Thermodyamics (Classical) for Biological Systems
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Module No. #03
Thermodynamics of Pure substances
Lecture No. #17
Fugacity Coefficient Estimation

Welcome. Today, we will look at the estimation of the fugacity coefficient using easy to measure variables. This will be the last aspect that we look at in this particular module on pure components.

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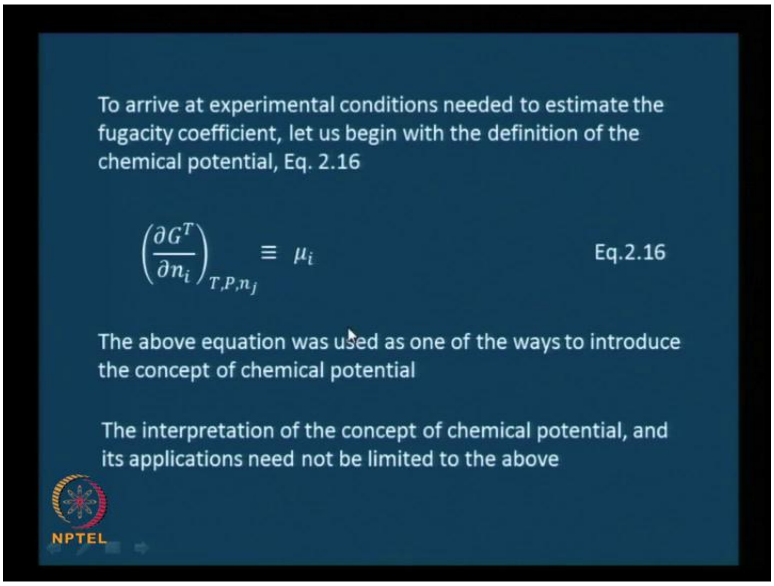

To arrive at experimental conditions needed to estimate the fugacity coefficient, let us begin with the definition of the chemical potential, Eq. 2.16

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq.2.16}$$

The above equation was used as one of the ways to introduce the concept of chemical potential

The interpretation of the concept of chemical potential, and its applications need not be limited to the above

We have already seen what a fugacity coefficient is; while going through this we will again take a look at what it is and then refresh ourselves, refresh our memories with what the fugacity coefficient is. Now, first to arrive at the experimental conditions needed to estimate the fugacity coefficient, we are going to begin with the definition itself. The definition of the chemical potential, which we had given in the previous module. If you remember, this was equation 2.16; we will mention this once again. dou G T dou n i at constant T, P, and all other j's different from i, all other n j's different from n i, this was defined as the chemical potential, when we first introduced or when we first strengthened the idea of the chemical potential.

This was equation 2.16, way back in the previous module. Again, to emphasize, this was only one of the ways that we used, to introduce the concept of chemical potential in the way we had organized our material. The chemical potential itself is a very powerful concept. And the interpretation of the concept of the chemical potential, and its applications are definitely not limited to the definition or the first level interpretation that one gets from this definition.

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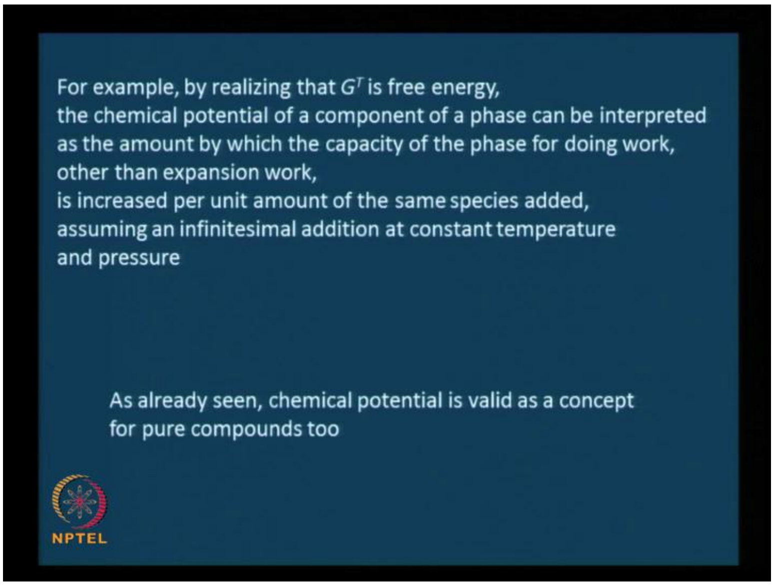

For example, by realizing that G^T is free energy,
the chemical potential of a component of a phase can be interpreted as the amount by which the capacity of the phase for doing work, other than expansion work,
is increased per unit amount of the same species added,
assuming an infinitesimal addition at constant temperature and pressure

As already seen, chemical potential is valid as a concept for pure compounds too

For example, by realizing that G T is the total free energy of the closed system, the chemical potential of a component of a phase can be interpreted also as the amount by which the capacity of the phase for doing work, other than expansion work, is increased per unit amount of the same species added, assuming an infinitesimal addition at the constant temperature and pressure. This is, … this comes from whatever we have seen earlier: dou G T dou n i at constant T, P, n j was given as a chemical potential. Now we are looking at G T as the free energy, apart from … or the capacity to do work apart from P V work.

