Thermodynamics (Classical) for Biological Systems

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Module No. # 03

Thermodynamics of pure substances

Lecture No. # 10

Equations of State-Virial Equations

After review of some concepts that we have already seen earlier, in the earlier classes, courses, in the first module, we looked at some relationships that would be fundamental to thermodynamics and their interrelationships in module number two. In this module, module three, we will look at thermodynamic properties of pure fluids.

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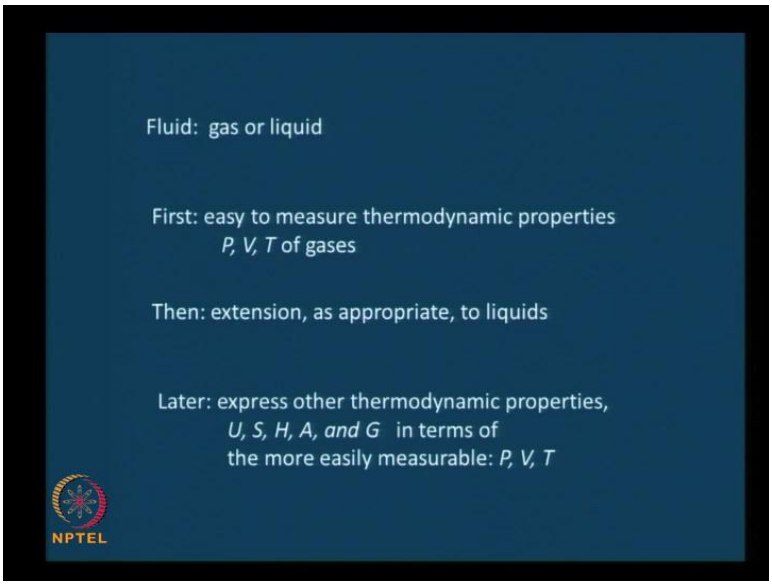

Fluid: gas or liquid

First: easy to measure thermodynamic properties
P, V, T of gases

Then: extension, as appropriate, to liquids

Later: express other thermodynamic properties,
U, S, H, A, and G in terms of
the more easily measurable: *P, V, T*

Fluid as may be known is either a gas or a liquid. And, let us continue the theme that we looked at in the later part of the previous module here also. First: easy to measure thermodynamic properties P, V, T of gases, we will look at. And then, we will do an extension, as appropriate, to liquids. Initially, it will be that of gases and then to liquids. And later, express other thermodynamic properties such as internal energy, U, entropy, S, enthalpy, H, Helmholtz free energy, A, and Gibbs free energy, G in terms of the more easily measurable pressure, specific volume and temperature.

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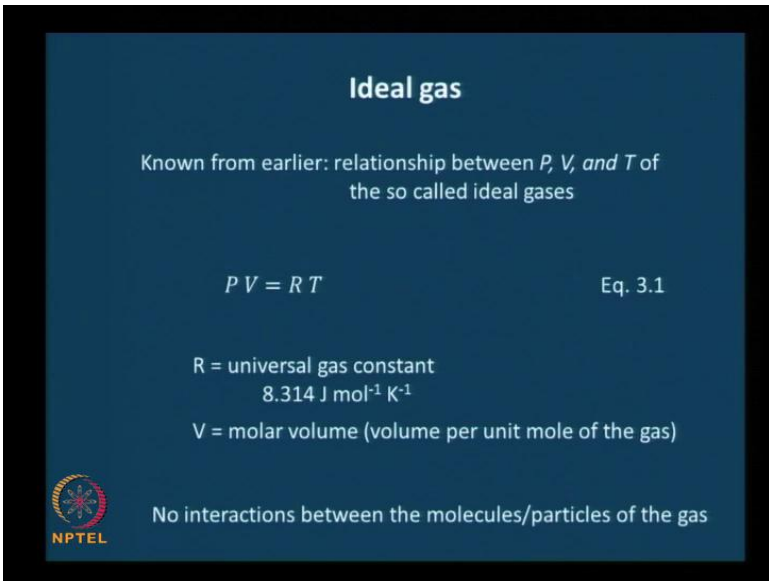

