Module 1

Thermodynamics and defects in solids

Concept of free energy, enthalpy and entropy

➢ **Gibb's free energy**, G can be expressed as G = H-TS

 H – enthalpy (J/mol) , T – temperature in K, S – entropy (J/mol.K)

➢ **Further** H= E+PV

 E – Internal energy (J/mol), P – Pressure (N/m^2) , V – Volume (m^3/mol)

➢ In the solid state, the term **PV** is in general **very small** (in the temperature and pressure range we consider) and can be neglected.

➢ To illustrate further at atmospheric pressure 1.01x 10^6 N/m^2, the typical molar volume of most of the metals could be in the range of 6x 10^{-6} - 10 x10^{-6} m^3/mol. If we take the higher side, PV term gives around 10.1 J/mol.

➢ On the other hand, internal energy of metals is in the order of kJ/mol. So PV term is less than even 1%.

➢**Internal energy** has two components:

 Potential energy , which depends on atomic bonds and

 Kinetic energy , which depends on the vibration of atoms at their lattice position

➢ The relation can be rewritten as   H = G + TS

➢ H measures the total energy of the body

➢ TS measures the useless energy that is the energy which can't be spent for any work or transformation.

➢ So the Gibb's free energy is defined as the energy that can be "set free" at a particular pressure to do the work or make a particular transformation possible

➢ Similarly at a particular volume the free energy is called Helmoltz free energy, F, expressed as

$$F = E - TS$$

➢ We shall consider the Gibb's free energy since we are going to consider the transformations under constant pressure.

➢ To determine Gibb's free energy, we need to determine enthalpy and entropy of the system.

Relation between enthalpy and specific heat

➢ **Let us first consider a single component system.**

➢ **If we keep the system isolated and do not allow it to interact with the surroundings, the internal energy of the system will not change.**

➢ **This is actually a closed system.**

➢ **However, if the system is allowed to interact with the surroundings (that is if it acts as a open system) internal energy might change.**

➢ **Suppose the system does work δW in the surroundings and takes heat δQ from the system, then according to the** *first law of thermodynamics*, **the change in internal energy of the system is**

$$dE = \delta Q - \delta W \qquad\qquad\qquad \text{(1)}$$

➢ **So after spending some energy for work, rest of the energy is added to the system to increase the internal energy.**

➢ **Here exact differential is used for energy because it does not depend on the path and function of the state only.**

➢ **On the other hand heat and work depend on the path.**

If a system changes its volume by dV at a constant pressure P, the work can be expressed as

$$dW = PdV$$

So Eq. 1 can be written as

$$dE = dQ - PdV \qquad\qquad (2)$$

Further we know

$$H = E + PV$$
$$dH = dE + PdV + VdP$$
$$dH = dQ + VdP$$

If we divide by dT, we get

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V\frac{dP}{dT}$$

Specific heat capacity, C_P at a constant pressure is defined as the heat required to increase the temperature of the system by one degree. So it can be expressed as

$$C_P = \left(\frac{\delta Q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \qquad \text{since dP = 0}$$

➢ **After integration, we can write**

$$\int_{H_o}^{H} dH = \int_{o}^{T} C_P dT$$

$$H_T = H_o + \int_{o}^{T} C_P dT$$

$$H_T = \Delta H_{298} + \int_{298}^{T} C_P dT$$

➢ H_T, H_o and ΔH_{298} are the enthalpies at temperature, **T, 0** and **298 K** respectively.

➢ **Note that we cannot measure the absolute thermodynamic values.**

➢ **We rather measure a relative value.** H_{298} **is considered as reference value.**

➢ **For pure elements it is considered as zero.**

Relation between entropy and specific heat

➢ As explained before, the knowledge on entropy (which cannot be spent to do a work) is required to determine how much energy is available (free energy) in a system to do useful work from the total heat content or enthalpy.

➢ Second law of thermodynamics states that the entropy of a system will either remain the same or try to increase.

