Thermodynamics: Classical to Statistical

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Lecture - 07

Clapeyron equation and phase transition; concept of fugacity

We know chemical potential of alpha phase is equal to chemical potential of beta phase,

$$\mu^{\alpha}(T,P) = \mu^{\beta}(T,P)$$

When phase α is in equilibrium with β phase

$$(\partial\mu^{\alpha} /\partial P)_T\, dP + (\partial\mu^{\alpha} /\partial T)_P\, dT = (\partial\mu^{\beta} /\partial P)_T\, dP + (\partial\mu^{\beta} /\partial T)_P\, dT$$

$$\Rightarrow \bar{V}^{\alpha}\, dP - \bar{S}^{\alpha}\, dT = \bar{V}^{\beta}\, dP - \bar{S}^{\beta}\, dT$$

$$(\bar{V}^{\alpha} - \bar{V}^{\beta})\, dP = (\bar{S}^{\alpha} - \bar{S}^{\beta})dT$$

$$\Rightarrow dP/dT = \Delta S_{tran}/\Delta V_{trans}$$

$$\Rightarrow dP/dT = \Delta H_{tran}/T\Delta V_{tran} \quad \Rightarrow \text{clapeyron equation}$$

Next we will consider the equation,

$$dP/dT = \Delta S_{trans}/\Delta V_{trans}$$

$$dP/dT = \Delta H_{trans}/T\Delta V_{trans}$$

it relates the slope of the two-phase boundary like in phase diagram (P-T plot) with the values of ΔH_{trans} and ΔV_{trans} for the transition between two phase.

$$dP/dT = \Delta\bar{S}_{trans}/\bar{V}_{trans}$$

for solid ice→liquid water transition

$$\Delta\bar{S}_{trans} = +\text{ ve}$$

$\Delta\bar{V}_{trans} = \bar{V}_{liqwater} - \bar{V}_{ice} = -$ ve $\Rightarrow dP/dT = -$ ve $\Rightarrow$ melting point of ice decreases with increasing pressure.

For liquid water→water vapour transition

$$\Delta S_{trans} = +\ ve$$

$$\Delta\bar{V}_{trans} = \bar{V}_{watervapour} - \bar{V}_{liquid\ water} = +ve \quad (dP/dT) = -\ ve$$

$\Rightarrow$boiling point of water increases with increase pressure.

Solid ice → Water vapour

$$\Delta S_{trans} = +\ ve$$

$$\Delta V trans = \bar{V}_{water\ vapour} - \bar{V}_{solid\ ice} = +\ ve$$

$(dP/dT) = +\ ve \Rightarrow (dT/dP) = +\ ve$…….. the sublimation temperature increases with increasing pressure.

Lets see and how they differ for these three transitions.

Now , we will plot pressure (P) versus temperature (T) for these transition (Figure 1),

$$(\Delta\bar{V}_{trans})_{liq\rightarrow vap} \approx (\Delta\bar{V} trans)_{solid\rightarrow vap}$$

$$(\Delta S_{trans}) liq\rightarrow vap < (\Delta S_{trans})_{solid\rightarrow vap}$$