Ideal gas

Known from earlier: relationship between *P, V, and T* of the so called ideal gases

$$P\,V = R\,T \qquad \text{Eq. 3.1}$$

R = universal gas constant
8.314 J mol^{-1} K^{-1}

V = molar volume (volume per unit mole of the gas)

No interactions between the molecules/particles of the gas

We all know what an ideal gas is. And, let us state it here for completeness. The relationship between P, V and T for the so-called ideal gases must be very familiar. It is P V equals R T. Let us register this as equation 3.1 here; because we will need to refer to this in the later parts of the module, or may be later too. R as may be known is the universal gas constant; the value of which in these set of units is 8.314 joule per mole per Kelvin. V is the molar volume or volume per unit mole of the gas that we have already seen.

And, this may or may not be known. In an ideal gas, we get such a simple relationship, because at the molecular level, … we consider no interactions between the molecules or the particles to make it general that comprise the gas. That is what led to the ideality of the gas – no interactions.

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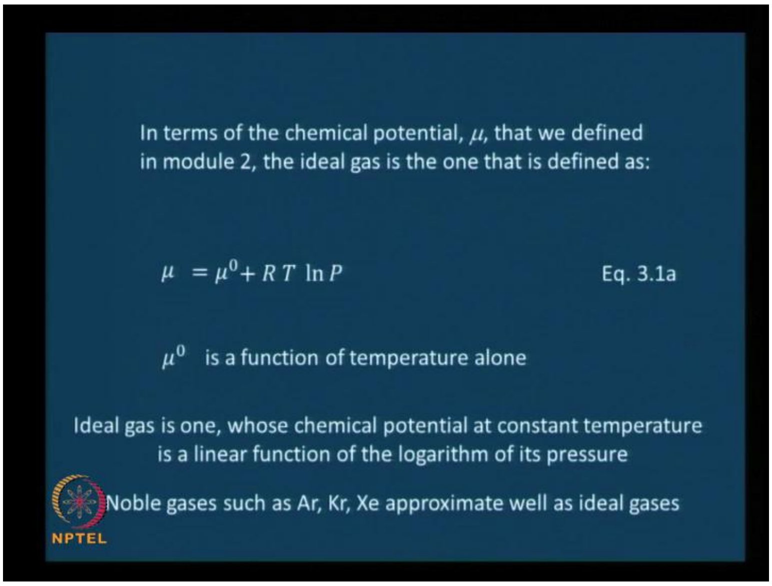

In terms of the chemical potential, μ, that we defined in module 2, the ideal gas is the one that is defined as:

$$\mu = \mu^0 + R\,T\,\ln P \qquad \text{Eq. 3.1a}$$

μ^0 is a function of temperature alone

Ideal gas is one, whose chemical potential at constant temperature is a linear function of the logarithm of its pressure

Noble gases such as Ar, Kr, Xe approximate well as ideal gases

Now, take a look at this. In terms of the chemical potential mu that we defined in module two, we can write the ideal gas or we can define the ideal gas as mu equals a certain mu naught plus R times T temperature times the natural log of the total pressure P. We will call this equation 3.1 a. Here, mu naught is a function of temperature alone. This mu naught is a function of temperature alone.

And therefore, another way of looking at this equation, interpreting this equation, is that ideal gas is one, whose chemical potential mu at constant temperature, which means this will be a constant – R T can be taken as a constant at constant temperature, is a linear function of the logarithm of its pressure, the natural logarithm of its pressure. It is one of the ways of interpreting the ideal gas in terms of the chemical potential. This may also be known that the noble gases such as argon, the krypton, xenon approximate well to ideal gases.