And then we said that, this is the amount by which it increases when you infinitesimally add one of the species at constant temperature, pressure, and all other species remaining constant. That is one of the ways to interpret; it is good to know this.

Let us look at it again from this background by realizing that G T is free energy, the chemical potential of a component of a phase can be interpreted as the amount by which the capacity of the phase for doing work, is increased or rather the work itself other than expansion work, is increased per unit amount of the same species added assuming an infinitesimal addition at a constant temperature and pressure. And of course, as we have already seen chemical potential is a valid concept for pure components also, although it was introduced using a multi component system.

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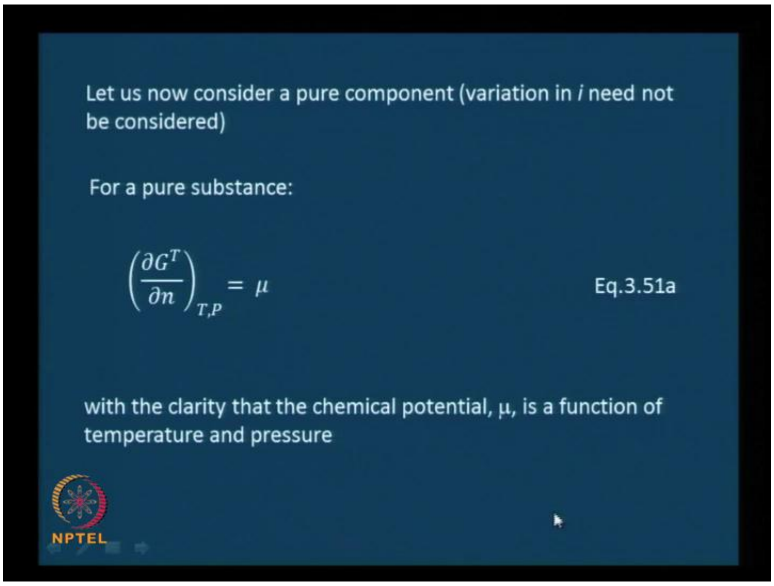

Let us now consider a pure component (variation in *i* need not be considered)

For a pure substance:

$$\left(\frac{\partial G^T}{\partial n}\right)_{T,P} = \mu \qquad \text{Eq.3.51a}$$

with the clarity that the chemical potential, μ, is a function of temperature and pressure

Now, let us consider a pure component, which means there is no i involved anymore. It is just one component there and therefore, variation in i need not be considered in the equations that we wrote earlier. For such a pure substance, dou G T by dou n at constant T and P would become the chemical potential of that substance. Let us call this equation 3.51 a. And, you know, we need to be clear here that chemical potential is a function of temperature and pressure too. Just that it is being held constant here, and we are defining it as the chemical potential.

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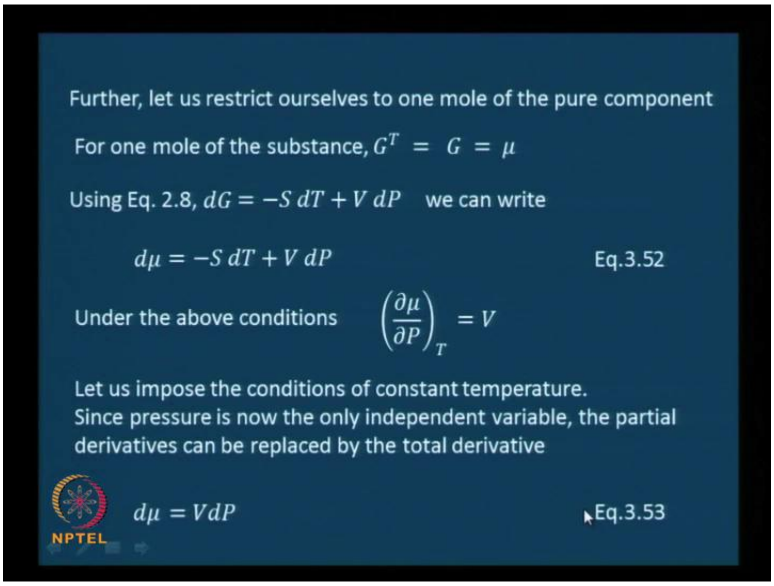

