Thermodynamics: Classical to Statistical

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Lecture - 35

Advance Problems - 3

Problem 19:

1 g of water is enclosed in a vial is placed in an evacuated flask maintaining 298 K temperature. By using a lever, the vial is broken so that the water is free to vaporize, and at equilibrium it is found that half of the water is vaporized. The vapor pressure of water at 25 ˚C is 24 mm of Hg and the enthalpy of vaporization is 2470 J g^{-1}. Calculate q, w, ΔH, ΔG and ΔS.

Solution:

The process is,

$$\frac{1}{2}g \text{ of } H_2O\text{ (l, 25°C, 24 mm)} \rightleftharpoons \frac{1}{2}g \text{ of } H_2O\text{ (g, 25°C, 24 mm)}$$

$$q = 2470 \times (1/2)\text{ J} = 1235\text{ J}$$

Let $q = q_v$, so $w = 0$, since no PV work.

Hence we can write $\Delta U = q$ which gives $\Delta U = 1235$ J.

$$\Delta H = q_p = q_v + P\,\Delta V$$

$$\text{Or,} \quad \Delta H = q_v + nRT$$

Now, $n = \frac{1}{2\times 18} = \frac{1}{36}$, hence we can write,

$$\Delta H = 1235 + \frac{1}{36} \times 8.314 \times 298$$

$$\text{Or,} \quad \Delta H = 1304\text{ J}$$

The q_{rev} (slow expansion against pressure P to vaporize half of water).

$$\Delta S = \frac{1304}{298} = 4.38\,J/K$$

Now $$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 1304 - 298 \times 4.38 = 0$$

It should because the process is in equilibrium.

Problem 20:

For a certain reaction,

$$\Delta G(cal/mol) = 13580 + 16.1T\log_{10} T - 72.59T$$

Find ΔS and ΔH of the reaction at 27 ˚C.

Solution:

Given that,

$$\Delta G(cal/mol) = 13580 + 16.1T\log_{10} T - 72.59T$$

Now, we know,

$$\Delta S = -\frac{\partial \Delta G}{\partial T}$$

$$\Delta S = -6.99\left[1 + \ln T\right] + 72.59$$

At 300 K,

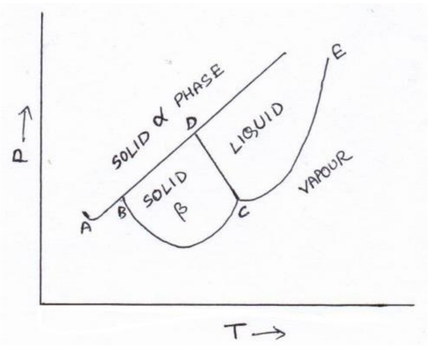
$$\Delta S = 25.72 \text{ cal K}^{-1} \text{ mol}^{-1} = 108.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = 15823.48 \text{ J mol}^{-1}$$

$$\Delta H = \Delta G + T\Delta S = 48.23 \text{ kJ mol}^{-1}$$

Problem 21:

The phase diagram of a one component system having solid phases (α, β) are shown below.



Starting from point A, indicate the phase observed if the system is heated at constant pressure. Calculate the degrees of freedom at points A and B.

Solution:

It is a one component system consisting of four phases, i.e., solid α and β, liquid and vapor phase. Now in the above P-T diagram,

- **Curve AB** is the sublimation or vapor pressure curve of solid α. Along this curve 2 phases, solid α and vapor phase are in equilibrium.
  The degrees of freedom, F = C - P + 2
  C = 1, P = 2 , hence, F = 1 – 2 + 2 = 1

- **Point B** is the point where α changes to β. Hence it is known as the transition temperature. Thus there are three phases [2 solid phases, α and β and 1 vapor phase]. So degrees of freedom F is C minus P plus 2, where C is 1, and phase is 3 here and it gives the number of degrees of freedom is 0.
  The degrees of freedom, F = C - P + 2
  C = 1, P = 3 , hence, F = 1 – 3 + 2 = 0

- **Curve BC** is vapor pressure or sublimation curve for β. On this curve 2 phases (β and vapor) are in equilibrium.
  The degrees of freedom, F = C - P + 2
  C = 1, P = 2 , hence, F = 1 – 2 + 2 = 1

- **Point C** represents the melting point of β. This is another triple point. At this point, 3 phases (β, vapor and liquid) are in equilibrium.

