Engineering Physics 1
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Module-05
Lecture-08
Vanderwaal's Equation of States– Part 03

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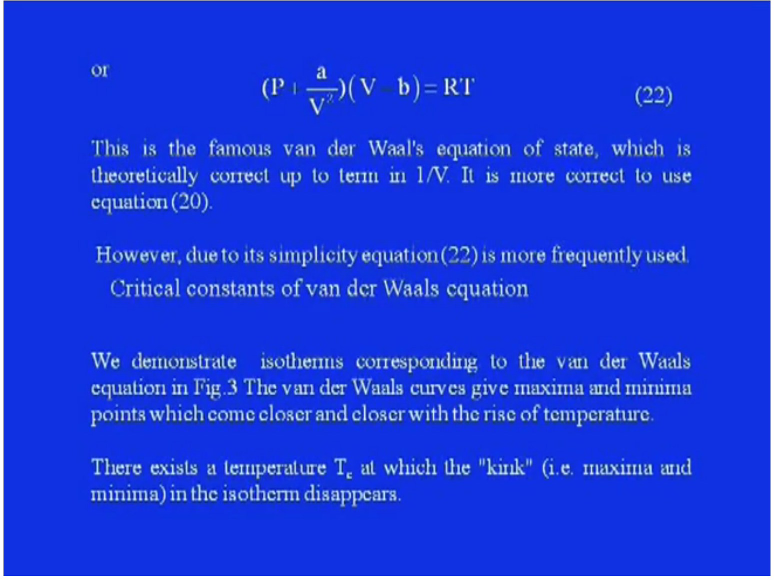

or

$$(P + \frac{a}{V^2})(V - b) = RT \qquad (22)$$

This is the famous van der Waal's equation of state, which is theoretically correct up to term in 1/V. It is more correct to use equation (20).

However, due to its simplicity equation (22) is more frequently used.

Critical constants of van der Waals equation

We demonstrate isotherms corresponding to the van der Waals equation in Fig.3 The van der Waals curves give maxima and minima points which come closer and closer with the rise of temperature.

There exists a temperature T_c at which the "kink" (i.e. maxima and minima) in the isotherm disappears.

So, let me switch over to how to calculate the critical constant in the Vanderwaal's equation of state means how to calculate the values of a and b. Because a and b represents the interaction, a represents the attractive interaction maybe it is weak between the atoms and molecule, b represents the repulsive interaction between atom molecules.So a and b the contains the molecular property.

So, molecular properties are encoded in the form of a and b, so let us calculate the form of a and b. So, we demonstrate isotherm corresponding to the Vanderwaal's equation in figure 3 from the theory. The Vanderwaal's equations gives maximum and minimum points which come closer with the rise of temperature that means just see it this is maximum if you are increasing the temperature.

Then this Maxima minima will come closer and closer and finally disappear ok, so here we learn two three things there exist temperature Tc which is a critical temperature we will tell you latter. At which the maxima or the minima in the isotherm disappear.

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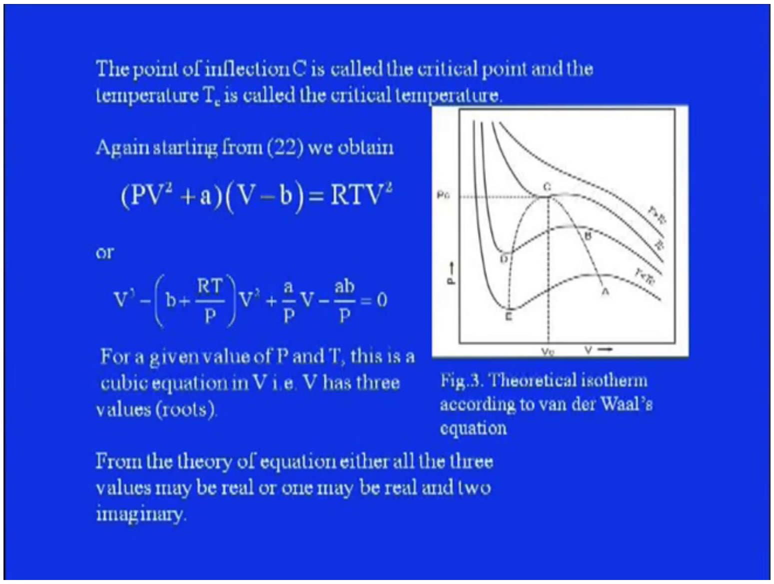
The point of inflection C is called the critical point and the temperature T_c is called the critical temperature.

Again starting from (22) we obtain

$$(PV^2 + a)(V - b) = RTV^2$$

or

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

For a given value of P and T, this is a cubic equation in V i.e. V has three values (roots).

Fig.3. Theoretical isotherm according to van der Waal's equation

From the theory of equation either all the three values may be real or one may be real and two imaginary.

So, another point which is point of inflection of C which is called the critical point and the temperature Tc which is called the critical temperature this point C. Then you start from this Vanderwaal's equation just you write P + a by b square into V - b = RT just write this equation you will get it Pb square + a into b - b = RTV square. Then you rewrite this equation in terms of volume, so we can write down the V cube - b + RT by P into V square + a by P V- ab by P =0.

This is the cubic equation so for a given value of P and T this is a cubic equation and V has three roots or three values. As you know from the theory of algebra all three roots may be real or one, two roots are real and one imaginary. So, let us see, so for a given P and T if less than the critical point.

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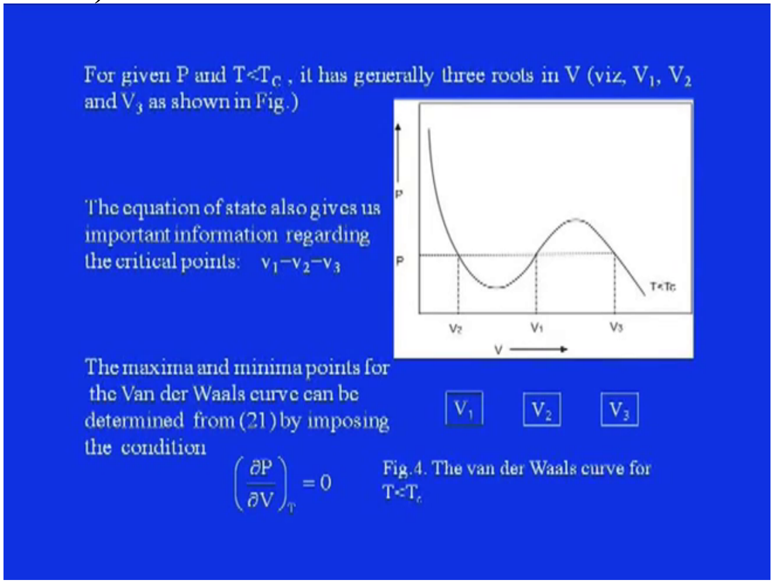
For given P and $T<T_C$, it has generally three roots in V (viz, V_1, V_2 and V_3 as shown in Fig.)

The equation of state also gives us important information regarding the critical points: $v_1 = v_2 = v_3$

The maxima and minima points for the Van der Waals curve can be determined from (21) by imposing the condition

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

$\boxed{V_1}$ $\boxed{V_2}$ $\boxed{V_3}$

Fig.4. The van der Waals curve for $T<T_c$

It has generally three roots V1, V2, V3 as shown in the figure 4. So, the equation of state also gives us important information regarding the critical points V1 = V2 = V3. So, the maximum minimum points for Vanderwaal's curve can be determined from the above equation from the equation 21 means from the Vanderwaal's equation 21 by imposing the condition del P by del V at constant = 0. So, this equation will give the maximum points of the maxima minima for Vanderwaal's curve

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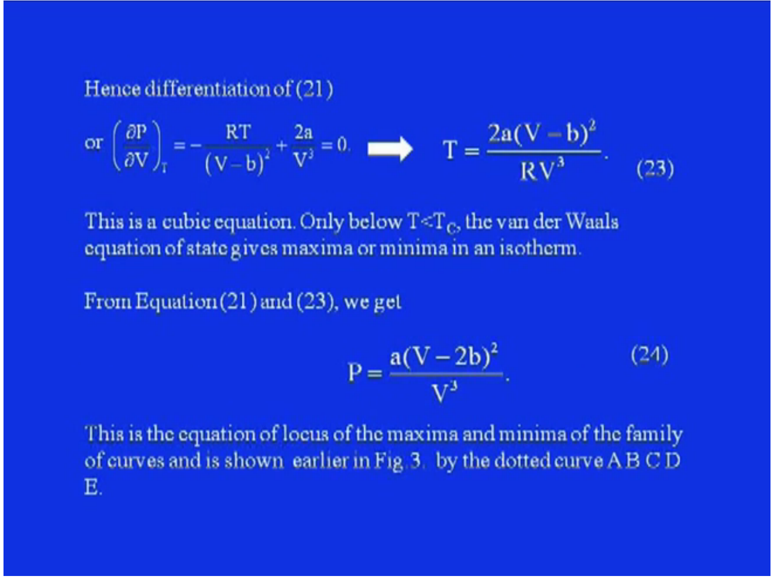

Hence differentiation of (21)

$$\text{or} \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0. \Rightarrow T = \frac{2a(V-b)^2}{RV^3}. \qquad (23)$$

This is a cubic equation. Only below $T<T_C$, the van der Waals equation of state gives maxima or minima in an isotherm.