Further, let us restrict ourselves to one mole of the pure component

For one mole of the substance, $G^T = G = \mu$

Using Eq. 2.8, $dG = -S\,dT + V\,dP$ we can write

$$d\mu = -S\,dT + V\,dP \qquad \text{Eq.3.52}$$

Under the above conditions $\left(\frac{\partial \mu}{\partial P}\right)_T = V$

Let us impose the conditions of constant temperature.
Since pressure is now the only independent variable, the partial derivatives can be replaced by the total derivative

$$d\mu = V dP \qquad \text{Eq.3.53}$$

We said we are considering only a pure component. Now, let us further restrict ourselves to one mole of that pure component. Please take … please pay some attention to this; this is where we are equating Gibbs free energy and chemical potential under these conditions. So, it is good to pay some attention to this. One mole of the pure substance for that G T which is the Gibbs free energy of the closed system, would become equal to the molar value G. And from the definition, dou n G T dou n i being equal to mu, you can actually say that this is equal to mu under the conditions that we are considering.

Now, using equation 2.8, which is for a closed system, we had written d G equals minus S d T plus V d P. Using this, we can actually write this in terms of mu. Therefore, d mu equals minus S d T plus V d P; let us call this equation 3.52. Under the above conditions, dou mu by dou P at constant T is nothing but V, because see d mu is a total differential. This is again an exact differential of a state variable, d mu is dou mu dou T at constant P d T and dou mu dou P at constant T, d P. Considering this term alone, we can write dou mu dou P at constant T equals the V that is given here, V is easily measurable. So, we will just look at that.

Since, we have a constant T here; let us impose the conditions of constant temperature. Let us also remind ourselves that, we are trying to get at a means of estimating the fugacity coefficient. For that we have started out with the chemical potential and we are getting there slowly. So, let us impose the conditions of constant temperature since it is

… since we have a T constant here. And once we do that, pressure becomes the only independent variable. We initially said we have constrained it to one mole of a pure substance already. And only variables that we can … we are concerned with now are the temperature and pressure. And now that we have also kept the temperature constant, pressure becomes the only variable.

If you have a single variable system, you do not have to look at partial derivatives anymore. They all become total derivatives because the variation is only with respect to one variable. And therefore, the partial derivatives can be replaced by the total derivative. Therefore, we can write d mu dP equals V, and therefore, d mu equals V d P. Equation 3.53.

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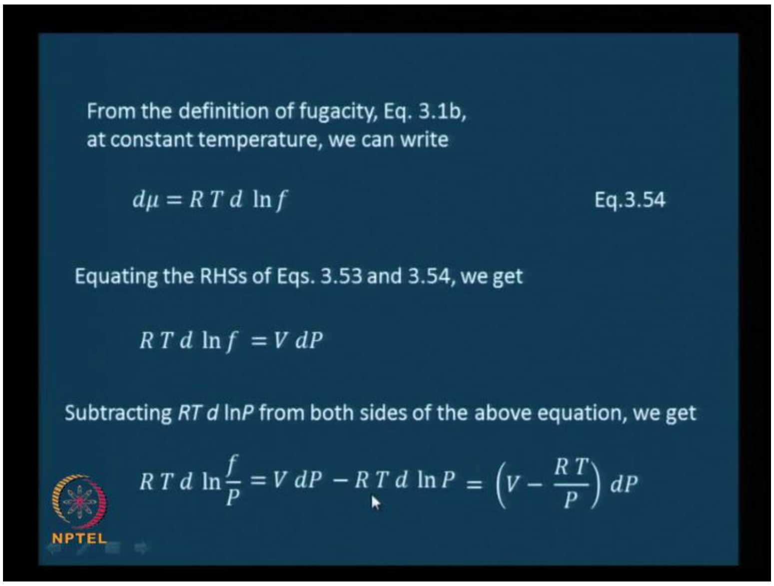

From the definition of fugacity, Eq. 3.1b, at constant temperature, we can write

$$d\mu = R\,T\,d\,\ln f \qquad \text{Eq.3.54}$$

Equating the RHSs of Eqs. 3.53 and 3.54, we get

$$R\,T\,d\,\ln f = V\,dP$$

Subtracting $RT\,d\ln P$ from both sides of the above equation, we get

$$R\,T\,d\,\ln\frac{f}{P} = V\,dP - R\,T\,d\,\ln P = \left(V - \frac{R\,T}{P}\right)dP$$

Now, from the definition of fugacity, which is equation 3.1 b, earlier in this module; at constant temperature, we can write d mu equals R T d ln f. This comes directly from the definition of the fugacity itself. This is equation 3.54. If you have some confusion, just go ahead and look back at equation 3.1 b; this will become very clear. Now, in this equation, we have d mu equals V dP, equation 3.53. And in equation, 3.54 we have d mu equals R T d ln f. And they are the same quantities on the left hand side. So, let us equate the right hand sides. If we do that – equating the right hand sides of equations 3. 53 and 3.54, the previous two equations, we get R T d ln f equals V dP.