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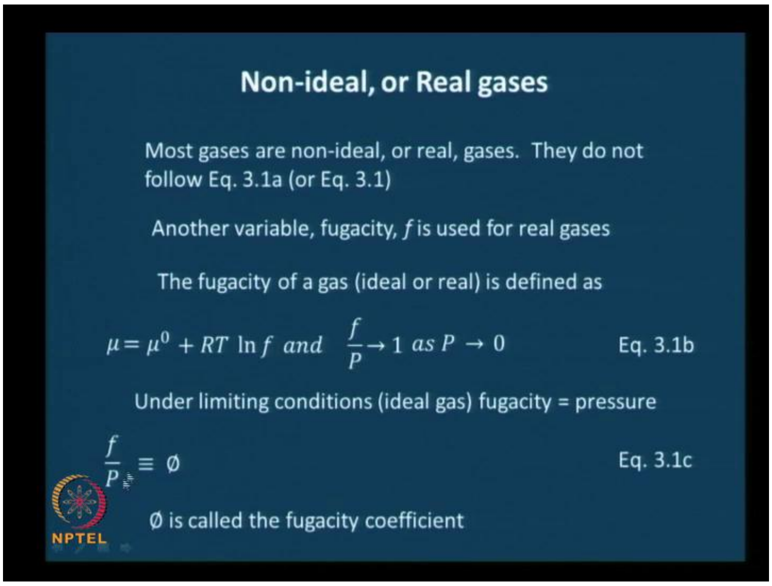

Non-ideal, or Real gases

Most gases are non-ideal, or real, gases. They do not follow Eq. 3.1a (or Eq. 3.1)

Another variable, fugacity, *f* is used for real gases

The fugacity of a gas (ideal or real) is defined as

$$\mu = \mu^0 + RT \ln f \ and \ \frac{f}{P} \to 1 \ as \ P \to 0 \qquad \text{Eq. 3.1b}$$

Under limiting conditions (ideal gas) fugacity = pressure

$$\frac{f}{P} \equiv \emptyset \qquad \text{Eq. 3.1c}$$

$\emptyset$ is called the fugacity coefficient

Most gases are non-ideal, or they can also be called as real gases. So, what is the formulation that we could use effectively for real gases? Also, … as may be apparent, if it is a real gas, it is not going to follow the ideal gas equation or in other words for real gases, P V is not going to be R T, equal to R T, or the chemical potential mu of an ideal pure gas cannot be expressed as mu naught plus R T ln P.

Therefore, we need another variable and that variable happens to be called fugacity f, which is used for real gases. The fugacity of a gas … in fact fugacity is a little general. If you are going to define it for real gases, it should be applicable to the ideal gas in the limiting case. That is always a case. Whenever you generalize, it should also take care of a special case.

Therefore, the fugacity of a gas, either ideal or real, is defined as, or it can be obtained from this … expression: the chemical potential mu equals mu naught plus R T ln f. Note that, for an ideal gas it was mu equals mu naught plus R T ln P. Here instead of P, we are using this fugacity here. This is not the complete definition. We should also add that f, fugacity, by total pressure, P, tends to 1 as the pressure tends to 0. This is the complete definition of a real gas, or of a gas; whether real or ideal. Let us call this equation 3.1 b.

And as mentioned earlier, under limiting conditions it should become an ideal gas. And of course, it is quite evident that mu equals mu naught … plus R T ln f should become mu equals mu naught plus R T ln P. And therefore, fugacity must equal pressure for the ideal gas. This f by P is an interesting quantity. And, let us define it as a separate quantity here, and indicate it by the letter phi. We will call this equation 3.1 c. And, phi is actually called the fugacity coefficient. f is fugacity; phi, which is the ratio of f to P is called fugacity coefficient.

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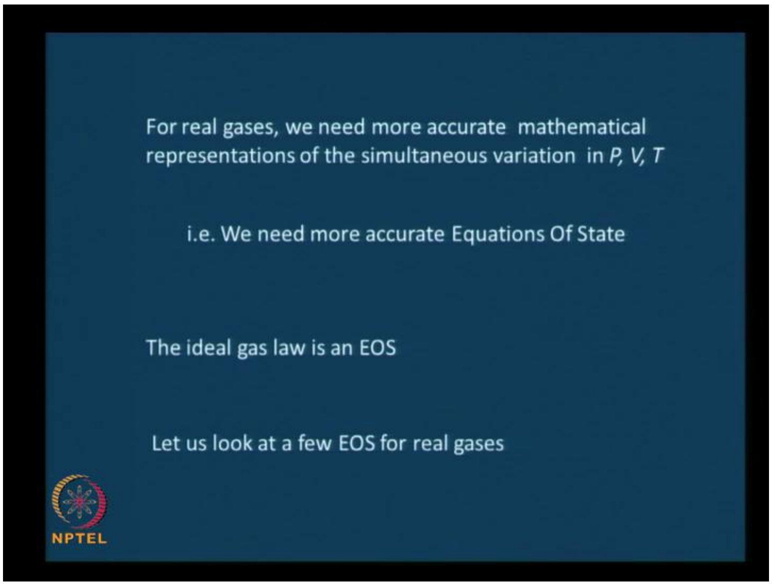