From Equation (21) and (23), we get

$$P = \frac{a(V-2b)^2}{V^3}. \qquad (24)$$

This is the equation of locus of the maxima and minima of the family of curves and is shown earlier in Fig. 3. by the dotted curve A B C D E.

So if you differentiate that equation what you will get del P by del V are constant T if you differentiate it then you will get – RT by V- b whole square + 2a by V cube. If you demand this is 0 that gives the critical value. So, if you demand it then you will get T = 2a into V - b whole square by RV cube this is a cubic equation only below T less than Tc than the Vanderwaal's equation of this state gives Maxima minima in an isotherm. But as T radius T beyond then Tc the maxima minima this will they will disappear ok.

So then from the above 2 equation 21 and equation 23 so if you just substitute the value of P so we get P = substitute value of T in the Vanderwaal's equation number 21. You will get P = a into V - 2b whole square by V cube then other remaining equation 23 and 24 we get the critical constant for the temperature as well as for the pressure which is known as Tc and Pc. Tc you will get 27 by Rb, Pc you will get a by 27 V square. So, finally we are able to determine the critical constant of the Vanderwaal's equation.

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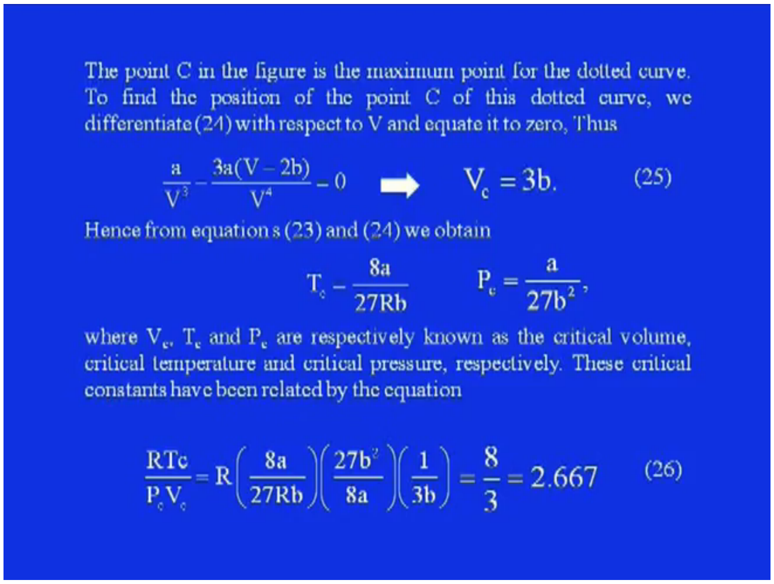

The point C in the figure is the maximum point for the dotted curve. To find the position of the point C of this dotted curve, we differentiate (24) with respect to V and equate it to zero, Thus

$$\frac{a}{V^3} - \frac{3a(V-2b)}{V^4} = 0 \Rightarrow V_c = 3b. \qquad (25)$$

Hence from equation s (23) and (24) we obtain

$$T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2},$$

where V_c, T_c and P_c are respectively known as the critical volume, critical temperature and critical pressure, respectively. These critical constants have been related by the equation

$$\frac{RTc}{P_cV_c} = R\left(\frac{8a}{27Rb}\right)\left(\frac{27b^2}{8a}\right)\left(\frac{1}{3b}\right) = \frac{8}{3} = 2.667 \qquad (26)$$

Pc, Vc and Tc in terms of the Vanderwaal's's constant a and b ok. So, that is what is Pc, Tc and Vc, Tc and Pc are respectively known as critical volume, critical temperature and critical pressure respectively. This critical constant have been related by beautiful equation RTc by PcVc just you substitute the value for Tc and PC and Vc. So, this Tc will come about 8 by 3 which is nothing but 2.667. This is a very beautiful ratio.

So if you will calculate the ratio for some system namely helium, hydrogen, neon, argon, oxygen, nitrogen etc you can calculate the values of Vc, Pc and Tc. so and then take their ration you see it will come around 3 to 3.5 days obviously it is sum how greater than the ratio of which is 2.667 ok. So, now let me see if you will perform experiment with that experimental results predict the experimental result it can be predicted with Vanderwaal's equation of state or not. So, let me just check it. The Vanderwaal's equation of state can be empirically applied to study the real gasses.

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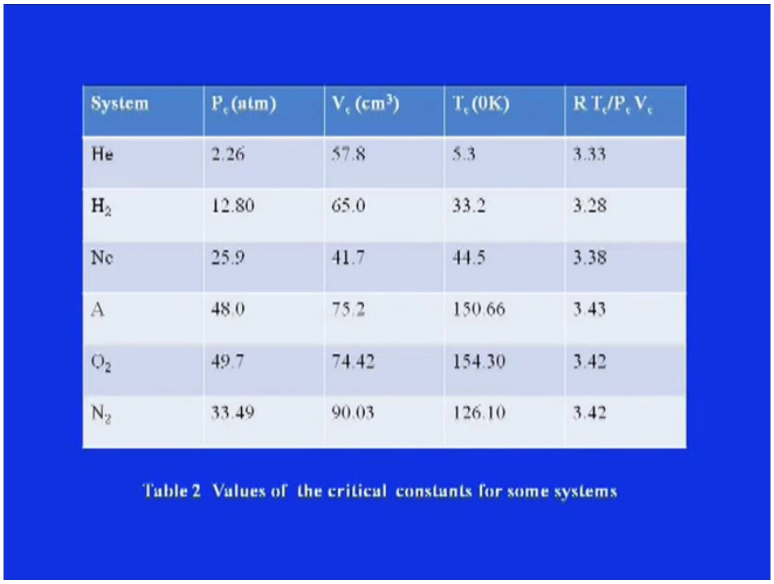

System	P_c (atm)	V_c (cm^3)	T_c (0K)	RT_c/P_cV_c
He	2.26	57.8	5.3	3.33
H_2	12.80	65.0	33.2	3.28
Ne	25.9	41.7	44.5	3.38
A	48.0	75.2	150.66	3.43
O_2	49.7	74.42	154.30	3.42
N_2	33.49	90.03	126.10	3.42

Table 2 Values of the critical constants for some systems

Over a wide range of densities and temperatures, so the theoretical curves are shown in the figure just see this figure P versus V it has been seen for different values of temperature 13.1for the carbon di oxide obviously, 13.2 just gradually increasing the temperature 21.5, 31.3, 35.5 and after that they are notting's at 48.1 degree centigrade's.

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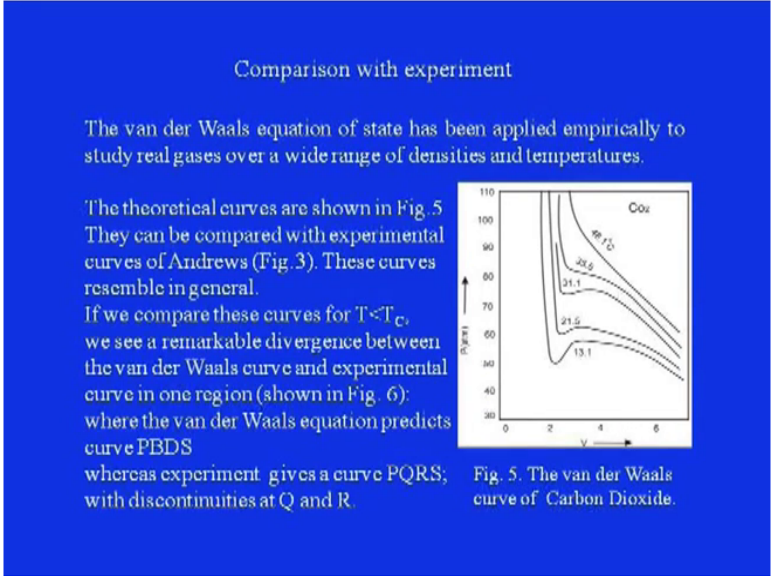

Comparison with experiment

The van der Waals equation of state has been applied empirically to study real gases over a wide range of densities and temperatures.

The theoretical curves are shown in Fig.5
They can be compared with experimental curves of Andrews (Fig.3). These curves resemble in general.
If we compare these curves for $T<T_C$,
we see a remarkable divergence between the van der Waals curve and experimental curve in one region (shown in Fig. 6):
where the van der Waals equation predicts curve PBDS
whereas experiment gives a curve PQRS; with discontinuities at Q and R.

Fig. 5. The van der Waals curve of Carbon Dioxide.