$$(dP/dT)_{solid\rightarrow vap} > (dP/dT)_{liq\rightarrow vap}$$

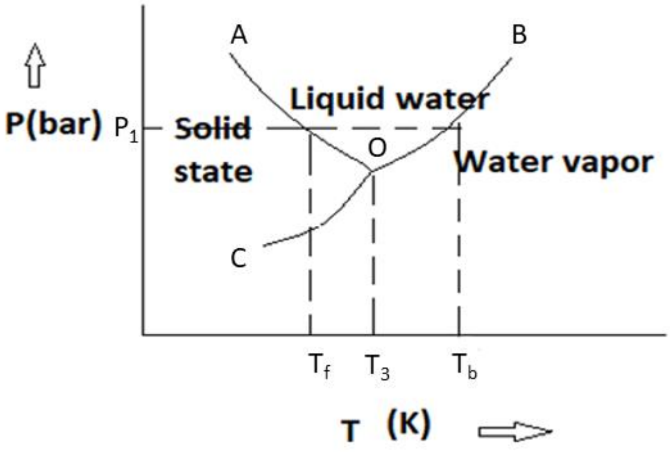

Figure 1

So here we get solid ice and this is water vapor and this is liquid water. If we draw line like this, we get a point it touches here is nothing but your boiling point and this is the melting point or freezing point whatever you say and this point, where all three phases here at this point they co-exist this is known as triple point or T_3. So T_3 is the triple point, T_b is the boiling point at pressure P bar. And T_f is the freezing point or freezing temperature at pressure P bar. This is suppose our point O here and we can level O, A, B, C. Along line OA solid ice and liquid water coexist. Similarly, along line OB or OB represents liquid water and water vapor coexistence line and so on. What we discuss so far? We derive Clapeyron equation with the help of Clapeyron equation we could able do draw the phase diagram of water or rather P-T diagram of water. So far whatever we discussed, we considered ideal gas.

Now we will consider not ideality. For non-ideal gas, **fugacity** is the measure of non-ideality of a gas. So what is fugacity we will discuss here. Fugacity is the mesure of non ideality of a gas .

We know,

$$\bar{G}(T,P) = G^0(T) + RT \ln P/P^0 \ \ldots\ldots\ldots(1)$$

We obtained this equation starting from

$$(\partial G/\partial P)T = \bar{V} \quad \ldots.(2)$$

$$\Rightarrow dG = \bar{V} dP$$

This is our equation 1 here, this is equation 2, and then what we did? On integrating we get this equation, so we will now generalize equation 1 to the case of a real gas.

We start with the virial expansion

$$P\bar{V}/RT = 1 + B_{2P}(T)P + B_{3P}(T)P^2 \ldots.$$

$$\bar{V} = RT\,[1/P + B_{2P}(T) + B_{3P}(T)P + \ldots.]$$

$$(\partial\bar{G}/\partial P)T = RT\,[1/P + B_{2P}(T) + B_{3P}(T)P + \ldots.]$$

$$\int_{Pid}^{P} dG = RT \int_{Pid}^{P} dPl + RT\ B2P(T) \int_{Pid}^{P} dPl + RT\ B_{3P}(T) \int_{Pid}^{P} PdPl + \ldots.$$

[where we are integrating from some low pressure, say P^{id} where the gas is sure to behave ideally, to some atbitary pressure ,P]

$$\Rightarrow\bar{G}(T,P) = G(T,P^{id}) + RT \ln P/P^{id}\ RTB_{2P}(T) + RT/2\ B_{3P}(T)P^2 \ \text{--------}(3)$$

From equation (1) we can write,

$$\bar{G}(T,Pid)=G^0(T) + RT\ln P^{id}/P^0$$

Where $G^0(T) \Rightarrow$ molar Gibbs free energy of an ideal gas at a pressure of P^0 bar

$$\bar{G}(T,P)= G0(T) + RT \ln Pid/P^0 + RT \ln P/P^{id} + RT\ B_{2P}(T)P + RT/2\ B_{3P}(T)P^2 \text{ --(4)}$$

Equation (4) is a general equation and is valid for all gases. Although equation 4 is an exact equation ,if differs for each gas, depending on the values of $B_{2P}(T)$, $B_{3P}(T)$, etc

From equation 4 we can write,

$$\bar{G}(T,P) = G^0(T)\ RT \ln f(P,T)/f_0 \quad \text{…..(5)}$$

Where,

$$f(P,T)/f_0 = P/P^0\ e^{[B2P(T)P\ +\ B3P(T)P2\ +\dots]} \quad \text{…..(6)}$$

$f(P,T) \Rightarrow$ fugacity$\Rightarrow$ non ideality is buried

$$f(P,T) \rightarrow P \text{ as } P \rightarrow 0$$

Note: the standard state in equation (1) and in equation (4) is taken to be the same quantity, thus the standard state of the real gas in equation (4) is taken to be the corresponding ideal gas at 1 bar pressure. In other words the standard state of the real gas is 1 bar after it has been adjusted to ideal behavior.

$$[f(P,T)/f^0 = P/P^0 \text{ when } B_{2P}(T) = B_{3P}(T)\text{……}= 0$$

$$F(P,T) \rightarrow P \text{ as } P \rightarrow 0 \text{ as all gases behave idaly when } P \rightarrow 0$$

So, at very low pressure all gases they behave ideally. The choice of standard state not only allow all gases to be brought to a single common state but also leads to a procedure to calculate f(P,T) at any pressure and temperature.