For real gases, we need more accurate mathematical representations of the simultaneous variation in *P, V, T*

i.e. We need more accurate Equations Of State

The ideal gas law is an EOS

Let us look at a few EOS for real gases

We already saw that real gases are not going to follow P V equals R T. And therefore, we need more accurate mathematical representations or more accurate models of the simultaneous variation in P, V, specific volume, and temperature. In other words, we need more accurate equations of state. In fact, the interrelationships between pressure, volume and temperature are called equations of state; P V equals R T is a very simple equation of state. We need more complicated equations of state … to represent real gases. Let us look at a few equations of state for real gas in this course. There are many, which have been developed over the past century or more. So, let us look at a few of them which are quite heavily used.

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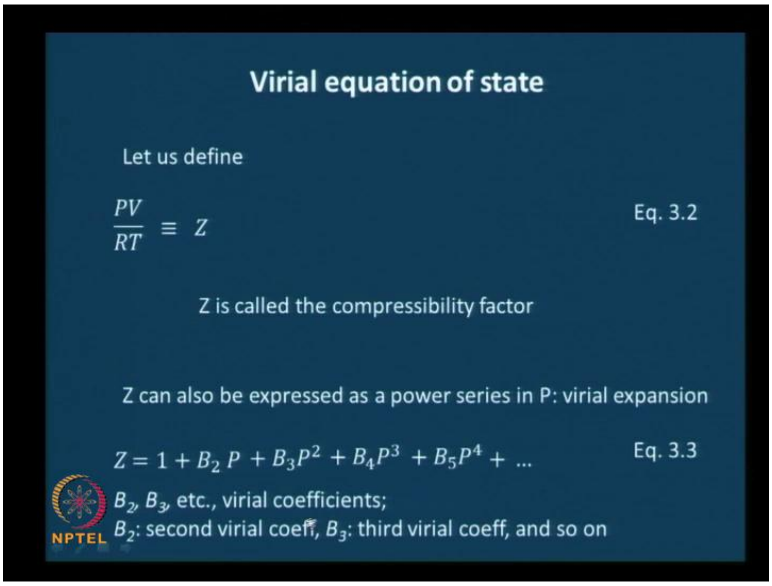

Virial equation of state

Let us define

$$\frac{PV}{RT} \equiv Z \qquad \text{Eq. 3.2}$$

Z is called the compressibility factor

Z can also be expressed as a power series in P: virial expansion

$$Z = 1 + B_2 P + B_3 P^2 + B_4 P^3 + B_5 P^4 + \ldots \qquad \text{Eq. 3.3}$$

B_2, B_3, etc., virial coefficients;

B_2: second virial coeff, B_3: third virial coeff, and so on

The first of those equations of state that we are going to look at is called the virial equation of state. To get to know what virial equation of state is, let us first define P V by R T. You know P V was equal to R T for an ideal gas. Let us define P V … by R T as a certain Z … let us call this equation 3.2. And, this Z is called the compressibility factor. This Z can also be expressed as a power series in P. You would have learnt about power series expansions in your Mathematics classes. And, if it is expressed as a power series it is called a virial expansion.

We will … first look at the expansion as a power series in pressure. Z can be written as one, plus a coefficient B 2 times P, plus B 3 times P squared, plus B 4 times P cubed, plus B 5 times P power 4, and so on. This is the power series expansion in pressure. And, this is called the virial expansion or virial equation of state for the particular component, which is represent … the particularity of the gas, comes about through B 2, B 3 and so on, as I will explain in a little while. We will call this equation 3.3. B 2, B 3 and so on are called virial coefficients; B 2 is called the second virial coefficient, B 3 is called the third virial coefficient, and so on.

