Chemical and Biological Thermodynamics: Principles to Applications

Prof. Nand Kishore
Department of Chemistry and Biochemistry
Indian Institute of Technology, Bombay

Lecture - 15
Fugacity

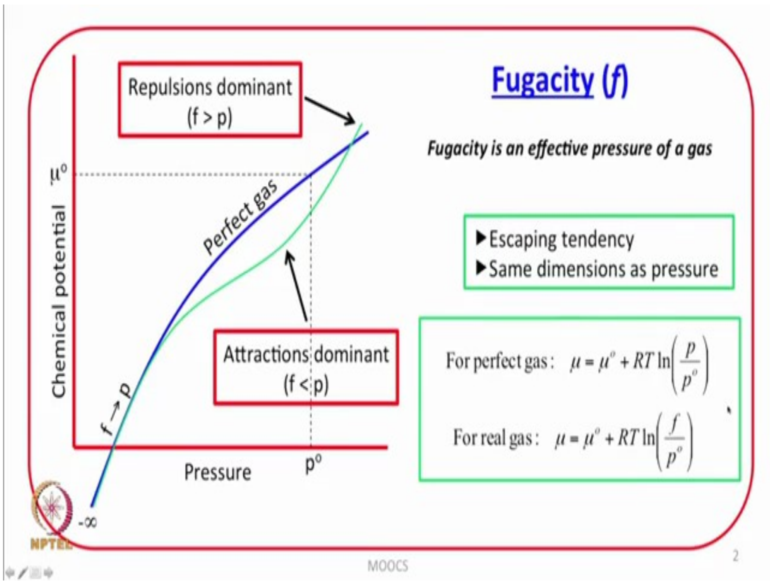
Last time we have discussed the properties of Free Energy or Gibbs Function, and we also discussed the Pressure Dependence of Gibbs Free Energy and came up with the definition of Chemical Potential for a Perfect Gas.

We all know what a perfect gas is an ideal gas is the one in which there is no intermolecular interaction, but as we know that the deviations from ideality do occur. So, therefore what should be the approach to develop equations for the systems which deviate from ideality? For example, last time we derived an equation for chemical potential. If you recall, it was mu is equal to mu naught plus R T log p by p naught for a perfect gas.

Now, a gas which deviates from ideal behavior, there are two ways, either you come up all together a new equation or you alter one of the parameters in the equation, existing equation which takes into account the deviation from ideality, and one of the ways is to use this approach. So, therefore the gases which show deviation from ideality for them instead of pressure, another term is used and that is called Fugacity.

What is fugacity? That is what we are going to discuss in detail in today’s lecture. Fugacity is an effective pressure of a gas.

(Refer Slide Time: 02:39)



Repulsions dominant
(f > p)

Attractions dominant
(f < p)

Fugacity (*f*)

Fugacity is an effective pressure of a gas

- Escaping tendency
- Same dimensions as pressure

For perfect gas: $\mu = \mu^{\circ} + RT\ln\left(\frac{p}{p^{\circ}}\right)$

For real gas: $\mu = \mu^{\circ} + RT\ln\left(\frac{f}{p^{\circ}}\right)$

See if there are no intermolecular interactions, then there is no question of talking about effective pressure. If there are intermolecular interactions, the interactions can be attractive.

Interactions can be repulsive and it does affect the pressure of a gas and that is why there is a need to use a term which is effective pressure which reflects effective pressure and that is called Fugacity. So, as said if there are intermolecular interactions, the interactions can be attractive or interactions can be repulsive. So, what is the escaping tendency? The escaping tendency will define the effective pressure of the gas. So, fugacity is also sometimes called as escaping tendency of the gas molecules. Another thing to remember is that fugacity has same dimensions as pressure.

Let us discuss a little more about the fugacity. As I was just discussing we have earlier derived this equation for a perfect gas, that is the chemical potential of a perfect gas is equal to standard state chemical potential plus RT log p by p naught, and this p naught is equal to 1 bar. Now, if the gas is not perfect, if the gas is not ideal, then as I said that this form of equation can still be retained provided we change the pressure by fugacity. So, what is done is you replace the pressure by fugacity. So, for a real gas, real gas means it allows for intermolecular interactions. For a real gas, the chemical potential will be defined as mu is equal to mu naught plus RT log f by p naught. So, please note here we are replacing the pressure by f. F is fugacity which we are calling as an effective pressure of the gas or escaping tendency, and once again please note here that the dimensions of fugacity will be same as that of the pressure.