➢ When system moves from one equilibrium state 1 to another equilibrium state 2 by changing heat of δQ, the entropy S in a reversible process can be defined as

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

➢ The value at zero Kelvin is zero and considered as the reference state for entropy, so that the entropy at any temperature T can be expressed as

$$S_T = \int_0^T \frac{\delta Q}{T}$$

➢ Previously we have seen from the relation H = E+PV and using the first law of thermodynamics

$$\delta Q = dH$$

➢ **Previously we have seen that** $dH = C_P dT$

➢ **So the entropy at T can be expressed as**

$$S_T = \int_o^T \frac{C_P}{T} dT$$

➢ **Sometimes value of the entropy at the standard state (298 K) is available and can written as**

$$S_T = \Delta S_{298} + \int_{298}^T \frac{C_P}{T} dT$$

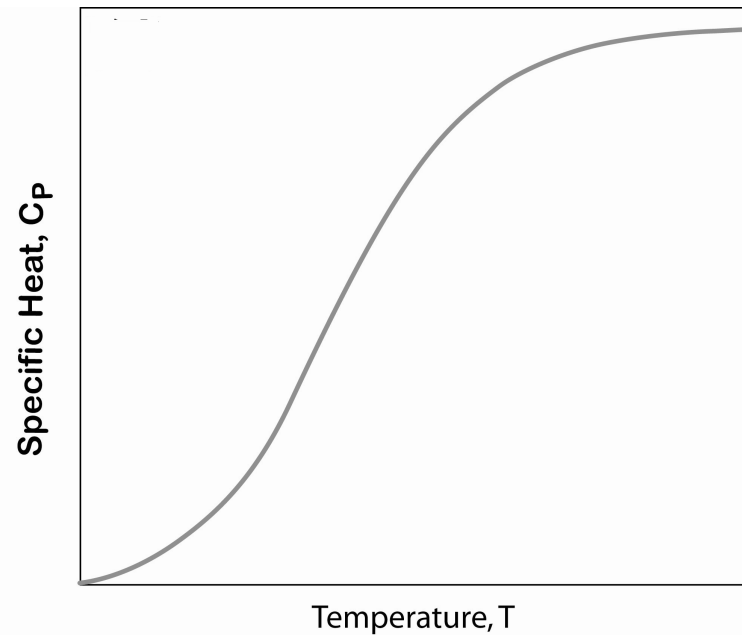➢ **So the free energy at temperature, T can be determined**

$$G_T = H_T - TS_T$$

$$G_T = \Delta H_{298} + \int_{298}^T C_P dT - T\left(\Delta S_{298} + \int_{298}^T \frac{C_P}{T} dT \right)$$

$$G_T = \int_{298}^T C_P dT - T\left(\Delta S_{298} + \int_{298}^T \frac{C_P}{T} dT \right) \quad \textbf{In pure elements}$$

➤ **Specific heat is expressed as**

$$C_p = A + BT - \frac{C}{T^2}$$

➤ **A, B and C are constants.**

➤ **Specific heat changes with temperature as shown in the figure**

Temperature, T

➤ **Specific heat is expressed in terms of empirical formula as expressed above.**

➤ **In general the constant values are available in the data book.**

➤ **So the free energy at temperature, T can be determined**

$$G_T = \int_{298}^{T} \left(A + BT - \frac{C}{T^2} \right) dT - T \left(\Delta S_{298} + \int_{298}^{T} \frac{A + BT - \dfrac{C}{T^2}}{T} dT \right)$$

$$= AT + \frac{B}{2}T^2 + C\left.\frac{1}{T}\right|_{298}^{T} - T\left[\Delta S_{298} + \left(A\ln T + BT + \left.\frac{C}{2T^2}\right|_{298}^{T} \right) \right]$$

➤ **From the known values, one can determine G at different temperatures and then plot the variation of G with T.**