Now, let us do some manipulations. Note that we are getting to the fugacity coefficient. So, we will have to arrive at that in some way. And, to do that, let us subtract R T d ln P … you know R T d ln P from both the sides of the above equation. Thinking of something like this: … we know that fugacity coefficient is f by P. So, somehow we need to get that into this kind of an expression. So, if we subtract R T d ln P from both sides of the above equation, we can write this as R T d ln f minus R T d ln P. Ln of a minus ln of b is ln of a by b. And therefore, we can write this is R T d ln f by P. And the right hand side, of course, is V dP minus R T d ln P. Now, d ln P is nothing but 1 by P dP, and therefore, V dP minus R T it is already here, by P d P, which can … if you take dP out common, we can write V minus R T by P, d P.

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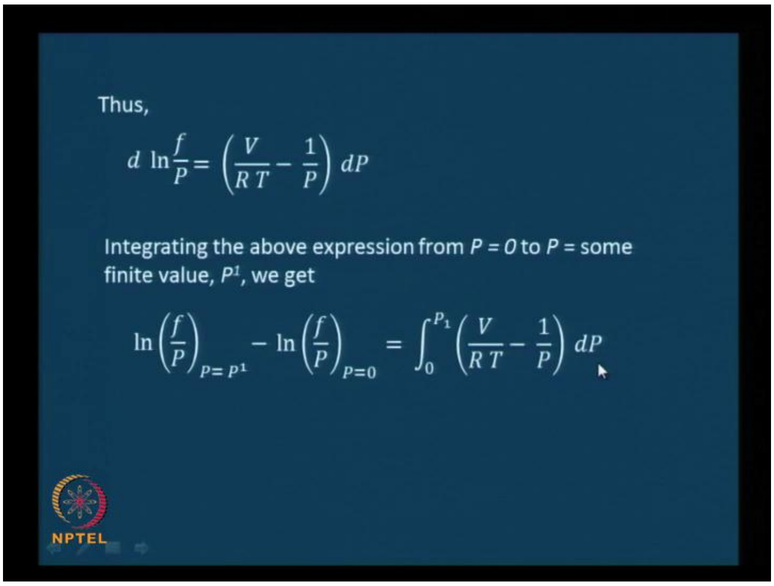

Thus,

$$d\ \ln\frac{f}{P} = \left(\frac{V}{R\,T} - \frac{1}{P}\right) dP$$

Integrating the above expression from $P = 0$ to $P =$ some finite value, P^1, we get

$$\ln\left(\frac{f}{P}\right)_{P=P^1} - \ln\left(\frac{f}{P}\right)_{P=0} = \int_0^{P_1}\left(\frac{V}{R\,T} - \frac{1}{P}\right) dP$$

Therefore, d ln f by P equals V by R T minus 1 by P, d P. … The need for writing this way will become very clear. We are trying to bring it in terms of compressibility factor; we know P V by R T is a compressibility factor. We will get to that in a little while. Before that, let us integrate the above expression from P equals 0 to P equals some finite value P 1. And if we do that, the integral of d, ln of f by P is nothing but ln f by P, and the upper limit at P equals P 1 minus ln f by P at the lower limit P equals 0, which equals right hand side integral of 0 to P 1, V by R T minus 1 by P d P.

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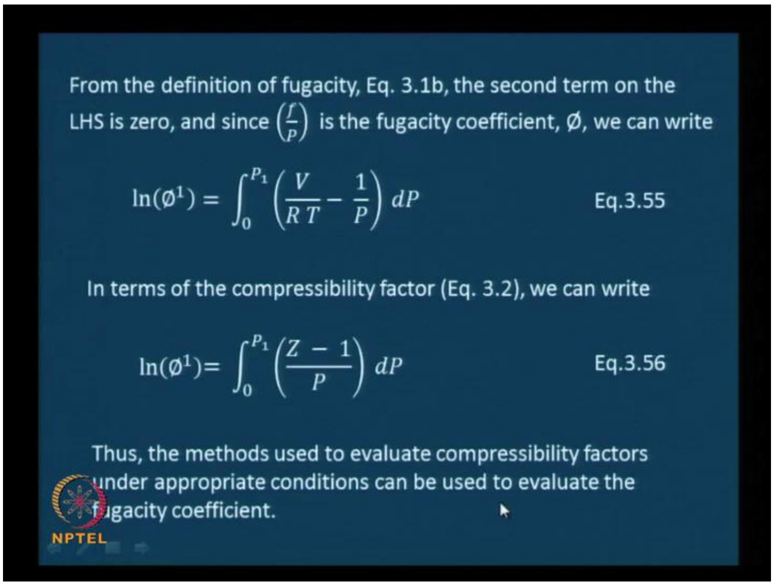