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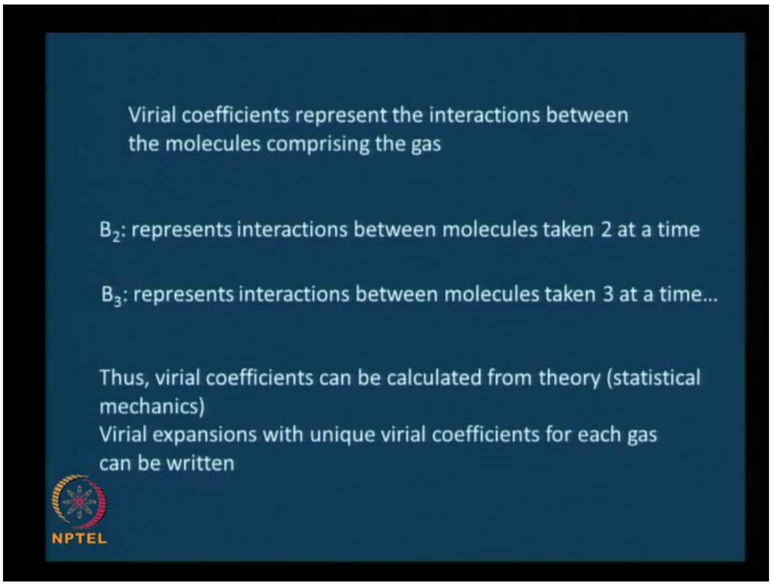

Virial coefficients represent the interactions between the molecules comprising the gas

B_2: represents interactions between molecules taken 2 at a time

B_3: represents interactions between molecules taken 3 at a time…

Thus, virial coefficients can be calculated from theory (statistical mechanics)
Virial expansions with unique virial coefficients for each gas can be written

These virial coefficients represent the interactions between the molecules or the particles that comprise the gas; typically molecules. For example, B 2 represents the interactions between particles in a gas taken two at a time, considered two at a time. B 3 represents interactions between molecules taken three at a time, and so on.

Therefore, the virial coefficients can be calculated from theory, which is actually Statistical Mechanics, which we will not be covering as a part of this course. But, Statistical Mechanics looks at the way of counting and way of accounting for a molecular… properties and so on, molecular doings and so on; and their relationship between two microscopic properties such as internal energy, entropy, and so on.

So, from very basic theory we can calculate B 2 and B 3. Here, I am not going to show you those calculations. I am just going to probably present the expressions, may be later on. And as mentioned earlier, virial expansions with unique virial coefficients for each gas can be written. Therefore B 2, B 3, B 4 and so on are going to be different for different gases.

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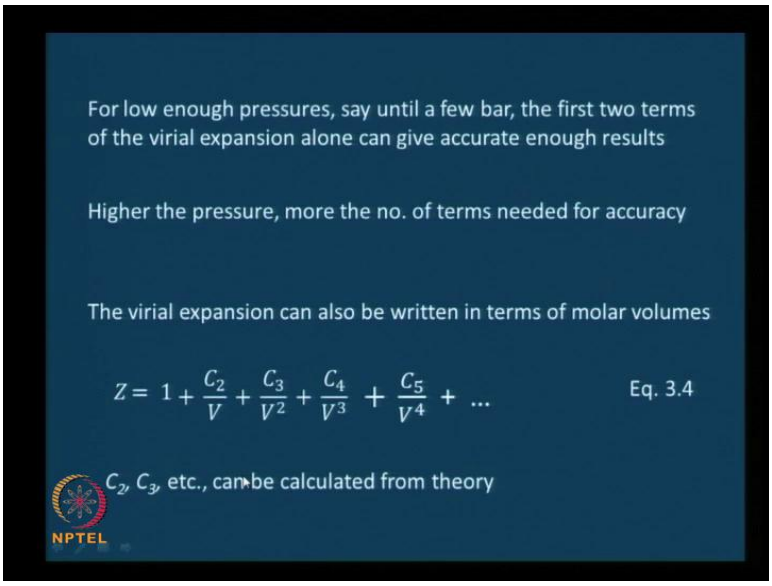

For low enough pressures, say until a few bar, the first two terms of the virial expansion alone can give accurate enough results

Higher the pressure, more the no. of terms needed for accuracy

The virial expansion can also be written in terms of molar volumes

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \frac{C_4}{V^3} + \frac{C_5}{V^4} + \ldots \qquad \text{Eq. 3.4}$$

C_2, C_3, etc., can be calculated from theory

For low enough pressures, say until a few bar, few atmospheres, the first two terms of the virial expansion alone are good enough to give accurate enough results. As we increase the pressure, we need to add more and more terms for the accuracy. What do I mean by accuracy? How close is the calculated value to the very carefully conducted experimental value. Higher the pressure; more the number of terms, more the number of virial terms needed for accuracy.