- **Curve CE** represents the liquid and vapor are in equilibrium.
  The degrees of freedom, F = C - P + 2
  C = 1, P = 2 , hence, F = 1 – 2 + 2 = 1

- **Curve BD** represents the equillibrium between the solid phases α and β.

- **Curve CD** represents β and liquid are in equilibrium.
  The degrees of freedom, F = C - P + 2
  C = 1, P = 2 , hence, F = 1 – 2 + 2 = 1

Problem 22:

The volume of a gas starts to expand at 5 L at a temperature of 400 K and a pressure of 1.12 bar. If the change in entropy was 0.787 $JK^{-1}mol^{-1}$, what was the final volume of the gas?

Solution:

Considering, $1\ bar \approx 1\ atm$ and $PV = nRT$, we get,

$$n = \frac{1.12 \times 5}{0.082 \times 400}$$

Now,

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

Where $\Delta S = 0.787\ \mathrm{JK^{-1}mol^{-1}}$, $R = 8.314\ \mathrm{JK^{-1}mol^{-1}}$ and $V_1 = 5\mathrm{L}$. Putting these values we can get the value of $V_2 = 8.7048$ L.

Problems on Statistical Thermodynamics

Problem 1:

'N' number of particles are distributed among three states having energies $E_1 = 0$, $E_2 = k_BT$ and $E_3 = 2k_BT$. If the total equilibrium energy of the system is $2000k_BT$, find the value of 'N'.

Solution:

Since the degeneracy of the states are not provided, we can consider the states are non degenerate. We know,

$$\frac{N_i}{N} = \frac{e^{-\beta E_i}}{Q}$$

where N_i represents the number of particles in any given state, N is the total number of particles N and Q is the partition function. Since N and Q are constants, we can write,

$$N_i \propto e^{-\beta E_i}$$

So,

$$N_1 : N_2 : N_3 = e^{-\beta E_1} : e^{-\beta E_2} : e^{-\beta E_3}$$

Or, $$N_1 : N_2 : N_3 = 1 : e^{-1} : e^{-2}$$

Hence,

$$N_1 = \frac{N}{1+e^{-1}+e^{-2}}$$

$$N_2 = \frac{N}{1+e^{-1}+e^{-2}} \times \frac{1}{e}$$

$$N_2 = \frac{N}{1+e^{-1}+e^{-2}} \times \frac{1}{e^2}$$

Now the average energy E is,

$$E = 2000k_B T = E_1 \times N_1 + E_2 \times N_2 + E_3 \times N_3$$

Putting the values, we get

$$N = 4709$$

Hence, the number of particles is 4709.

Problem 2:

The density of zinc (whose electronic configuration is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$) is 7130 kgm^{-3} and its atomic weight is 65.4. Calculate the Fermi energy. The effective mass of a free electron in zinc crystal is 7.7×10^{-31} kg and Avogadro's number is 6.02×10^{23}.

Solution:

The electronic configuration of zinc in ground state shows that each atom of Zn has 2 valence electrons.

The number of atoms per unit volume is

$$= \frac{N}{\frac{M}{\rho}} = \frac{6.02 \times 10^{23}}{\frac{65.4 \times 10^{-3}}{7130}} = 6.56 \times 10^{28} m^{-3}$$

The number of free electrons per meter cube volume $= 2 \times 6.56 \times 10^{28} m^{-3}$

So Fermi energy, E_F, is

$$E_F = \frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{\frac{2}{3}} = 94.25eV$$

So the value of Fermi energy is 94.25 eV.