From the definition of fugacity, Eq. 3.1b, the second term on the LHS is zero, and since $\left(\frac{f}{P}\right)$ is the fugacity coefficient, Ø, we can write

$$\ln(\emptyset^1) = \int_0^{P_1} \left(\frac{V}{RT} - \frac{1}{P}\right) dP \qquad \text{Eq.3.55}$$

In terms of the compressibility factor (Eq. 3.2), we can write

$$\ln(\emptyset^1) = \int_0^{P_1} \left(\frac{Z-1}{P}\right) dP \qquad \text{Eq.3.56}$$

Thus, the methods used to evaluate compressibility factors under appropriate conditions can be used to evaluate the fugacity coefficient.

Now, let us recall the definition of the fugacity … fugacity itself. This is again from equation 3.1 b. … If you look at the definition of fugacity, it will say that f tends to P as P tends to 0, or f by P tends to 1 as P tends to 0. And note that this is nothing but the evaluation of ln of f by P at … P going to 0, or P being equal to 0. In such a case, we have a ln 1 here, which is nothing but 0. And therefore, the second term on the left hand side of the previous equation is 0. And f by P is the fugacity coefficient at 0.1, in this case. … Therefore, ln of P 1, or phi 1 you know here, we have evaluated f by P which is phi at P equals P 1 and therefore, we will call it ln of phi 1. … Ln phi 1 equals the right hand side, which is integral of 0 to P 1 V by R T minus 1 by P, d P.

Let us call this equation 3.55. We are almost there. In terms of the compressibility factor … because we have so many methods for compressibility factor, now, let us try to expresses this also in terms of the compressibility factor. We know that P V by R T is a compressibility factor. We can write of ln of phi 1 as integral of 0 to P 1 this is Z by P this is 1 by P therefore, this becomes Z minus 1 by P d P. Let us call this equation 3.56.

Let us take a look at this equation, ln of phi 1 equals integral of 0 to P 1 Z minus 1 by P, d P. We have on the right hand side all that can be evaluated. We already know methods for evaluating the compressibility factor starting right from the initial part of this module. And therefore, by evaluating this, we can get an estimate of the fugacity coefficient, at a particular point. In this case one denotes the particular point at which the estimation is made. Let us, … same thing … the methods used to evaluate compressibility factors under appropriate conditions can be used to evaluate the fugacity coefficient. So, whatever information that we have gathered so far, in terms of evaluating Z, estimating Z, can directly be ported on here, to evaluate the fugacity coefficient.

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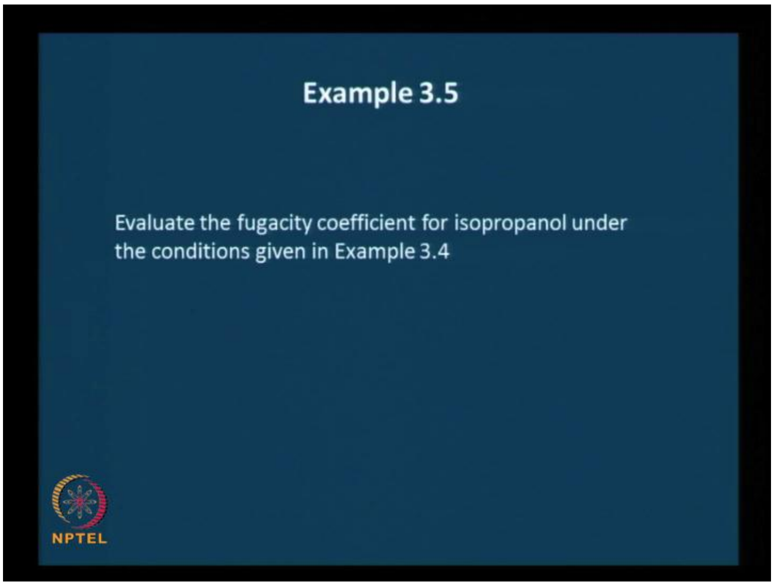

Example 3.5

Evaluate the fugacity coefficient for isopropanol under the conditions given in Example 3.4

To appreciate this a lot better, let us work out an example. This is example 3.5. Let me first, read out the example. Evaluate the fugacity coefficient for our, you know popular modal system, isopropanol, under the conditions given in example 3.4. The same temperature, the same pressure … I think it is 200 degrees C and 10 bar, which is given in 3.4. What I would like to tell you first is that this problem is not trivial, although it is just one line there: evaluate the fugacity coefficient for isopropanol. That is because, on the basis of whatever we have seen so far, whatever we have learnt so far, the skills that are required to arrive at an acceptable solution to this problem calls for our slightly higher level skills; it requires some integration also.