How? The chemical potential varies with pressure for a perfect gas. We have taken a look at that in the previous lecture, but today let us see when the chemical potential dependence on pressure, all chemical potential dependence on fugacity is plotted in the same figure. How do they look like? Let us take a look at that. This is how it look like. This figure shows the variation of chemical potential against pressure. The blue curve, this is the variation of chemical potential with pressure for a perfect gas and the green curve is for a real gas.

The interesting observations to be noted in this figure r that there is a deviation from the ideal behavior. See the deviation in this region as we see at very low pressure, both the green and blue curve match overlap at moderate pressures. We see there is a deviation, the chemical potential for a real gas. Green one is for a real gas is lower than the chemical potential for a perfect gas and when the pressure is very high, you see the chemical potential for a real gas becomes higher than the chemical potential for a perfect gas.

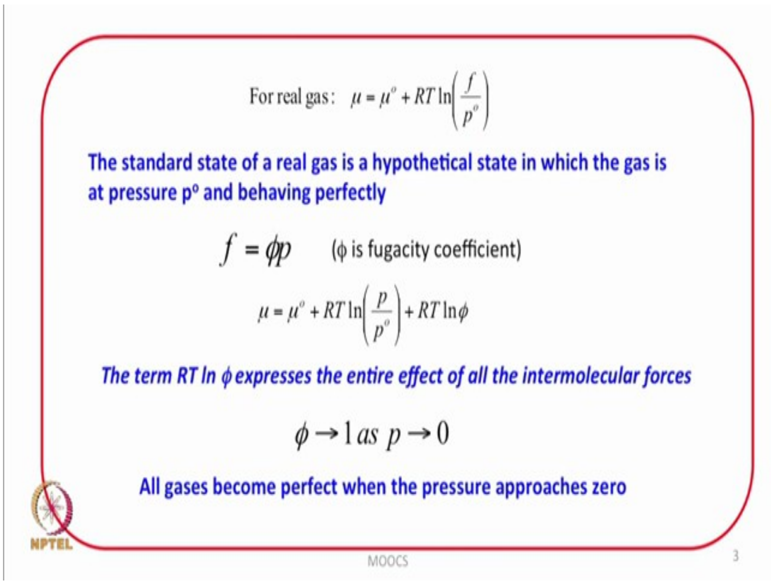
Let us discuss what could be the reason for that. As we just discussed that fugacity is an escaping tendency, it is an effective pressure. When the pressure is very low, very low means the molecules of the gas are far apart and the intermolecular interactions can be ignored. So, we can say that at very low pressure, the gases tend to behave in a perfect manner or gases behave ideal.

Now, when you increase the pressure at moderate pressures, there will be attractive interactions between the gas molecules in the real gas electrons and nucleus. So, when there are attractive interactions between the gas molecules, obviously the escaping tendency will be less because the molecules will like to stick to each other and that is what is shown in this figure over here that at moderate pressures, we see that the attractions are dominant and the chemical potential of a real gas is less than the chemical potential of a perfect gas because fugacity is lower than pressure. The escaping tendency is lower than pressure.

Now, when you further increase the pressure and the molecules are almost touching each other, now the repulsive interactions will begin and when the interactions are repulsive.

That means the escaping tendency of the gas molecules is more because they like to repair. So, if the escaping tendency f becomes more than p, obviously the chemical potential for the real gas will become higher than the chemical potential for a perfect gas and that is what is seen here.

(Refer Slide Time: 10:18)



For real gas: $\mu = \mu^{o} + RT\ln\left(\frac{f}{p^{o}}\right)$

The standard state of a real gas is a hypothetical state in which the gas is at pressure p° and behaving perfectly

$f = \phi p$ (ϕ is fugacity coefficient)

