . \quad . \; (1)$$

So, we write dG is VdP minus SdT. This is very very important expression. Why we will see now.

$$(\partial G/\partial P)T = V....(2)$$

$$(\partial G/\partial T)P = -S....(3)$$

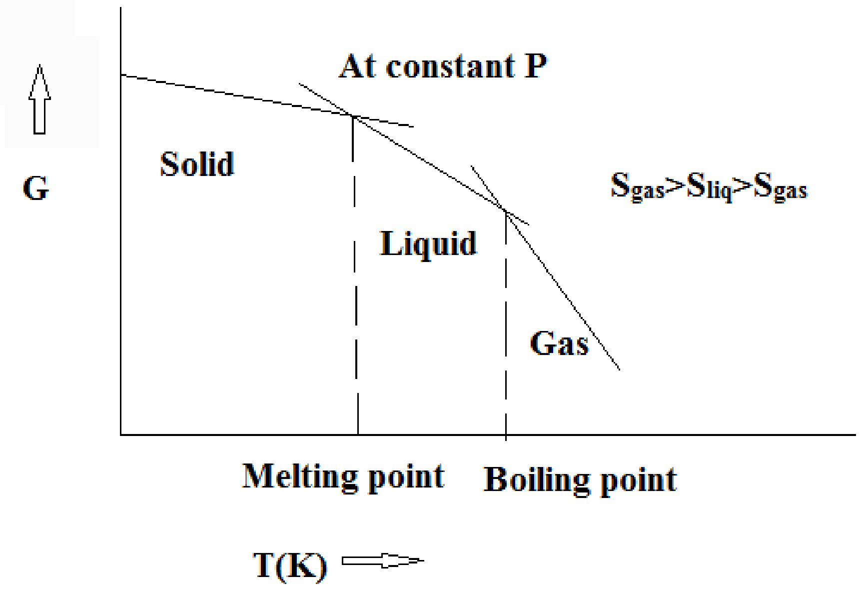

**Figure 3**

Now first we consider this expression 3. Now if we plot G verses temperature in kelvin (Figure 3), expression 3 says variation of Gibbs free energy with temperature at constant pressure. If we look at expression 3 here we get that the slope of the curve is negative, because absolute entropy is a positive quantity. So, the slope of G verses T plot will be having negative slope. So we get like this.

If you look at the figure carefully, what you observe. You observe that the slope is different up to this point, again from this point to this point, after this point the slope is also different here. So this is known as melting point and this is boiling point. Why the slopes are different here? The slopes are different here because S gas (absolute entropy for gas molecule) is much much higher than S liquid is greater than S solid. That is why we get different slops here. So this region is our solid region, this is liquid region, and this is gas region. So, this is at constant pressure. When pressure is constant we get this kind of plot, if we plot G verses T.

From Equation (2) ,

$$\int_{G1}^{G2} dG = \int_{P1}^{P2} V\ \mathrm{dP}$$

For ideal gas V= nRT/P

$$\Delta G = G_1\text{-}G_2 = nRT\ \ln P_2/P_1$$

$$\Delta G = nRT\ln\ V_2/V_1$$

So, we get another good expression, another nice expression for calculating delta G here.

$$dU = \partial q_{rev} + \partial W_{rev} = TdS - PdV$$

$$(\partial U/\partial S)_V = T \text{ and } (\partial U/\partial V)_S - P$$

$$dH = TdS + VdP$$

$$(\partial H/\partial S)_P = T \text{ and } (\partial H/\partial P)_S = V$$

$$dA = dU\text{-}\ TdS - SdT = TdS/\partial q - PdV/\partial W - TdS\text{-}SdT$$

$$dA = \text{-}PdV\text{-}SdT$$

$$(\partial A/\partial V)_T = \text{-}\ P \text{ and } (\partial A/\partial T)_V = \text{-}\ ST$$

$$dG = dH - SdT - TdS$$

$$dG = (dU+PdV)/\partial q + VdP - SdT - TdS/\partial q$$

$$dG = VdP - SdT$$

$$(\partial G/\partial P)_T = V \text{ and } (\partial G/\partial T)_P$$

So, we have obtained so far 8 important expressions. So, from these expressions we can derive Maxwell’s relationships.