So, what I will do is give you a lot of time to do this. Take about 5 minutes to think about this and the first hint is very clear. You will need to use the expression for the fugacity coefficient of course, but may not be very directly. So, take about 5 minutes think about this and then I will give you some hints and lead you through the solution process. This is this is not as straight forward as the solutions that we have seen so far. Go ahead please – 5 minutes.

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Now, that you have, taken the time to think through this. … We would have connected some expressions for the fugacity coefficient, the one that we just saw, ln of phi 1 equals 0 to P 1, Z minus 1 by P, dP and so on. Maybe we will have to use that, but I already warned you – not very directly. So, let me start giving you some hints.

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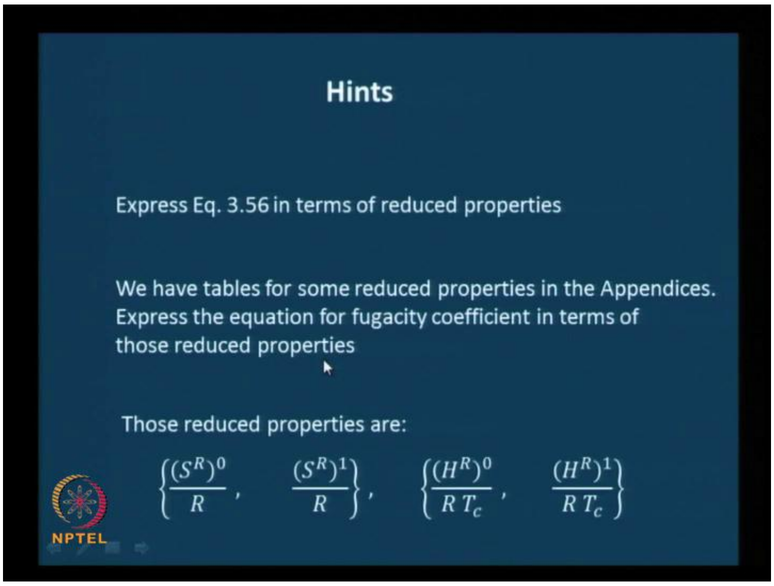

Hints

Express Eq. 3.56 in terms of reduced properties

We have tables for some reduced properties in the Appendices. Express the equation for fugacity coefficient in terms of those reduced properties

Those reduced properties are:

$$\left\{\frac{(S^R)^0}{R}, \quad \frac{(S^R)^1}{R}\right\}, \quad \left\{\frac{(H^R)^0}{R\,T_c}, \quad \frac{(H^R)^1}{R\,T_c}\right\}$$

The first hint is, try to express that equation 3.56 that we just saw, the expression for ln of phi 1, in terms of reduce properties, you know T R, P R, and so on. Because, if you do that, then the data, the amount of data that is needed significantly goes down. Because, in terms of reduced variables, those are applicable for a wide variety of substances, pure substances. And therefore, try to express this in terms of reduced properties. Go ahead, take about ten minutes and try to express the equation in terms of reduced properties and then I will give you the second hint.

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Probably you are ready for the second hint now. We will see the solution when we work out the complete details, but let me give you a hint so that you can start thinking in that direction and pick up such skills, which require thinking in one angle and thinking in another angle, putting them together for the purpose at hand. The hint is something like this; we have tables for reduced properties in the appendices. Express the equation for the fugacity coefficient in terms of those reduced properties. This is a very big hint. So, go ahead ten minutes, and see how you can express the equation for that fugacity coefficient, which is already been converted to a reduced property form, in terms of these reduced properties the values of which are available in the appendices.

Let me probably give you a third hint now, it might help you. Those reduced properties are S R 0 by R, S R one by R, H R 0 by R T c, H R one by R T c. We have already seen that these are available in the tables of your appendix. So, take about 15 minutes and link this up, you know, in terms of the expression for the fugacity coefficient, in terms of these reduced properties to these reduced properties. Take 15 minutes to do it. Go ahead please.

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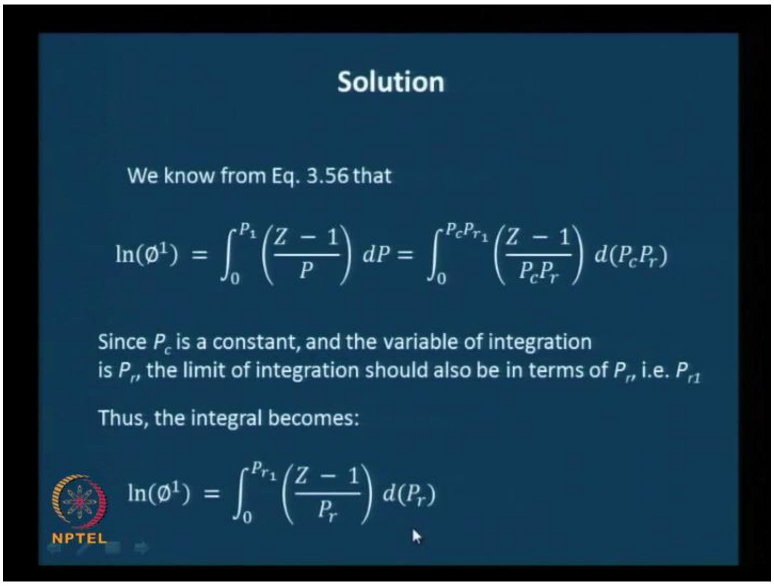