The virial expansion as we said is nothing but a power series expansion. It can be written in terms of molar volumes also. For example, Z can be written as one, plus C 2 by V, plus C 3 by V squared, plus C 4 by V cubed, plus C 5 by V power 4 and so on. This is a power series expansion in V or 1 by V. And, we will call this equation 3.4. C 2, C 3 and so on can also be calculated from theory, similar to the calculation of B 2, B 3 and so on.

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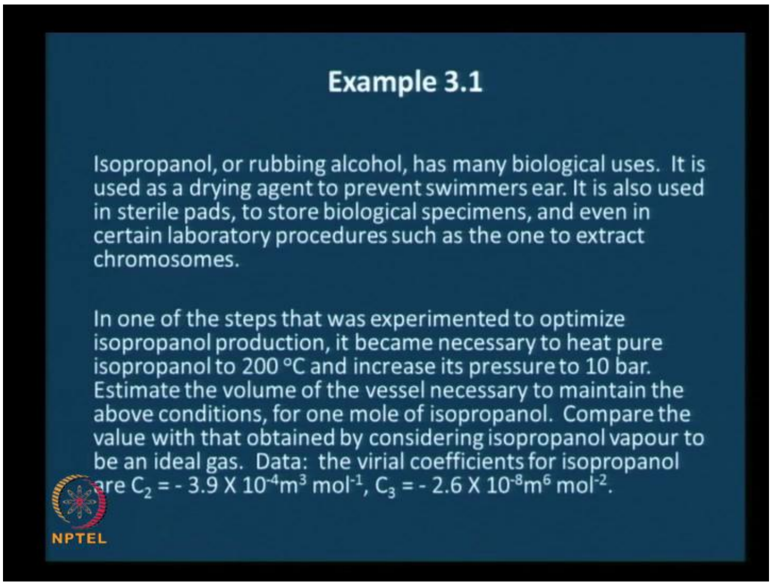

Example 3.1

Isopropanol, or rubbing alcohol, has many biological uses. It is used as a drying agent to prevent swimmers ear. It is also used in sterile pads, to store biological specimens, and even in certain laboratory procedures such as the one to extract chromosomes.

In one of the steps that was experimented to optimize isopropanol production, it became necessary to heat pure isopropanol to 200 °C and increase its pressure to 10 bar. Estimate the volume of the vessel necessary to maintain the above conditions, for one mole of isopropanol. Compare the value with that obtained by considering isopropanol vapour to be an ideal gas. Data: the virial coefficients for isopropanol are $C_2 = -3.9 \text{ X } 10^{-4} m^3 \, mol^{-1}$, $C_3 = -2.6 \text{ X } 10^{-8} m^6 \, mol^{-2}$.

Now, we have looked at some new information. So, let us workout an example or an exercise to understand this and apply and gather the skills of application a little bit. This is example 3.1. Isopropanol or rubbing alcohol has many biological uses. It is used as a drying agent to prevent swimmers ear. It is also used in sterile pads to store biological specimens. And, even in certain laboratory procedures such as the one to extract chromosomes. So, it has very many applications. And, you will find that we will be using isopropanol as one of our model substances for presenting the applications in this course. We will use a quite heavily.

In one of the steps that was experimented to optimize isopropanol production, it became necessary to heat pure isopropanol to 200 degrees Celsius and increase its pressure to 10 bar. What is required here is, estimate the volume of the vessel necessary to maintain the above conditions for one mole of isopropanol. Compare the value … with that obtained, by considering isopropanol vapor to be an ideal gas. So, that would quickly give you what are the kind of variations that you would expect when something is real and you use an ideal gas expression to represent it. And to do that, we will need the virial coefficients for isopropanol. These are available in the appendix of your textbook at the back. For ease, let me present it here itself. C 2 is, … remember C the coefficients and the virial expansion with respect to V. So, C 2 equals minus 3.9 into 10 power minus 4 meter cube mole; C 3 is minus 2.6 into 10 power minus 8 meter power six per mole squared.