So this can be compared with experimental curves of Andrew and which is which is which is this is the experimental curve obtain by Andrew, if you want to compare if you want to compare so if you want to compare this curves T less than Tc s we see a remarkable divergence of the difference between the Vanderwaal's curve and the experimental curve in one region. So, let me see that region, this is the figure 6.

From there you can from there you can see that what the Vanderwaal's predict predicted curvess PBDS whereas experimental gives curve PQRS with discontinuity at Q and R just you see. This is this the PBDS, this is the ah ah theoretical curve, PQRS which is the experimental curve. So, experimentally the portion Q are corresponds to the heterogeneous portions where pressure is the main constant.

On the region BD you see the if the pressure increases with the volume so del P by del V is less than 0.Then the system cannot be in the stable equilibrium at any point in this region. Hence this region cannot be in a stable state and we cannot realise this region in practice. This is not obtained in the Andrews experiment. So, in the region QVRD the pressure decreases with increase volume del P by del V less than 0 and hence the corresponding state can physically exist ok.

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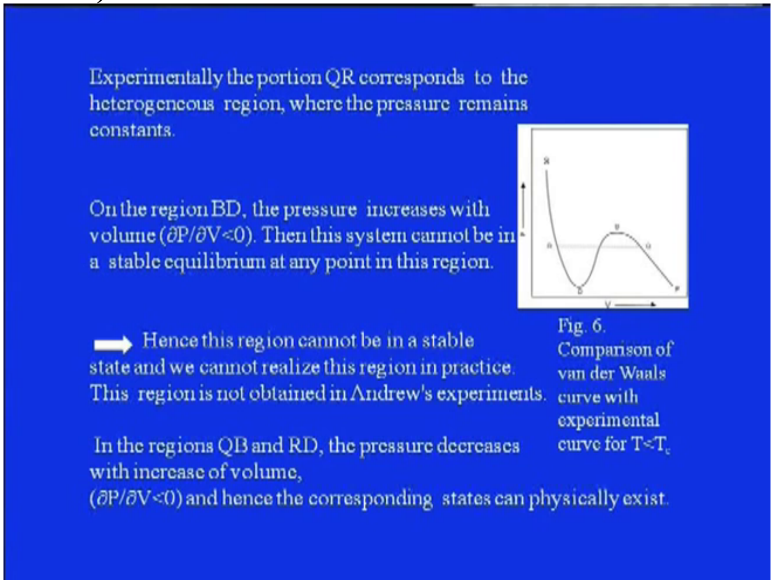

Experimentally the portion QR corresponds to the heterogeneous region, where the pressure remains constants.

On the region BD, the pressure increases with volume ($\partial P/\partial V < 0$). Then this system cannot be in a stable equilibrium at any point in this region.

→ Hence this region cannot be in a stable state and we cannot realize this region in practice. This region is not obtained in Andrew's experiments.

In the regions QB and RD, the pressure decreases with increase of volume, ($\partial P/\partial V < 0$) and hence the corresponding states can physically exist.

Fig. 6. Comparison of van der Waals curve with experimental curve for $T < T_c$

So, the region QVRD requires cool vapour and super heated liquid respectively. Thus we can explain the difference between the theoretical and experimental isotherm. So, the general agreement between theory and experiment is remarkable. However the quantitative agreement is not expected from such simple theory. However Vanderwaal's equation is the first step to explain the deviation from the ideal behavior.

Any way in this context I should tell, I should give Simple explanation of QVRD this can be understood in a much rigorous theory of history which is known as the Bubble Nucleation theory.

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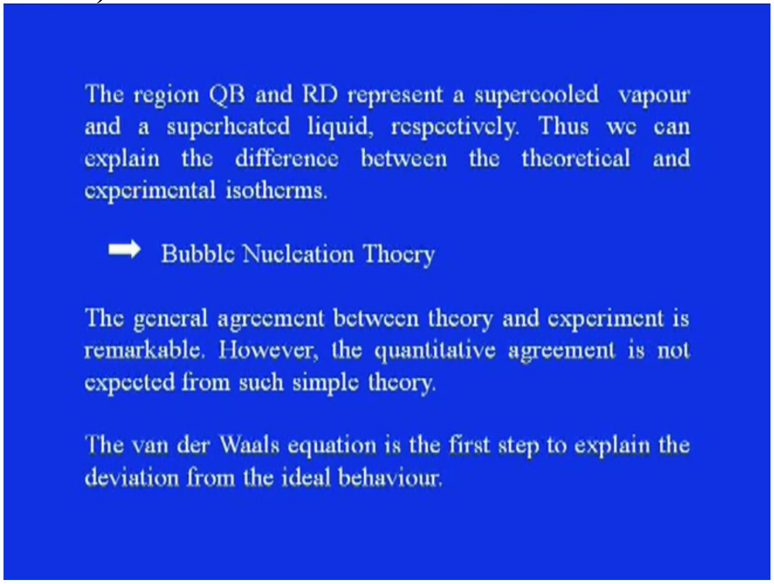

The region QB and RD represent a supercooled vapour and a superheated liquid, respectively. Thus we can explain the difference between the theoretical and experimental isotherms.

➡ Bubble Nucleation Theory

The general agreement between theory and experiment is remarkable. However, the quantitative agreement is not expected from such simple theory.

The van der Waals equation is the first step to explain the deviation from the ideal behaviour.

In the Bubble Nucleation theory tells, let me tell you suppose if you want to study the surface tension of liquid, water to steam. So, you take the water as a system then is gradually increasing the temperature as you know as from our commonsense as T will reach at 100 degree centigrade means critical temperature. Then this water is started to convert it to the steam phase. But what happens exactly out of his as you know this is a first order phase transition.

First order phase transition is not an instantaneous what will happen as you increasing the temperature of the water phase around T= 100 degree centigrade what will happen that some of this steam bubble, because of the local fluation because of the local thermal fluctuation some of this steam bubble will be produce and then they will started grow and finally they collide each other and then quails each other and from a bigger bubble.

And gradually more and more steam bubble will be produced and they will collide and quails to each other and finally the total water phase you will be converted to the steam phase. So, in this way you can understand the concept of super heat, superheated water vapour or super cool vapour when you understand the phase transition from vapour to water that time it will be super cool vapour ok. So, this is this idea ok.

So, now how to calculate the Vanderwaal's's constant a and b. So, let me start it, a simple and more accurate method of determining the constant a and b is based on measuring the temperature dependents on pressure gas at constant volume. So, from Vanderwaal's equations let me calculate del P by del T constant V = R by V – b as you know R is a molar gas constant. So, then what is from this equation what is b, b is nothing but the V – R by del P by del T at constant V.

The constant a can be determined from Vanderwaal’s equation which can be written as a = V square into RT by V- b –P, this is simple from Vanderwaal’s equation. Then if you substitute this equation in 27 we get a = V square into T del P by del T at constant V – P.

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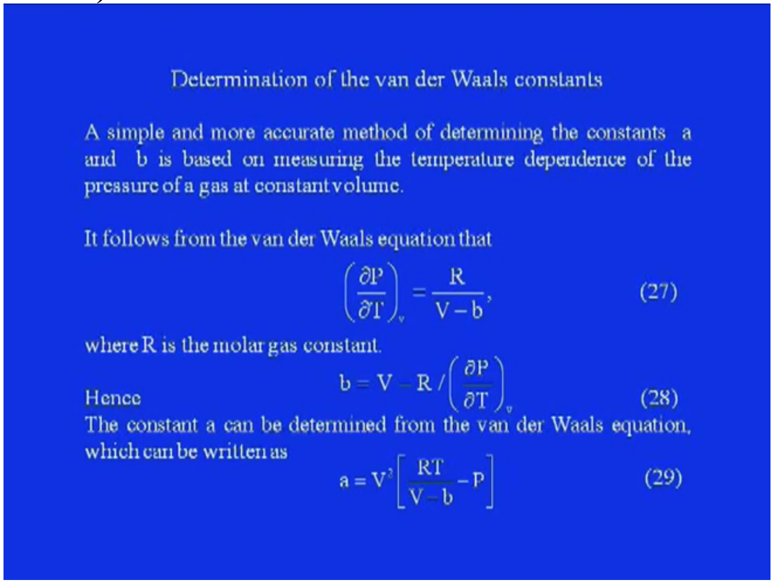

Determination of the van der Waals constants

A simple and more accurate method of determining the constants a and b is based on measuring the temperature dependence of the pressure of a gas at constant volume.

It follows from the van der Waals equation that

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{V-b}, \qquad (27)$$

where R is the molar gas constant.

Hence

$$b = V - R / \left(\frac{\partial P}{\partial T}\right)_v \qquad (28)$$

The constant a can be determined from the van der Waals equation, which can be written as

$$a = V^2\left[\frac{RT}{V-b} - P\right] \qquad (29)$$

So, where V is the molar volume which can be expressed as capital V = V naught small m by capital M where small n is the molar mass and capital N is the mass of the gas in the vessel of volume V naught. So, if the gas is taken in closed vessel of volume V naught and provided with a manometer, the pressure of the gas is measured at different temperatures from these experiment a graph P as a function of temperature is plotted at which gives del P by del T at constant V.