Problem 3:

An ice cube of volume 1 dm^3 is melted slowly (reversibly) at 0°C. How many times more micro states are associated with the liquid phase (water) than the solid phase (ice).

[Given, the latent heat of melting of ice is 3.34×10^5 Jkg^{-1} and the density of ice is 1 gcm^{-3}.

Solution:

The mass of ice cube = density × volume

where density is 1 gcm^{-3} and volume is 1 dm^3. So we get the mass of ice is

$$= 1\ g\ cm^{-3} \times 1\ dm^3 = 1000\ \text{gram} = 1\ \text{kg of ice cube.}$$

The latent heat of melting, $\Delta H = 3.34 \times 10^5\ Jkg^{-1}$.

Thus, the heat absorbed by the ice cube,

$$\begin{aligned} q_{rev} &= \text{latent heat} \times \text{mass} \\ &= 3.34 \times 10^5\ J\ kg^{-1} \times 1\ kg \\ &= 3.34 \times 10^5\ J \end{aligned}$$

At temperature T = 0°C = 273 K.

$$\Delta S = \frac{q_{rev}}{T} = \frac{3.34 \times 10^5}{273}\ JK^{-1}$$

We know,

$$\Delta S = k_B \ln \frac{w_2}{w_1}$$

where w represents the number of micro states. Equating the above two expressions we get,

$$\frac{w_2}{w_1} = e^{8.8655 \times 10^{25}}$$

Hence the number of micro states in the liquid phase is higher than the number of micro states in the solid phase.

Problem 4:

For grand canonical ensemble, show that

$$\frac{\partial < N >}{\partial \mu} = \beta \Delta \overline{N}^2$$

Where $\Delta \overline{N}^2 = < N^2 > - < N >^2$.

Solution:

The grand canonical partition function is given

$$\Xi(\mu,V,T)=\sum_N\sum_j e^{-\beta E_{N_j}(V,T)}e^{\beta\mu N}$$

The average number of particle N is

$$<N>=\frac{1}{\beta}\left(\frac{\partial\ln\Xi}{\partial\mu}\right)_{V,T}$$

Or, $$<N>=\frac{1}{\beta}\times\frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\mu}\right)_{V,T}$$

Or, $$<N>=\frac{1}{\beta}\frac{1}{\Xi}\sum_N\sum_j e^{-\beta E_{N_j}}e^{\beta\mu N}\times\beta N$$

Or, $$<N>=\frac{1}{\Xi}\sum_N\sum_j Ne^{-\beta E_{N_j}}e^{\beta\mu N}$$

Differentiating,

$$\frac{\partial<N>}{\partial\mu}=\left(-\frac{1}{\Xi^2}\sum_N\sum_j e^{-\beta E_{N_j}}e^{\beta\mu N}\times\beta N\right)\times\left(\sum_N\sum_j Ne^{-\beta E_{N_j}}e^{\beta\mu N}\right)+\frac{1}{\Xi}\sum_N\sum_j Ne^{-\beta E_{N_j}}e^{\beta\mu N}\times\beta N$$

$$\frac{\partial<N>}{\partial\mu}=-\beta\left(\frac{1}{\Xi}\sum_N\sum_j Ne^{-\beta E_{N_j}}e^{\beta\mu N}\right)\times\left(\frac{1}{\Xi}\sum_N\sum_j e^{-\beta E_{N_j}}e^{\beta\mu N}\right)+\beta\times\frac{1}{\Xi}\sum_N\sum_j N^2e^{-\beta E_{N_j}}e^{\beta\mu N}$$

Or, $$\frac{\partial<N>}{\partial\mu}=-\beta<N>^2+\beta<N^2>$$

Or, $$\frac{\partial<N>}{\partial\mu}=\beta\left(<N^2>-<N>^2\right)$$

Or, $$\frac{\partial<N>}{\partial\mu}=\beta\Delta\bar{N}^2$$