So, please go ahead and work this out. Take about ten minutes. After about ten minutes … to think through the problem, to see what is available, what is needed, how do you make the link between what is available and what is needed. Go through all your notes, the previous slides here. And then, I will start giving you some hints. And then, give you more time and then probably present the solution. Go ahead, ten minutes please.

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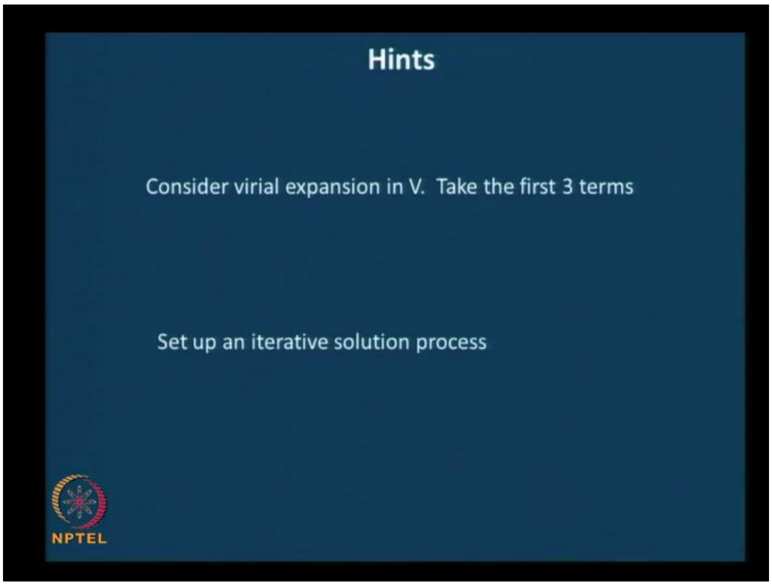

Hints

Consider virial expansion in V. Take the first 3 terms

Set up an iterative solution process

Ok. Let me give you some hints to work out the problem. The first hint, which was quite obvious, once you thought through it is: consider a virial expansion in V. And the real hint is, take the first three terms. And, let me also give you the second hint and leave you for another ten minutes to work things out. And, that is the solution is not a very straightforward solution. It involves an iterative solution. So, set up an iterative solution process for V, or in terms of V; because the specific volume is what we are looking at. The volume of the vessel that will hold one mole of the substance, which is essentially the specific volume is what we are looking for. And, so set up an iterative solution process for the same. Go ahead, please take another ten minutes.

Let me present a part of the solution and give you some more time because I am not very sure how comfortable you are with the iterative solution process. So, to get more comfortable with that, I probably need to give you more time. But, first let me present the initial part of the solution.

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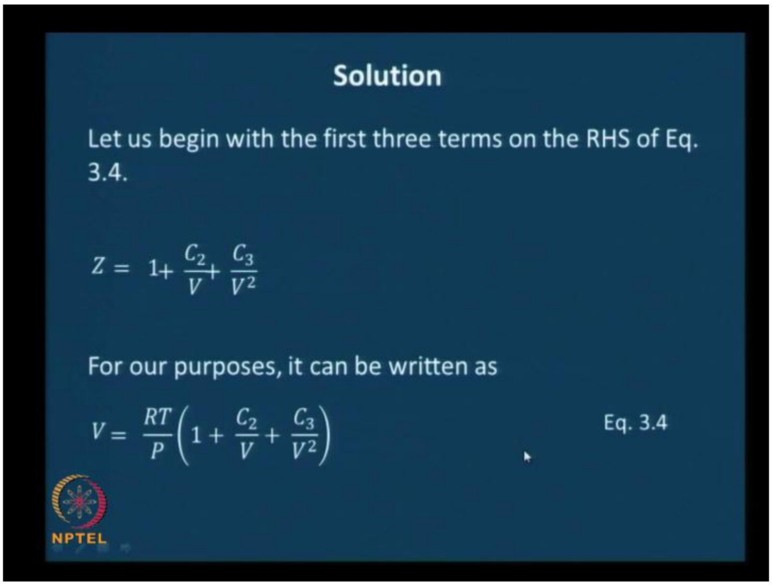

Solution

Let us begin with the first three terms on the RHS of Eq. 3.4.

