

Third Law of Thermodynamics

Entropy of the perfectly crystalline solids at absolute 0 temp. (OK)

Solid (0.K pressure) \rightarrow Solid (T, p)

$$\Delta S = S_T - S_{OK} = \int_{OK}^T \frac{C_p dT}{T}$$

$$S_T = S_{OK} + \int_{OK}^T \frac{C_p dT}{T}$$

(Entropy at 0 temp.)

$$S_T = \int_{OK}^T \frac{C_p dT}{T}$$

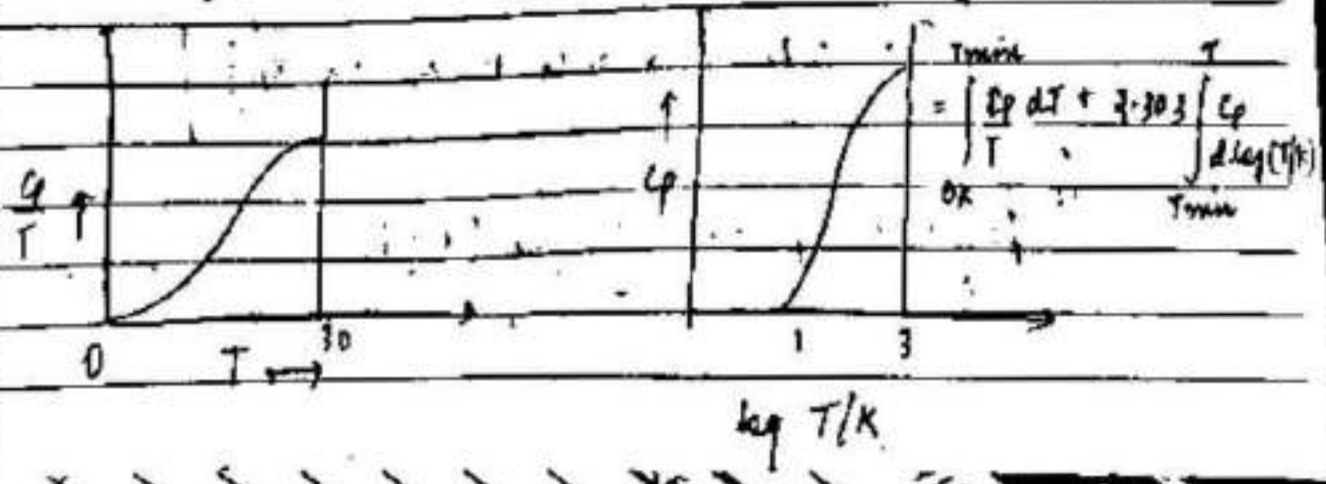
Absolute Entropy

$$S_T^0 = \int_{OK}^T \frac{C_p dT}{T} \quad P = 1 \text{ bar}$$

0 to 15K (values known hold for within this temp. range)

Below this temp. $C_p = AT^3$
 \rightarrow Debye - T-cubed law

$$S_T = \int_0^{T_{min}} \frac{C_p dT}{T} + \int_{T_{min}}^T \frac{C_p dT}{T} = \int_{OK}^T \frac{C_p dT}{T} + \int_{T_{min}}^T \frac{C_p d(T/K)}{(T/K)}$$



Derivation of 3rd law of Thermodynamics

$$S = k \ln w$$

$$w = \frac{N!}{N_1! N_2! \dots}$$

$$S = k \ln(w) \equiv 0 \quad (T \rightarrow 0) \quad (\text{Third law of Thermodynamics})$$

$w = \text{max. no. of microstates}$

$= \text{possible no. of arrangements}$

Explanation

$$w = \frac{N!}{N_a! N_b!}$$

if molecule have diff. kind of atoms

Residual Entropy

$$S_{\text{residual}} = k \ln \frac{N!}{N_a! N_b!}$$

if N is very large - by using Stirling approximation

$$\ln N! \approx N \ln N - N$$

$$S = k \ln [(N \ln N - N) - (N_a \ln N_a - N_a) - (N_b \ln N_b - N_b)]$$

since, $N_a + N_b = N$

$$S = -k [N_a \ln N_a + N_b \ln N_b - N \ln N]$$

in terms of mole fraction

$$S = -k [N_a \ln N_a + N_b \ln N_b - (N_a + N_b) \ln N]$$

$$= -k [N_a (\ln N_a - \ln N) + N_b (\ln N_b - \ln N)]$$

$$= -k \left[N_a \ln \frac{N_a}{N} + N_b \ln \frac{N_b}{N} \right]$$

$$S = -Nk [x_a \ln x_a + x_b \ln x_b]$$

(perfectly immiscible solids - a & b)