Then you plug-in the values of del P by del T at constant V in the expression a and b, so then you can find out what is a and b.

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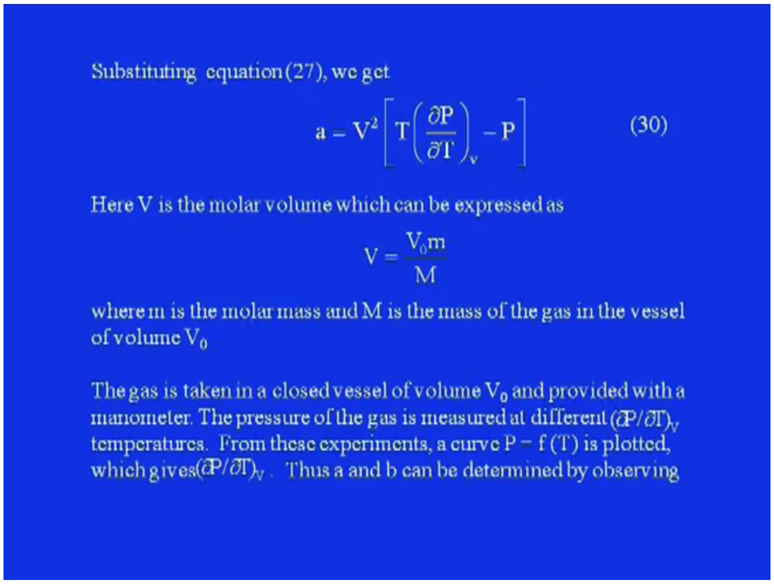

Substituting equation (27), we get

$$a = V^2\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \qquad (30)$$

Here V is the molar volume which can be expressed as

$$V = \frac{V_0 m}{M}$$

where m is the molar mass and M is the mass of the gas in the vessel of volume V_0

The gas is taken in a closed vessel of volume V_0 and provided with a manometer. The pressure of the gas is measured at different $(\partial P/\partial T)_V$ temperatures. From these experiments, a curve $P = f(T)$ is plotted, which gives $(\partial P/\partial T)_V$. Thus a and b can be determined by observing

You see in equation a; b which is nothing but V- R by del P by del T at constant V if you plug-in the values of del P by del T at constant V then you will get the; similarly get the values of a also. So, this is the way you can get the constant a and b. so, now there is another way how to determine the a and b from the critical constant. So I have told you few minutes back before the value of a and b can also be obtained from critical gas of a constant means Pc and Vc and Tc for a gas obeying the Vanderwaal's equation.

The critical constant just few minutes before told you this equal to 3V Tc = 8a by 7Rb, Vc = a by 27V square just from this we can obtain a and V in terms of Tc and Pc, a is nothing but the 27 R square by 64 Tc square by Pc. Similarly b is R by Tc by Pc, so finally a and b could also be written in calculator determined in terms of Tc and Pc because R is constant we know its value from the experimental know what is value of Pc and Tc.

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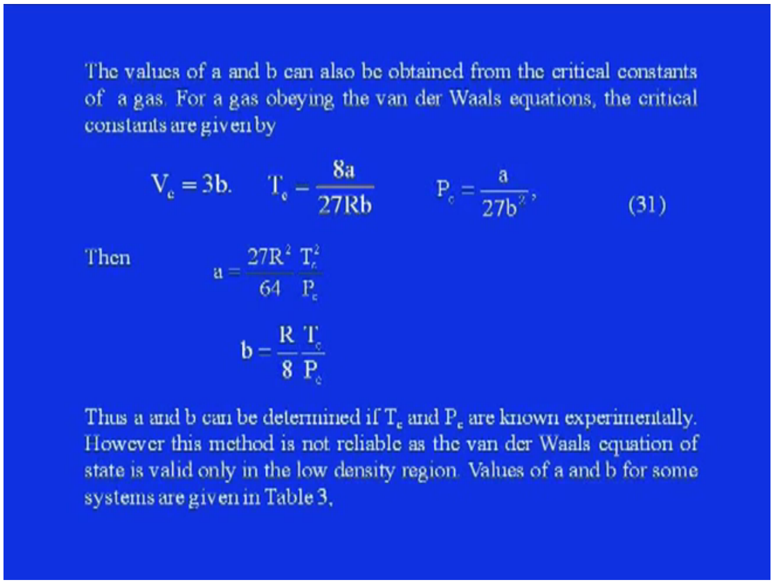

The values of a and b can also be obtained from the critical constants of a gas. For a gas obeying the van der Waals equations, the critical constants are given by

$$V_c = 3b, \quad T_c = \frac{8a}{27Rb} \quad P_c = \frac{a}{27b^2}, \qquad (31)$$

Then

$$a = \frac{27R^2}{64}\frac{T_c^2}{P_c}$$

$$b = \frac{R}{8}\frac{T_c}{P_c}$$

Thus a and b can be determined if T_c and P_c are known experimentally. However this method is not reliable as the van der Waals equation of state is valid only in the low density region. Values of a and b for some systems are given in Table 3.

Plug in the expression a and b we can find out a and b. So, thus we can conclude it and can be determined if Tc and Pc are known experimentally however this method is not reliable as a Vanderwaal's's equation of state is valid only in the low density region values of a and b for some systems are given in the table for your kind perusal where it is the values from one mole of system at NTP.

So, for the helium, hydrogen, argon, oxygen, nitrogen, carbon di oxide the values of a and b has been tabulated, the Vanderwaal's equation constants a and b are not constant they are found to vary with temperature and exactly that is what it is expected from the physics point of view. So, this can be explained from the molecular structure. So, it is now evident that the molecules do not behave as hot sphere as assumed by the Vanderwaal's but have some softness, so, just to check it, how it depends on temperature or intermolecular interaction.

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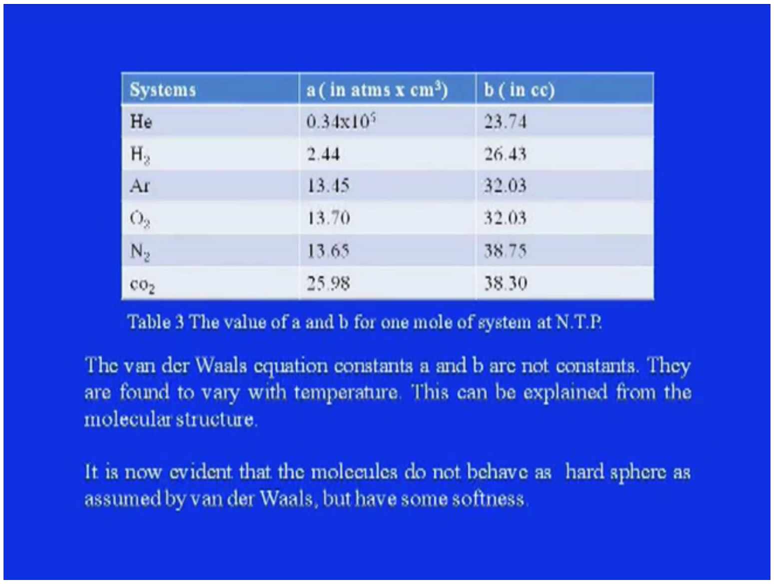

Systems	a (in atms x cm^3)	b (in cc)
He	$0.34x10^5$	23.74
H_2	2.44	26.43
Ar	13.45	32.03
O_2	13.70	32.03
N_2	13.65	38.75
co_2	25.98	38.30

Table 3 The value of a and b for one mole of system at N.T.P.

The van der Waals equation constants a and b are not constants. They are found to vary with temperature. This can be explained from the molecular structure.

It is now evident that the molecules do not behave as hard sphere as assumed by van der Waals, but have some softness.

So, naturally distance of closest approach between the centres of the molecules will vary with temperature and hence the main function of temperature. However thus for constant a can be let me write down equation we have already seen the equation 8, 8 where we have written down the expression a in terms of intermolecular potential just to show this is a actually this is the a we have told you this is a is – 2Pi this thing. So, let me see what is a? So then values a is -2.5 square KT 0 to infinity 1- exponential ur- KT r square dr.

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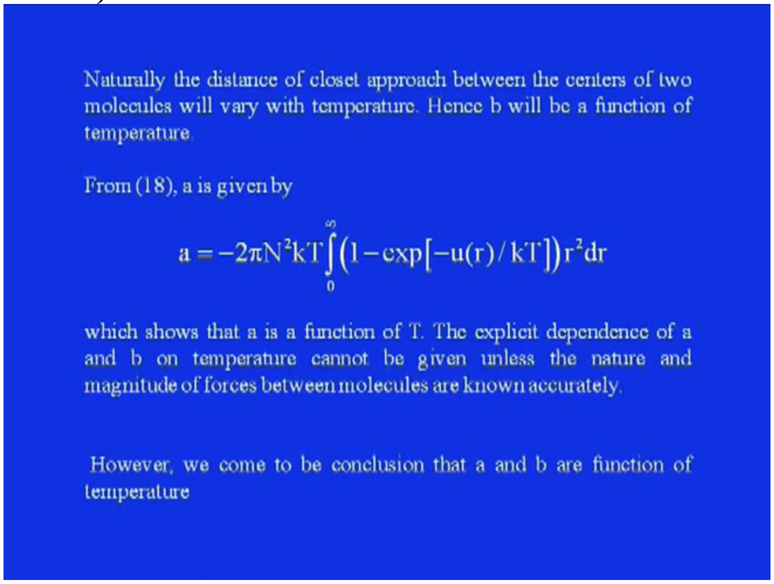

Naturally the distance of closet approach between the centers of two molecules will vary with temperature. Hence b will be a function of temperature.