Solution

We know from Eq. 3.56 that

$$\ln(\emptyset^1) = \int_0^{P_1}\left(\frac{Z-1}{P}\right)dP = \int_0^{P_cP_{r_1}}\left(\frac{Z-1}{P_cP_r}\right)d(P_cP_r)$$

Since P_c is a constant, and the variable of integration is P_r, the limit of integration should also be in terms of P_r, i.e. P_{r1}

Thus, the integral becomes:

$$\ln(\emptyset^1) = \int_0^{P_{r_1}}\left(\frac{Z-1}{P_r}\right)d(P_r)$$

Some of you would have arrived with the solution which is very good. Let us look at the way of going about the solution. We have already seen from equation 3.56, the first step was to express this in terms of reduced properties. We have we already known that, ln of phi 1 as an integral from 0 to p 1 Z minus 1 by P d P; this we already know.

Now, the way to express this in terms of reduced properties is to replace these actual variables in terms of the reduced variables. We now that P is P c P r and dP as we already seen is P c, which is a constant, times d P r. I have written down the steps here P c P r and d of P c P r. And the P c, when it comes out common here it will get cancelled with this. And now, since P c is a constant and the variable of integration is P r, the limit of integration should also be in terms of P r. This, that makes sense because, you have this in terms of dP r. We do that and it goes from 0 to P r 1, ln of phi 1 becomes integral of 0 to P r 1, Z minus 1 by P r dP r. It is quite straight forward and no major complications in converting this expression from the actual quantities to reduced variables.

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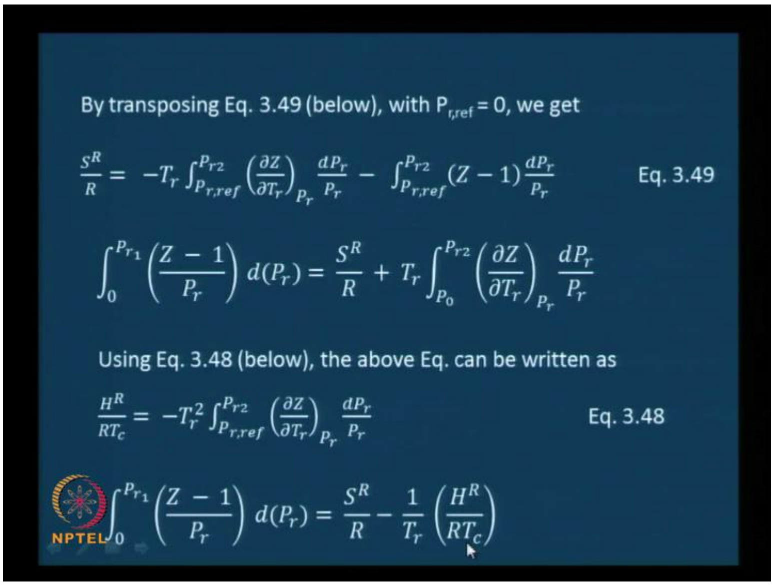

By transposing Eq. 3.49 (below), with $P_{r,ref} = 0$, we get

$$\frac{S^R}{R} = -T_r \int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_{P_{r,ref}}^{P_{r2}} (Z-1) \frac{dP_r}{P_r} \qquad \text{Eq. 3.49}$$

$$\int_0^{P_{r_1}} \left(\frac{Z-1}{P_r}\right) d(P_r) = \frac{S^R}{R} + T_r \int_{P_0}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

Using Eq. 3.48 (below), the above Eq. can be written as

$$\frac{H^R}{RT_c} = -T_r^2 \int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad \text{Eq. 3.48}$$

$$\int_0^{P_{r_1}} \left(\frac{Z-1}{P_r}\right) d(P_r) = \frac{S^R}{R} - \frac{1}{T_r} \left(\frac{H^R}{RT_c}\right)$$

Now, by transposing equation 3.49 below, you have think of the second hint that was given. Try to express it in terms of the other reduced properties S R and H R and so on. The 3.49 equation is given here for a quick reference. 3.49 was S R by R equals minus T r reference to P r two integrated dou Z dou T r at constant P r by P r, dP r minus integral of P r reference to P r 2, Z minus 1 by P r, dP r. And this can be written as, integral of Z minus 1 by P r dP r, which is this, equals S R by R plus T r into integral of P 0 to P r 2 or 0 to P r 2, dou Z dou T r at constant P r dP r by P r.