$$\mu = \mu^{o} + RT\ln\left(\frac{p}{p^{o}}\right) + RT\ln\phi$$

The term RT ln ϕ expresses the entire effect of all the intermolecular forces

$$\phi \to 1 \; as \; p \to 0$$

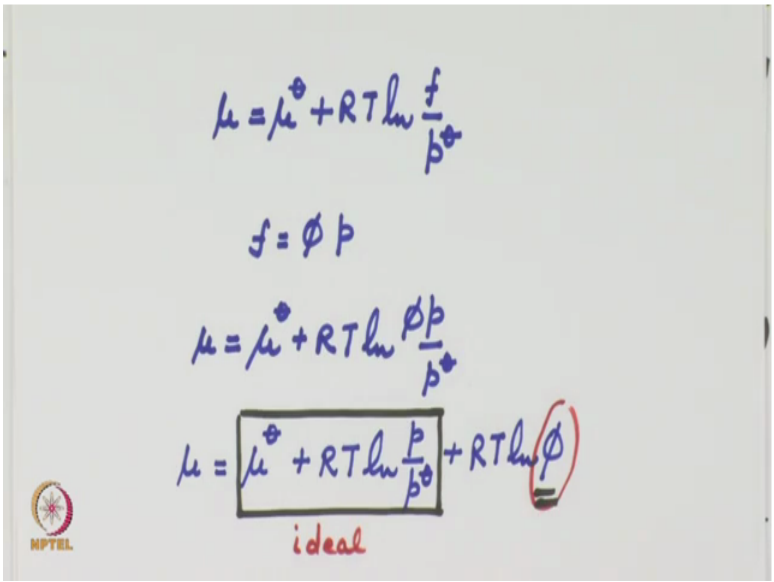
All gases become perfect when the pressure approaches zero

So, now we can write that for a real gas, the chemical potential is equal to mu naught plus R T log f by p naught and mu naught here is a hypothetical standard state so; obviously, we are taking the initial state as a standard state. So, what is the standard state for a real gas the standard state of a real gas is a hypothetical state in which the gas is at pressure p naught and behaving perfectly.

So, for real gases the normalized reference standard state is the one it is in hypothetical state where the gases behave perfectly and the pressure is equal to p naught p naught is one bar fugacity can be related to pressure by this expression fugacity is equal to fugacity coefficient into pressure fugacity has the same dimensions as that of pressure, therefore fugacity coefficient is a dimensionless quantity

Now, if i substitute this f is equal to phi times p over here. So, in this equation let us substitute f is equal to phi p what do we get we get this expression.

(Refer Slide Time: 12:19)



$$\mu = \mu^{\ominus} + RT \ln \frac{f}{p^{\ominus}}$$

$$f = \phi p$$

$$\mu = \mu^{\ominus} + RT \ln \frac{\phi p}{p^{\ominus}}$$

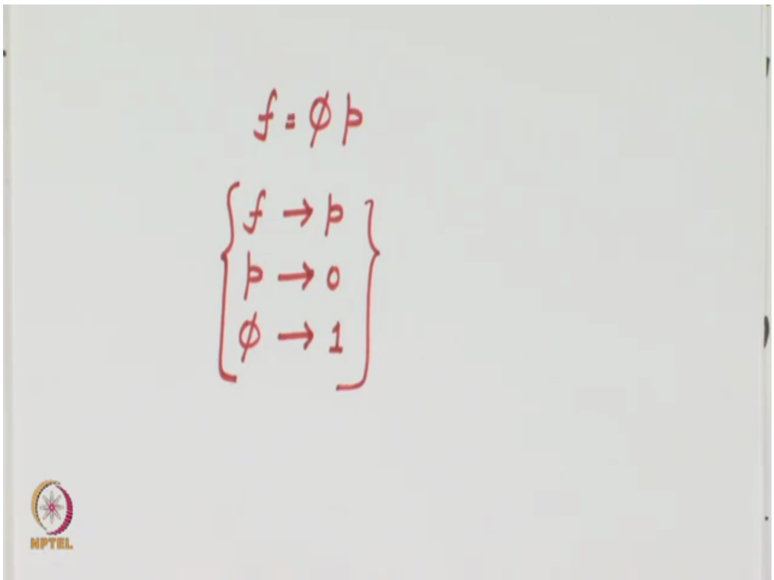
$$\mu = \underset{\text{ideal}}{\boxed{\mu^{\ominus} + RT \ln \frac{p}{p^{\ominus}}}} + RT \ln \underline{\phi}$$

So, what we are doing is, we are taking this equation mu is equal to mu naught plus R T log f by p naught. This is for a real gas and as we just discussed, fugacity is equal to fugacity coefficient into pressure. Now, I substitute for f. So, what I have is mu is equal to mu naught plus R T log phi times p over p naught.

So, then I can expand this. If I keep p by p naught together, then log a into b is log a plus log b. So, once I use that, I end up with the equation mu is equal to mu naught plus R T log p by p naught plus R T log phi. The point to be noted over here is that this part is the same as chemical potential for an ideal gas what is an additional term because of the non-ideality is the fugacity coefficient. That means, all the deviations from ideality are captured in this term because this is same as that for ideal case. Mu is equal to mu naught plus R T log p by p naught. So, additional intermolecular interaction effect is captured in the term log phi and hence the phi.