From (18), a is given by

$$a = -2\pi N^2 kT \int_0^\infty \left(1 - \exp\left[-u(r)/kT\right]\right) r^2 dr$$

which shows that a is a function of T. The explicit dependence of a and b on temperature cannot be given unless the nature and magnitude of forces between molecules are known accurately.

However, we come to be conclusion that a and b are function of temperature

So, this is from equation 8 s just you please see the equation 8 and this is the a. Just from there it is obvious that a depends on temperature T and it depends on the intermolecular potential which is u of r, so this is shows that is a function of temperature be explicitly dependent on a and b the temperature cannot be given unless the nature and magnitude of the force is between the molecules are known accurately because u of r is sitting inside the integration until and unless u of r is not known exactly precisely you cannot tell what is the exact dependence on of a on temperature ok.

However we come to the conclusion that a and b are function of temperature ok. So, now I will spend a couple minutes on the law of corresponding states ok. Let the pressure, our idea is, beautiful ideas is there any way to get rid of the arbitrariness or get rid of the arbitrariness of the a and b of the Vanderwaal's constants this is the idea of this law of corresponding states.

Let the pressure, volume and temperature are measured on units of Pc, Tc, Vc let me modify and redefine variable P by Pc = Pr, V by Vc =Vr, T by Tc = Tr then where Pr, Vr and Tr reduce pressure, reduce volume and reduce temperature respectively they are obviously of dimensionless quantity. So, P is nothing but in terms of Pc into Pr, V= Vc into Vr, T =Tc into Tr ok.

So, if you substitute the values of P, V, T in the Vanderwaal's equation what you will get, you will get Pr + 3 by Vr square into Vr – one third = 8 by 3 into Tr. You see immediately if you inspect the equation immediately you feel happy.

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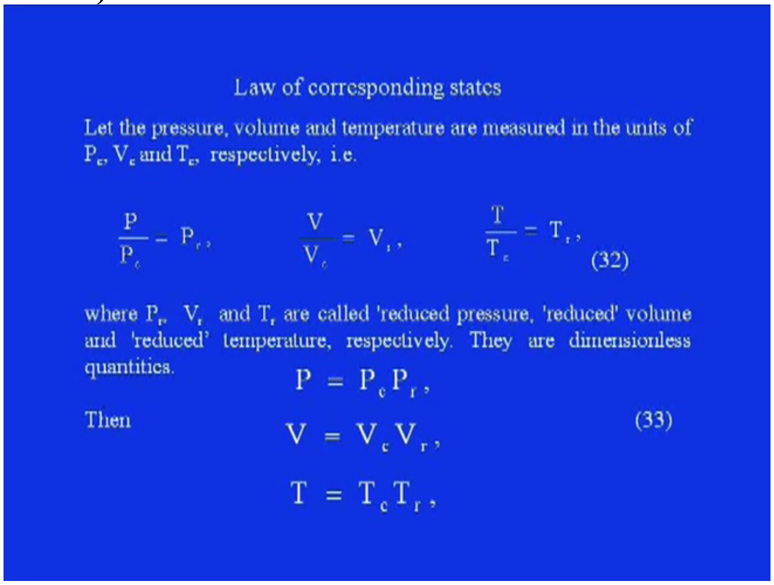

Law of corresponding states

Let the pressure, volume and temperature are measured in the units of P_c, V_c and T_c, respectively, i.e.

$$\frac{P}{P_c} = P_r, \qquad \frac{V}{V_c} = V_r, \qquad \frac{T}{T_c} = T_r, \qquad (32)$$

where P_r, V_r and T_r are called 'reduced pressure, 'reduced' volume and 'reduced' temperature, respectively. They are dimensionless quantities.

Then

$$P = P_c P_r, \quad V = V_c V_r, \quad T = T_c T_r, \qquad (33)$$

Because there are no a and b are sitting inside the equation ok it is there, but it is not, it is it has not appear directly there are no end. So, this equation does not contain the constant a and b which are characteristic of a system therefore it is a universal equation valid for all substances.

This equation is known as reduced equation of state of the Vanderwaal's gas. So, these equation states that if any two of the quantities from Pr, Vr to Tr are the same.

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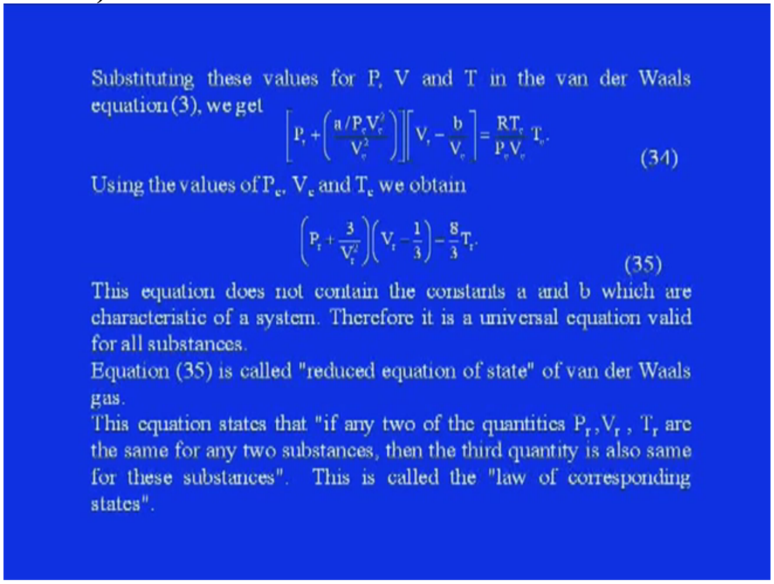

Substituting these values for P, V and T in the van der Waals equation (3), we get

$$\left[P_r + \left(\frac{a/P_cV_c^2}{V_r^2}\right)\right]\left[V_r - \frac{b}{V_c}\right] = \frac{RT_c}{P_cV_c}T_r. \qquad (34)$$

Using the values of P_c, V_c and T_c we obtain

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r. \qquad (35)$$

This equation does not contain the constants a and b which are characteristic of a system. Therefore it is a universal equation valid for all substances.

Equation (35) is called "reduced equation of state" of van der Waals gas.

This equation states that "if any two of the quantities P_r, V_r, T_r are the same for any two substances, then the third quantity is also same for these substances". This is called the "law of corresponding states".

For any two substances when the third quantity is also same for these substances. So this is called law of corresponding states. So, let me repeat it again if any two of the quantities are Vr, Pr and Tr at the same for any two substances then third quantity is also same for the substances. This is known as law of corresponding states. So, it expresses the fact that by using the reduced parameter the isotherm of all substances we made to coincide.

Not only that the law of corresponding states can be used to determine unknown isotherms of the gases if there critical constants are known. The law of corresponding states is not restricted to the Vanderwaal's equation only. Any equation of state may predict certain method of corresponding states provided the equation contains 3 constants such as a, b, r. So, the reduced equation of state may be expressed in terms of other variables instead of critical constant. So, let me look for some other thing.

So let us consider some gaseous system which molecule which interact with Pr potential of equation

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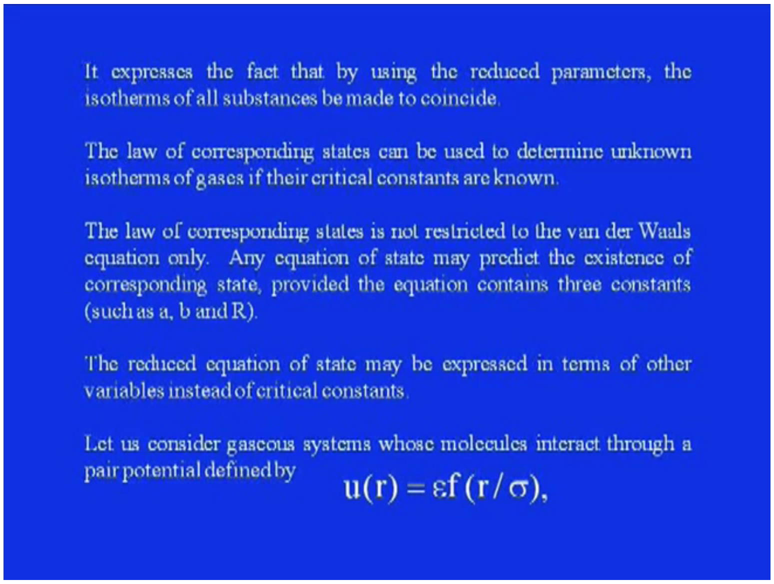

It expresses the fact that by using the reduced parameters, the isotherms of all substances be made to coincide.