This was actually our fugacity coefficient expression, that we had gotten earlier … in terms of reduced quantities. So, we have this in terms of S R and something else here. Now if you can take care of this then, we have a means of calculating our fugacity coefficient. Now, what is this? To get at this, let us look at 3.48, which has again being given here for convenience. If you recall 3.48 … you can go back and take a look at that,

that will be h R by R T c equals minus T r squared integral … P r reference to P r 2, dou Z dou T r at constant P r into one by P r dP r.

Therefore, this integral here which is somewhat this here can be written as minus, you know, here take a look at this here this is T r squared here you have a T r and therefore, minus one by T r into H R by R T c becomes this integral that we are looking for. And therefore, the fugacity coefficient estimation, integral of 0 to P r 1, Z minus 1 by P r dP r becomes S R by R minus this term has become 1 by T r H R by R T c.

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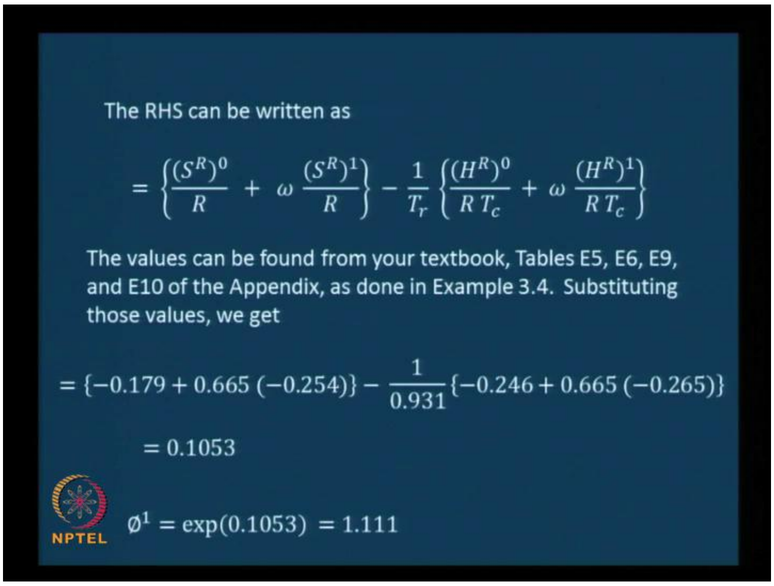

The RHS can be written as

$$= \left\{\frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R}\right\} - \frac{1}{T_r}\left\{\frac{(H^R)^0}{R\,T_c} + \omega \frac{(H^R)^1}{R\,T_c}\right\}$$

The values can be found from your textbook, Tables E5, E6, E9, and E10 of the Appendix, as done in Example 3.4. Substituting those values, we get

$$= \{-0.179 + 0.665\,(-0.254)\} - \frac{1}{0.931}\{-0.246 + 0.665\,(-0.265)\}$$

$$= 0.1053$$

$$\emptyset^1 = \exp(0.1053) = 1.111$$

Now, the RHS can be written as, … this is where the link between what is available to us … we have values available in terms of S R 0, S R 1, H R 0, H R 1. Therefore, we need to relate whatever we have in terms of S R and H R to these H that was here you know you have your S R by R minus 1 by T r H R by R T c. We link it up to whatever is available. We can write that as S R 0 by R plus omega times S R 1 by R, which is nothing but S R by R minus 1 by T r H R 0 by R T c plus omega times H R 1 by R T c; the one within this flower bracket is nothing but H R by R T c. Now, we can take these values from the tables available in the appendix. These are appendices or tables E 5, E 6, E 9 and E 10 of appendix E from your text book, Smith VanNess and Abbot.

This is pretty much similar to what we did in example 3.4. Substituting these values, we get S R 0 by R as 0.179, and so on. Omega is 0.665, S R 1 by R was minus 0.254; we have already seen this in the previous example. And … minus 1 by T r is minus 1 by

0.931. This term, H R 0 by R T c was minus 0.2466 plus omega times H R 1 by R T c, minus 0.265; this turns out to be 0.1053. What was on the left hand side was ln of phi 1 and therefore, phi 1, which is a fugacity coefficient at 1 is the exponential of 0.1053, which turns out to be 1.111. So, we have kind of integrated, whatever we knew in terms of, whatever was available and got an estimate of the fugacity coefficient. If you want you can go through this solution again to see the various ways and which we went about doing it. And in the next class, we will do a review of whatever … we have done in this module, before we go on to the next module. See you then.