Now, let us go back to our slides and that is what is commented over here that the term R T log phi expresses the entire effect of all the intermolecular forces. We know that the gases will start behaving perfectly when the pressure approaches 0. So, obviously when the pressure approaches 0, the value of fugacity coefficient will approach 1 and then fugacity will approach pressure.

(Refer Slide Time: 15:38)



$$f = \phi p$$

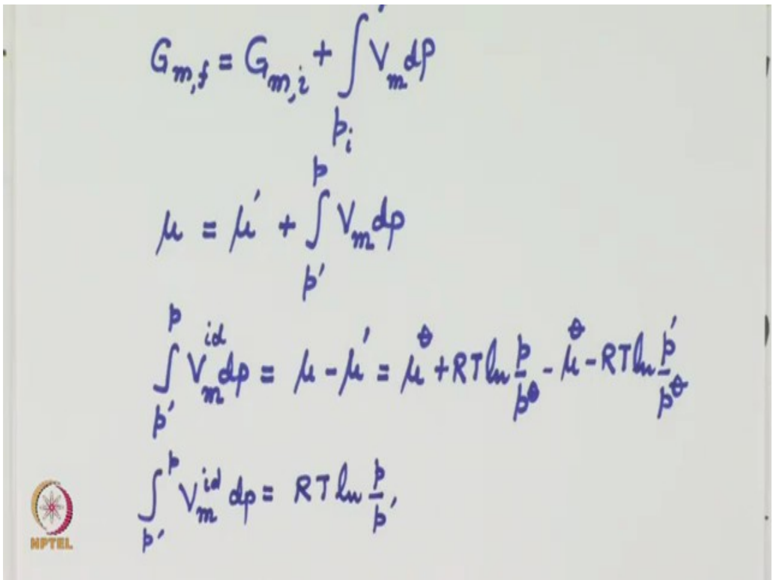
$$\left\{ \begin{array}{l} f \to p \\ p \to 0 \\ \phi \to 1 \end{array} \right\}$$

So, please do remember this condition that since we have discussed that fugacity is equal to fugacity coefficient time pressure, fugacity can be replaced by pressure. When pressure approaches a value of 0 and at that time, the value of fugacity coefficient will approach a value of 1.

So, these condition must be remembered which in other words can be interpreted as when the pressure approach is 0, the gases start behaving ideally and instead of fugacity, we can use pressure because at that under those conditions, the fugacity coefficient value will be equal to 1, ok.

Now, let us work towards deriving an expression for fugacity coefficient. Here again we will use our previous discussion. Let us remember this expression G m final is equal to G m initial plus p i to p f V m d p.

(Refer Slide Time: 17:01)



$$G_{m,f} = G_{m,i} + \int_{p_i} V_m dp$$

$$\mu = \mu' + \int_{p'}^{p} V_m dp$$

$$\int_{p'}^{p} V_m^{id} dp = \mu - \mu' = \mu^\ominus + RT\ln\frac{p}{p^\ominus} - \mu^\ominus - RT\ln\frac{p'}{p^\ominus}$$

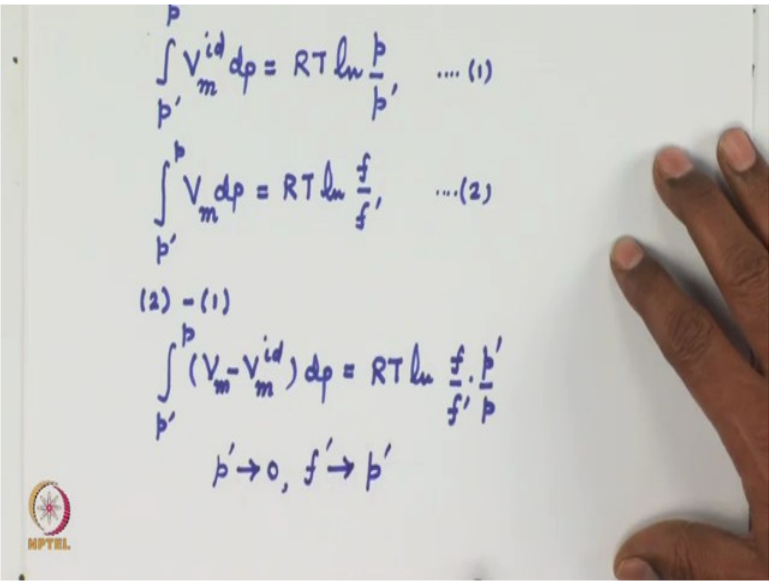
$$\int_{p'}^{p} V_m^{id} dp = RT\ln\frac{p}{p'}$$