The law of corresponding states can be used to determine unknown isotherms of gases if their critical constants are known.

The law of corresponding states is not restricted to the van der Waals equation only. Any equation of state may predict the existence of corresponding state, provided the equation contains three constants (such as a, b and R).

The reduced equation of state may be expressed in terms of other variables instead of critical constants.

Let us consider gaseous systems whose molecules interact through a pair potential defined by

$$u(r) = \varepsilon f(r/\sigma),$$

Ur = epsilon f as a function of some a new variable by sigma, where sigma as you know the diameter of the molecules. Which depends upon 2 molecular parameter we introduce new reduced variable defined as P star = P sigma cube by epsilon, V star = V by sigma cube, T star = KT by epsilon which are also dimensionless quantity is like Pr, Vr, Tr and so obviously we can see KT is the unit of energy, epsilon is the energy.

So, these are all dimensionless quantities sigma is the diameter of sigma Q as a dimension of volume. So, obviously from there is a all three P star, Vstar, T star are dimensionless variables. So, taking is reduced variable in terms of P star, V star and T star reduced equation of state may also be retained in another form P star = as a function of V star and T star.

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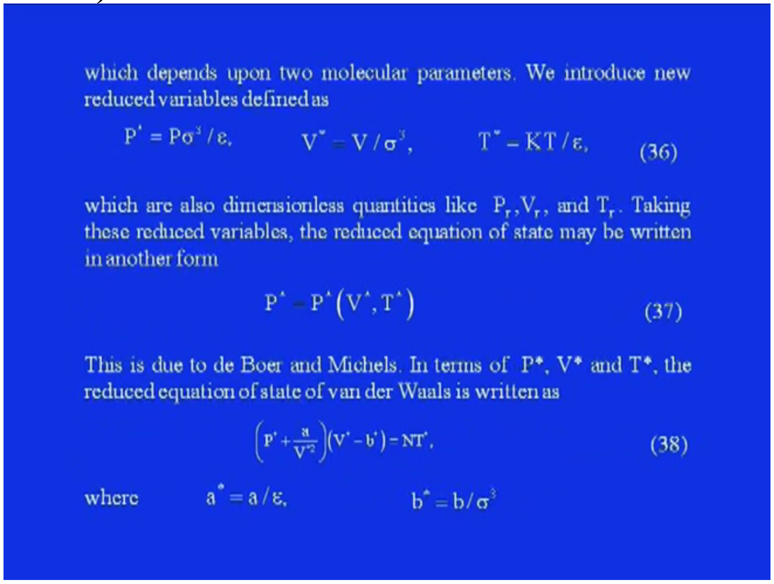

which depends upon two molecular parameters. We introduce new reduced variables defined as

$$P^* = P\sigma^3/\varepsilon, \qquad V^* = V/\sigma^3, \qquad T^* = KT/\varepsilon, \qquad (36)$$

which are also dimensionless quantities like P_r, V_r, and T_r. Taking these reduced variables, the reduced equation of state may be written in another form

$$P^* = P^*(V^*, T^*) \qquad (37)$$

This is due to de Boer and Michels. In terms of P^*, V^* and T^*, the reduced equation of state of van der Waals is written as

$$\left(P^* + \frac{a}{V^{*2}}\right)(V^* - b^*) = NT^*, \qquad (38)$$

where $a^* = a/\varepsilon,$ $b^* = b/\sigma^3$

These is due to De Boer and Michels in terms of P star, V star and T star the reduced T star – V star = NT star where a star is nothing but a by epsilon, b star is nothing but b by sigma cube ok. So, there is a printing mistake I think it is P star + a star by V star square ok, sorry we check it, please correct it. So De Boer further generalized the law of corresponding state for quantum fluids the deviation from the classical or due to quantum effects depends on the dimensionless quantum parameter lambda star .

Which is defined lambda star = 8 upon sigma into m epsilon to the power 1 by half so which is a characteristic k of the substance considered ok. Then the new law of corresponding states will be a function it will be a function of other variable which is lambda star takes into account the quantum correction P star = P star as a function of the T star and further other variable lambda star obviously lambda star = 0 limit reduces to the classical which is nothing but which where P star the function only V star and T star.

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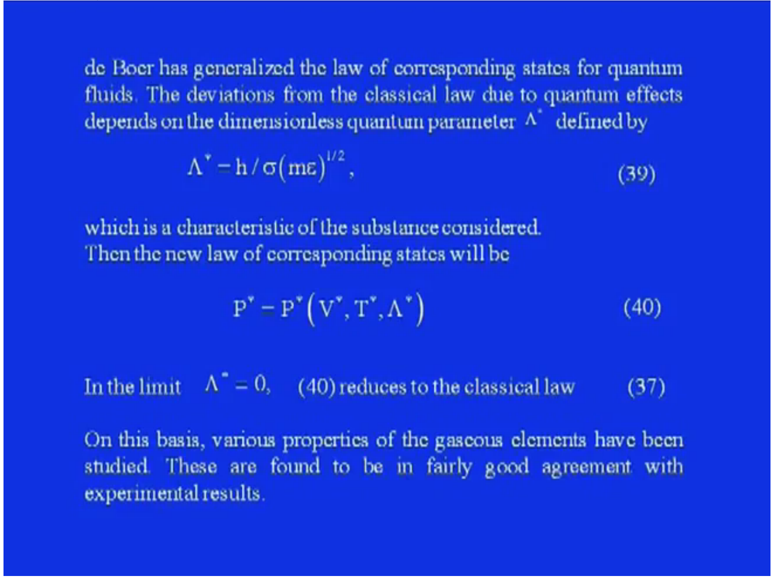

de Boer has generalized the law of corresponding states for quantum fluids. The deviations from the classical law due to quantum effects depends on the dimensionless quantum parameter Λ^* defined by

$$\Lambda^* = h/\sigma(m\varepsilon)^{1/2}, \qquad (39)$$

which is a characteristic of the substance considered.
Then the new law of corresponding states will be

$$P^* - P^*\left(V^*, T^*, \Lambda^*\right) \qquad (40)$$

In the limit $\Lambda^* = 0$, (40) reduces to the classical law (37)

On this basis, various properties of the gaseous elements have been studied. These are found to be in fairly good agreement with experimental results.

On the basis various properties of gaseous elements have been studies these are found to be really good agreement with the experimental result. So, now we are almost at the end of this lecture on Vanderwaal’s. So, finally to conclude it we should know what are the defects and limitation of the Vanderwaal’s equation of state means the regions, what are regions where Vanderwaal’s gives good prediction and what are region where Vanderwaal’s is not able to gives the prediction which are, which exist with the experimental results.

So, I will know it so let me tell one by one ok, all the Vanderwaal’s equation of state discuss the general features of the liquid gas system. So, its quantitative to prediction deviate from experimental result will consider important discrepancies below. So, in the region we know from the first order phase transition either ice to water or water to gas. We know whenever there is a phase transition obviously first order phase transition.

So, whenever water goes to steam it cannot abruptly phase will be changes from one phase to another phase it will go some meta stable phase of which is known as the co existence where initially dominated by the what phase but very less amount of steam phase and at the end of at the end of phase transition.

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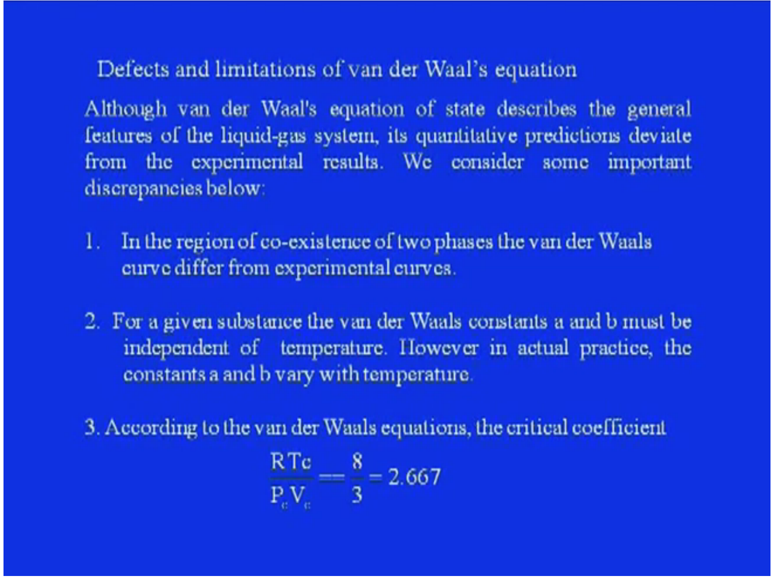

Defects and limitations of van der Waal's equation

Although van der Waal's equation of state describes the general features of the liquid-gas system, its quantitative predictions deviate from the experimental results. We consider some important discrepancies below:

1. In the region of co-existence of two phases the van der Waals curve differ from experimental curves.
2. For a given substance the van der Waals constants a and b must be independent of temperature. However in actual practice, the constants a and b vary with temperature.
3. According to the van der Waals equations, the critical coefficient

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.667$$

And as the phase transition proceeds then gradually the steam phase will be more compare to the water and at the end of its transition it will be purely steam phase. So, this phase is known as coexistence phase where both phases exist together for pressure and temperature remains constant during this coexistence region. So, in the region of coexistence of two phases the Vanderwaal's differs from experiment of as we have already seen.