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2}$$

For our purposes, it can be written as

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right) \qquad \text{Eq. 3.4}$$

Let us begin with the first three terms on the right hand side of equation 3.4. 3.4, if you want you can go back and check your slides. It is nothing but the virial expansion in V, or the compressibility factor Z expressed in terms of the powers of V or 1 by V. Z equals one, plus C 2 by V, plus C 3 by V squared. Let us start with this. It will turn out to be decent enough. We are trying to find out the volume. And therefore, we need to express this in terms of the volume. Therefore for our purposes, it can be written as, … you know Z is nothing but P V by R T. Therefore, if you multiply both sides by R T by P we get V.

V remains here, the remaining gets cancelled out. R T by P into one, plus C 2 by V, plus C 3 by V squared. Let us call this equation 3.4. I will check the numbering a little bit. The same; pretty much the same, with just three terms taken.

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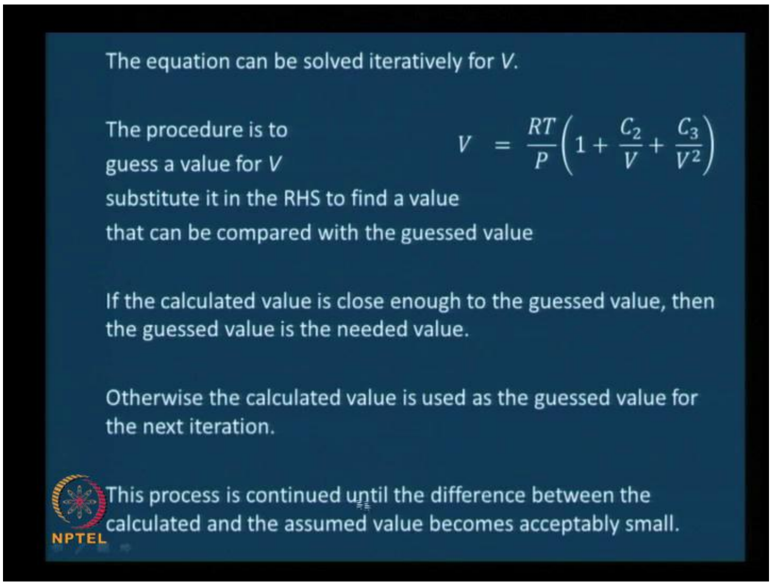

The equation can be solved iteratively for V.

The procedure is to
guess a value for V
substitute it in the RHS to find a value
that can be compared with the guessed value

$$V = \frac{RT}{P}\left(1 + \frac{C_2}{V} + \frac{C_3}{V^2}\right)$$

If the calculated value is close enough to the guessed value, then the guessed value is the needed value.

Otherwise the calculated value is used as the guessed value for the next iteration.

This process is continued until the difference between the calculated and the assumed value becomes acceptably small.

This is the equation and this can be solved iteratively for V. Let me give you the algorithm to do it; because we need to do very many calculations. And, once I present the algorithm, I would like you to take the remainder of this lecture, may be another ten minutes or eight minutes to work that out. Maybe you will need a little bit more time. It takes a few steps to converge.

Let me present the algorithm first, or the procedure. First, guess a value for V. Substitute it into the right hand side to find a value … you know … in terms of C 2, C 3 and R T by P, and so on. Guess a value for V; substitute it here to get a value. And, compare that with the guessed value. Remember that V was something that we guessed to begin with the first time, and then we substituted the same V here to find out this value. And now, compare the right hand side with the left hand side.

If the calculated value, the right hand side is close enough – you know the operative term here is close enough. You know, you might be working with 10 power minus 3 and so on and so forth. If all the values are in the range of 10 power minus 3, it does not really, it is not really close enough. Close enough to the guessed value. Then, the guessed value is the needed value. Otherwise, the calculated value is used as the guessed value for the next generation.

Whatever you calculated here you put it here and then substitute back here to get another calculated value. And then, you check how close this is to the guessed value or the value in the previous step. The process is continued till the difference between the calculated and the assumed value becomes acceptably small. Please go ahead and do this. Try it doing for about five steps. That is the hint. So, try it doing for about five steps. And, when we begin the next class, I will give you the complete solution.