This I am using from our previous discussing. I am expressing everything into molar quantities and we also know that for pure substances, Molar Gibbs Free Energy is equal to its chemical potential. So, if I write now mu is equal to mu prime, I am using initial state as prime plus p prime to p V m d p which I can rearrange and write as integration p prime to p V m d p is equal to mu minus mu prime.

Let me extend this further is equal to mu is equal to mu naught plus R T log p by p naught and next minus mu prime mu naught minus R T log. Here what it will be? It will be p prime by p naught. Now, you remember p, that mu is equal to mu naught plus R T log p by p naught is the definition of chemical potential for an ideal gas and for an ideal gas, let me put a subscript ideal. So, that means what I have now is p prime to p V m ideal d p is equal to R T log p by p prime.

Now, let me continue this. I will use this result also in the same way. If I use it for real gases, then instead of pressure, I will have to use fugacity because mu is equal to mu naught plus R T log f by p naught.

(Refer Slide Time: 20:38)



$$\int_{p'}^{p} V_m^{id}\, dp = RT \ln \frac{p}{p'}, \quad \dots (1)$$

$$\int_{p'}^{p} V_m\, dp = RT \ln \frac{f}{f'}, \quad \dots (2)$$

(2) - (1)

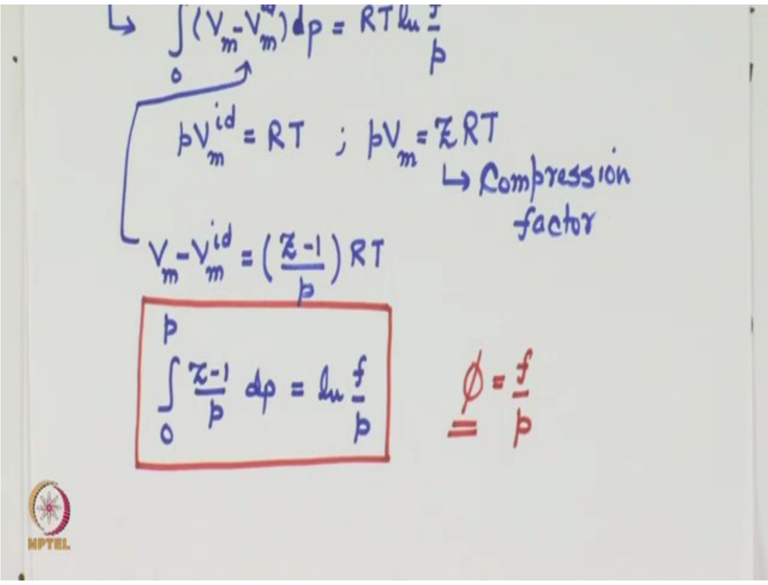
$$\int_{p'}^{p} (V_m - V_m^{id})\, dp = RT \ln \frac{f}{f'} \cdot \frac{p'}{p}$$

$$p' \to 0, \ f' \to p'$$

So, if the same expression I were to write integration p prime to p V m ideal, d p is equal to R T log p by p prime and same equation for real gas is R T log f by f prime.

Let us put this as equation number 2 and let us put this as equation number 1. Now, 2 minus 1, what does it give? It gives me p prime to p V m minus V m ideal d p is equal to R T log. I am subtracting this minus this. So, f by f prime into p prime by p and we need to simplify this integral. An easy way to simplify such an integral is that let us say p prime. When p prime approaches 0, then obviously f prime will approach p prime because we just discussed that when the pressure approach is 0, the gases start behaving ideally and in place of fugacity, we can use pressure that is what I am doing here.