For a given substance the Vanderwaal's constant a and b must be independent of temperature it should be however we know in a actual practice the constant a and b vary with temperature. So, third but not the least according to the Vanderwaal's equation the critical constant this RTc by Pc Vc = 8 by 3 which is nothing about 2.667 but we know which is a universal constant for all the substance. However in actual practice we have already seen.

It changes its values substance to substance in general the predictions of Vanderwaal's equation is better for light gases then for heavy gases. Fourth as we have already told you somewhere

Vanderwaal’s equation is gives the critical values of the which is bc is 3Vwhich is not overt experimentally more exact values of the bc of the order of 2 times b. So, the Vanderwaal’s equation is only an approximate equation of state.

It is expected to provide a better agreement when you compare the behaviour at the low densities. It never claimed to hold at high density such as the critical region ok. So, now we just tell how to determine the critical constants experimentally ok

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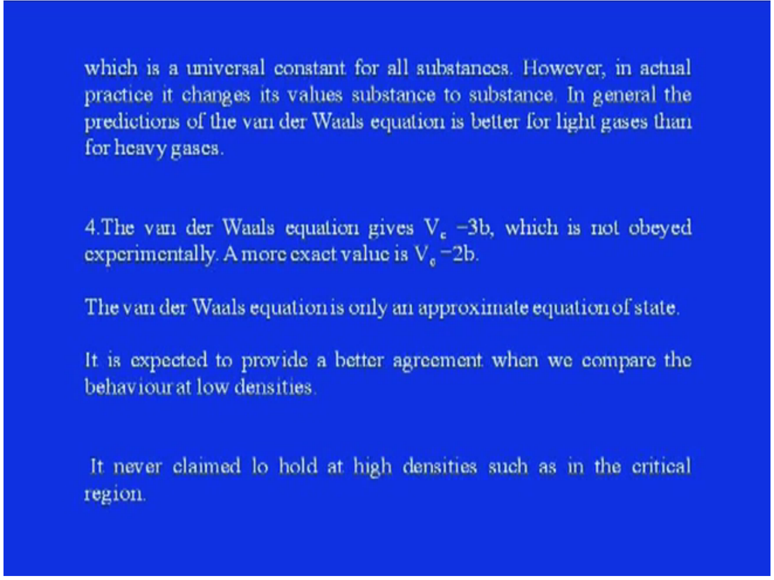

which is a universal constant for all substances. However, in actual practice it changes its values substance to substance. In general the predictions of the van der Waals equation is better for light gases than for heavy gases.

4.The van der Waals equation gives $V_c = 3b$, which is not obeyed experimentally. A more exact value is $V_c = 2b$.

The van der Waals equation is only an approximate equation of state.

It is expected to provide a better agreement when we compare the behaviour at low densities.

It never claimed to hold at high densities such as in the critical region.

Experimentally the critical constant or characteristics of a as you know what is the idea motivation to determine the critical constant is that the critical constant are characteristic of a substance because it changes from one substance to other substance their determination is a fundamental importance as they occur in certain equation of state. So we describe a simple method to determine the critical constant of a substance.

The first how to start it, first the liquid is introduced in a hard glass tube of connected Andrew separators to a manometer this is the Andrews apparatus. So, if you just see it then the tube is surrounded by thermostat whose temperature is continuously changing. The temperatures at which the liquid disappeared and reappeared are noted. The mean of these two temperatures give the critical temperature Tc.

The manometers reading at the temperature at which the liquid just disappear give the critical pressure P. So, finally we got the values of Tc.

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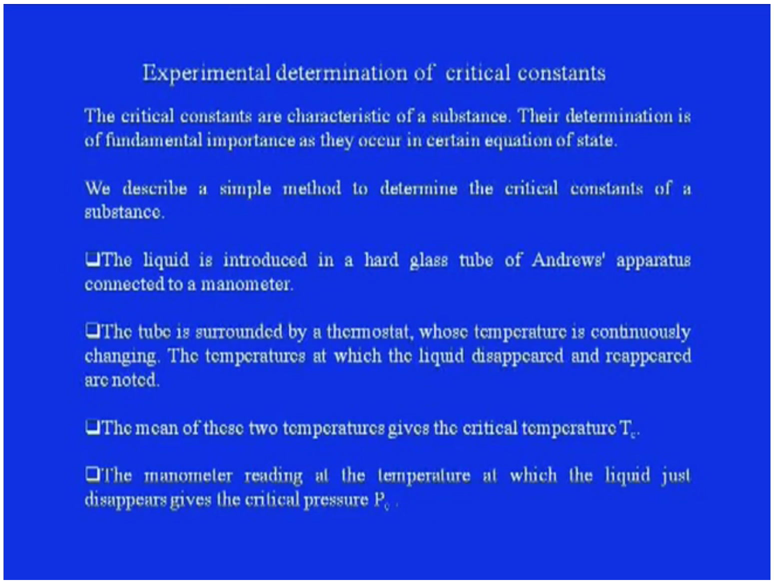

Experimental determination of critical constants

The critical constants are characteristic of a substance. Their determination is of fundamental importance as they occur in certain equation of state.

We describe a simple method to determine the critical constants of a substance.

❑The liquid is introduced in a hard glass tube of Andrews' apparatus connected to a manometer.

❑The tube is surrounded by a thermostat, whose temperature is continuously changing. The temperatures at which the liquid disappeared and reappeared are noted.

❑The mean of these two temperatures gives the critical temperature T_c.

❑The manometer reading at the temperature at which the liquid just disappears gives the critical pressure P_c .

And got the values of the Pc, how are the determination of the critical constant this is more difficult as a reason is because you feel change change the temperature in small amount it causes a lot change in volume. So, the substance is kept strictly at Tc to measure Vc, so that Cailletet and Mathias used the most accurate method for the determine determination of the critical volume, so, how they have determine, so the density of the liquid and it saturated vapour are determined accurately at different temperatures.

So, then they are plotted density as a function of temperature. So, the density of the; as you see from this figure the density of the liquid and vapour are approaching each other as temperature increases till they become equal at the critical temperature.

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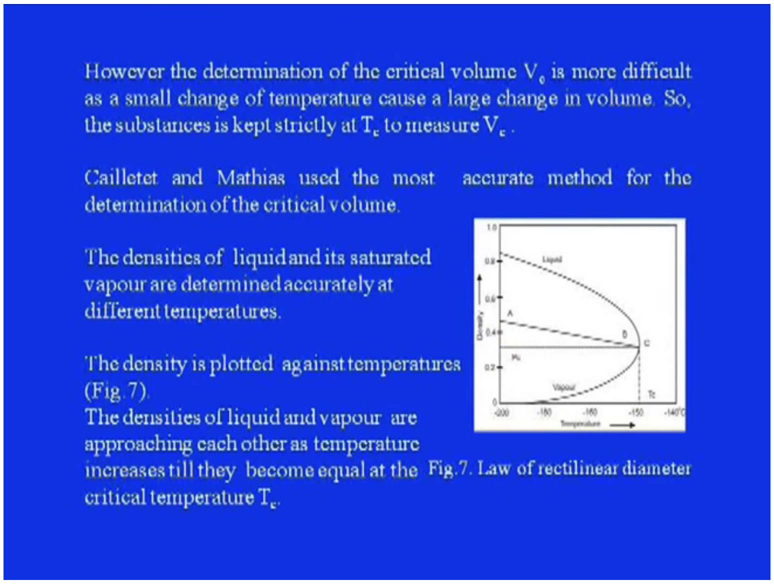

However the determination of the critical volume V_c is more difficult as a small change of temperature cause a large change in volume. So, the substances is kept strictly at T_c to measure V_c .

Cailletet and Mathias used the most accurate method for the determination of the critical volume.

The densities of liquid and its saturated vapour are determined accurately at different temperatures.

The density is plotted against temperatures (Fig.7).

The densities of liquid and vapour are approaching each other as temperature increases till they become equal at the critical temperature T_c.

Fig.7. Law of rectilinear diameter

So at the critical temperature the densities of liquid as well as vapour become equal. So, these carob a and b represents a line of mean of the liquid and vapour density which will pass through the critical temperature obviously. It is found to be straight line for all substance. So, now let me parameterized, so if Rho l and Rho v be the densities of the liquid and vapour respectively. The equation of this line in this curve density vs temperature can be written as a linear function of temperature.