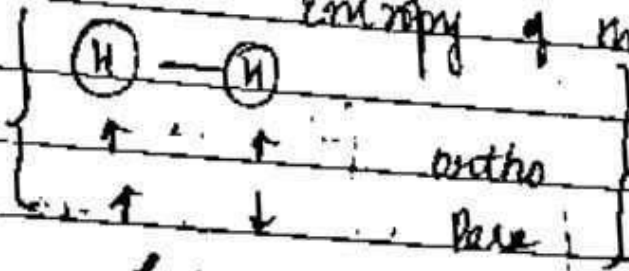
pure a + pure b \rightarrow mix (a + b)

$$\Delta S_{\text{mix}} = S_{\text{mix}} - (S_{\text{pure a}} + S_{\text{pure b}})$$

$$\Delta S_{mix} = S_{mix} - S$$

$$\Delta S_{mix} = -R \ln (x_a \ln x_a + x_b \ln x_b)$$

Entropy of the mixture is always +ve.



Free Energy

$\Delta \rightarrow$ Helmholtz Free Energy

$$A = U - TS$$

$$dA = dU - Tds - SdT$$

$$\because dq = dU + dw \quad (FDOT) \quad dU = dq + dw$$

for reversible isothermal change

$$dA = dU - Tds \quad \because \left(\frac{dq_{rev}}{T} = ds \right)$$

$$dA = dq_{rev} + dw_{rev} - Tds$$

$$dA = Tds + dw_{rev} - Tds$$

$$(dA)_T = dw_{rev}$$

$$(\Delta A)_T = W_{rev} \text{ for finite change}$$

$$= (\Delta A)_T = -W_{rev} \text{ work done by the system}$$

decrease in Helmholtz energy:

maximum amt of work is equal to maximum amount of work which a system can do isothermally and reversibly because of relationship b/w ΔA and W , Helmholtz free energy is called work function.

Gibbs free energy $\rightarrow G$

$$G = H - TS$$

$$dG = dH - Tds - SdT$$

$$dH = dU + PdV$$

at constant pressure $\rightarrow VdP$

$$dG)_p = dU + PdV - Tds - sdT$$

$$dG)_p = dq_{rev} + dw_{rev} + PdV - Tds - sdT$$

$$dG)_p = Tds + dw_{rev} + PdV - Tds - sdT = 0$$

at constant temp.

$$(dG)_{T,P} = dw_{rev} + PdV$$

$$(dG)_{T,P} = [dw_{rev} - (-PdV)] \text{ i.e. non-mechanical work}$$

(include all types of work)

$$(dG)_{T,P} = dw_{net}$$

$$\Delta G)_{T,P} = w_{net}$$

$$(-\Delta G)_{T,P} = -w_{net}$$

A decrease in Gibbs free energy is equal to the amount of work which a system can do isothermally & isobarically over and above the expansion work against constant pressure.

We know that, in an adiabatic process, the entire energy change (ΔE) in a system is converted into work.

$$dU = dq + dw$$

$$dq = 0$$

$$dU = dw$$

However, under other conditions less than the entire energy change can be converted into work, the amount which is just unavailable can be converted into work is Tds because this amount is used to increase the randomness of the system at constant temp.

The difference in $\Delta F + T\Delta S$ or $\Delta H - T\Delta S$ are the free energies in the sense that if all the processes are reversible and isothermal then the complete conversion of free energy is possible.

Variation of Free Energy with temp. & Pressure

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

$$G = H - TS$$

$$H = U + PV \quad (1)$$

$$G = U + PV - TS \quad (2)$$

$$dG = dU + PdV + VdP - TdS - SdT \quad (3)$$

$$dU = dq + dw$$

$$dq = dU - dw$$

$$-PdV$$

$$dq = dU + PdV$$

$$dq = VdP - SdT$$

$$\left(\frac{dS}{dT} = \frac{dq_{rev}}{T} \right)$$

if P is constant, $dP = 0$

$$dq_p = -SdT$$

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

if T is constant, $dT = 0$

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

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

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

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

$$\Delta G = RT \ln \frac{V_1}{V_2}$$

$$\Delta G = nRT \ln \frac{V_1}{V_2}$$