(Refer Slide Time: 22:56



$$\hookrightarrow \int_0 (V_m - V_m^{id})\,dp = RT \ln \frac{f}{p}$$

$$pV_m^{id} = RT \;;\; pV_m = zRT$$

↳ Compression factor

$$V_m - V_m^{id} = \left(\frac{z-1}{p}\right) RT$$

$$\boxed{\int_0^p \frac{z-1}{p}\,dp = \ln \frac{f}{p}}$$

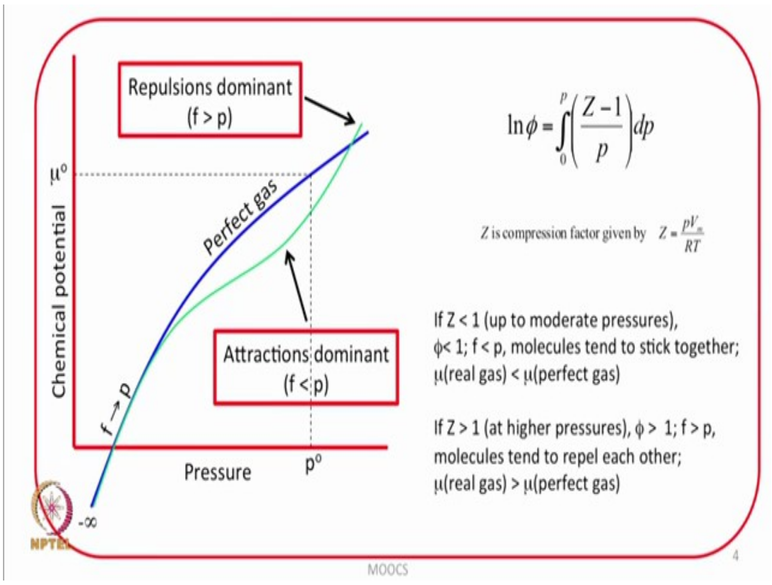
$$\underline{\underline{\phi}} = \frac{f}{p}$$

So, therefore when I continue from here, now what I will do is, I will use this and from 0 to p V m minus V m ideal, this is ideal into d p is equal to R T log f by p because f prime and p prime will be cancelled.

Now, we are close to the end result p V m ideal is equal to R T and p V m real is equal to z R T, where z you know is compression factor. So, therefore V m minus V m ideal will be equal to from here z minus 1 over p into R T V m. I get from here V m ideal. I get from here, I substitute it becomes z minus 1 over p into R T and this can now be substituted here.

So, what I have now is integration 0 to p z minus 1 over p d p is equal to log f by p because R T and R T will get cancelled and this is the result that we were looking for that.

(Refer Slide Time: 25:41)



$$\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right)dp$$

Z is compression factor given by $Z = \frac{pV_m}{RT}$

If Z < 1 (up to moderate pressures), ϕ< 1; f < p, molecules tend to stick together; μ(real gas) < μ(perfect gas)

If Z > 1 (at higher pressures), ϕ > 1; f > p, molecules tend to repel each other; μ(real gas) > μ(perfect gas)

Now, let us go back to our slide that we were trying to establish this or derive this equation that log phi phi is a f over p log phi is equal to 0 to p z minus 1 over p into d p, where z is the compression factor.

So, in order to get the information on the fugacity coefficient, we need the information on compression factors and compression factors for example, if it is an ideal gas in terms of p V is equal to some you know p V is equal to R T and if it is a van der Waals gas, we can always get an expression for z compression factor and substitute over here.

Now, let us go back to this figure at moderate pressures, where the attractions are dominant. The value of z is less than 1 that we understand from elementary chemistry that at moderate pressures when the attractions are dominant, the value of compression factor is less than 1. So, obviously if z is less than 1, the value of this integral is going to be negative. If value of integral is going to be negative, that means phi is going to be less than 1 and phi is equal to f by p. If phi is less than 1, then fugacity will be less than pressure and that is what is seen over here. If fugacity is less than pressure, then by the same arguments that we discussed in the beginning that the chemical potential will be less than the chemical potential for a real gas will be less than the chemical potential for an ideal gas.

On the other hand, when the compression factor is higher than 1, then this integral is positive means phi will be greater than 1 phi. Greater than 1 means fugacity is greater than pressure and that is what we were discussing earlier when we use fugacity greater than pressure in chemical potential equation, then here we see the escaping tendency or fugacity chemical potential for a real gas will be more than the chemical potential for the ideal gas. So, this is a region where attractions are dominant and this is the region where the repulsions are dominant.

So therefore, the knowledge of fugacity or in other words, fugacity coefficient allows us to discuss the system in terms of possible intermolecular interactions, and we must keep in mind that it is phi, it is fugacity which contains the information about deviations from ideality, and deviations from ideality in its own term provides lot of information which we will discuss later in more details.

Thank you.