Where y = half Rho l by Rho v by 2 equal to which is nothing but alpha + beta t. So, it looks like a linear relation. At the critical temperature we know the density of liquid should be = density of the vapour. Let call this Rho c;

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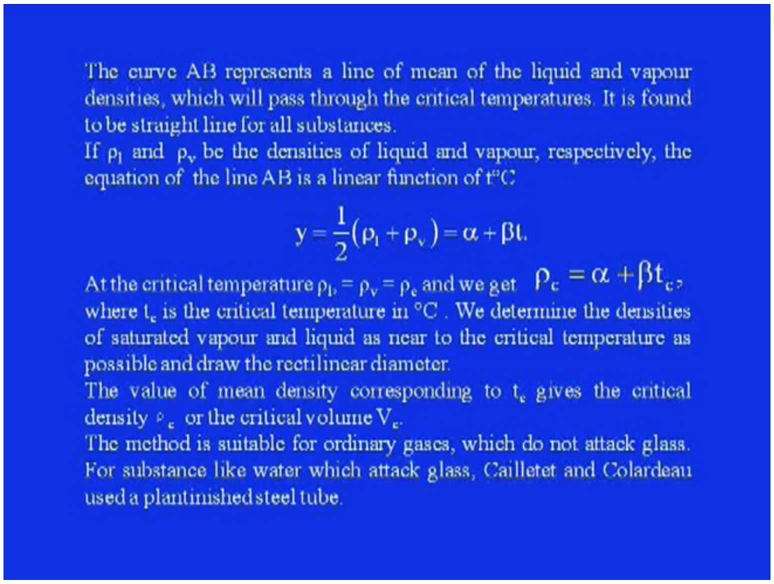

The curve AB represents a line of mean of the liquid and vapour densities, which will pass through the critical temperatures. It is found to be straight line for all substances.

If ρ_l and ρ_v be the densities of liquid and vapour, respectively, the equation of the line AB is a linear function of t°C

$$y = \frac{1}{2}(\rho_l + \rho_v) = \alpha + \beta t.$$

At the critical temperature $\rho_l = \rho_v = \rho_c$ and we get $\rho_c = \alpha + \beta t_c$, where t_c is the critical temperature in °C . We determine the densities of saturated vapour and liquid as near to the critical temperature as possible and draw the rectilinear diameter.

The value of mean density corresponding to t_c gives the critical density ρ_c or the critical volume V_c.

The method is suitable for ordinary gases, which do not attack glass. For substance like water which attack glass, Cailletet and Colardeau used a plantinished steel tube.

So, we get Rho c = alpha + beta times tc, t should be replaced by tc because c stands for the critical point. So, where tc is the critical temperature in degree centigrade. So, we determine the density of the saturated vapour and liquid as near to the critical temperature as possible and draw the rectilinear diameter. The mean or mean density corresponding to tc gives the critical density Rho c or critical volume Vc.

So, these method is suitable for ordinary gases who is do not attack glass for substances like water which attack glass so, Caillitate and Colardeau platinised steel tubes to get rid of this problem ok. So, now let me tell you give you some idea of some quantities which causes the division of deviation from the ideal equation of state. If you see first two three transfer we have retained PV by RT =1 + BP+ TP square + some higher order term.

At the low pressure only first order w with the higher order term will be neglected so but exactly even at the low pressure are moderately higher pressure the higher order terms is also there. So, let me see how the higher order term looks like. So, that we will feel why that there will be deviation from the ideal equation of state, so, let me; that is the reason let me estimate the form of second virial coefficient which is a measure from the deviation of the idea equation of state.

So, equation of state of fluid may be expressed in the virial form keeping the second time only PB by RT = 1 + BT by V where BT is the second virial coefficient of the fluid. So, the Vanderwaal's equation can be written as PV = RT by 1 + a by PV square into 1 – b by v, so if you rewrite it, if you bring to the numerator so what you will see RT into 1 + b by v ok – a by PB square. So, if you write it again so RT then RT by V into b – a by PV, so obviously from this equation you see that PV= RT, so we will compare it with the first equation.

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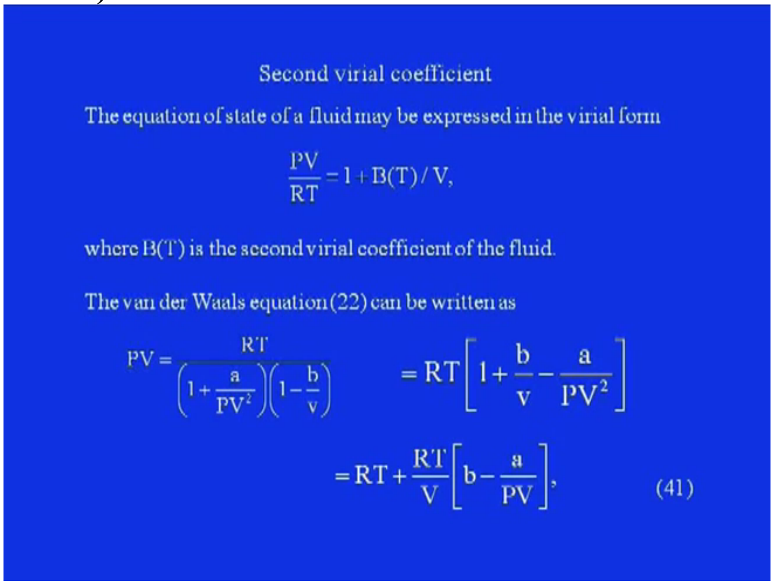

Second virial coefficient

The equation of state of a fluid may be expressed in the virial form

$$\frac{PV}{RT} = 1 + B(T)/V,$$

where B(T) is the second virial coefficient of the fluid.

The van der Waals equation (22) can be written as

$$PV = \frac{RT}{\left(1+\frac{a}{PV^2}\right)\left(1-\frac{b}{V}\right)} = RT\left[1+\frac{b}{V}-\frac{a}{PV^2}\right]$$

$$= RT + \frac{RT}{V}\left[b - \frac{a}{PV}\right], \qquad (41)$$

Then it gives the values of b which is nothing but the second virial coefficient. So, so, by comparing it what you will see is b = b by a – RT, so the temperature so from this equation of states there you see b = 0 or a= 0 then it reduces to the ideal equation of state and which is which it should be. Because you know a and b are the causes the deviation from the ideal equation of state. So, the temperature at which V= 0 is called the wall temperature TV, Tb. So, we can estimate the wall temperature Tv =27 by 8 Tc.

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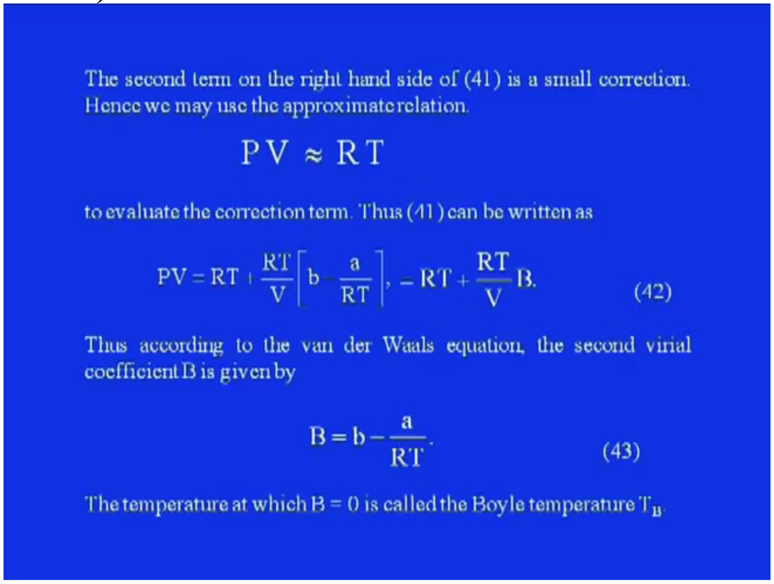

The second term on the right hand side of (41) is a small correction. Hence we may use the approximate relation.

$$PV \approx RT$$

to evaluate the correction term. Thus (41) can be written as

$$PV = RT + \frac{RT}{V}\left[b - \frac{a}{RT}\right], = RT + \frac{RT}{V}B. \qquad (42)$$

Thus according to the van der Waals equation, the second virial coefficient B is given by

$$B = b - \frac{a}{RT}. \qquad (43)$$

The temperature at which B = 0 is called the Boyle temperature T_B

The agreement is not satisfactory the discrepancy is due to the fact that the Vanderwaal's equation does not represent the actual gas accurately. So, which we have told many times that it cannot capture properties of the actual gases exactly. So, actually the second virial coefficient is nothing is but BT is 2 Pi N 0 to infinity 1 – exponential – ur by KT r square dr.

So, from this expression it seems that second virial coefficients depends on correct knowledge of intermolecular potential ok. So, if you will; we can write from this equation if you will plug in this form of u of r.

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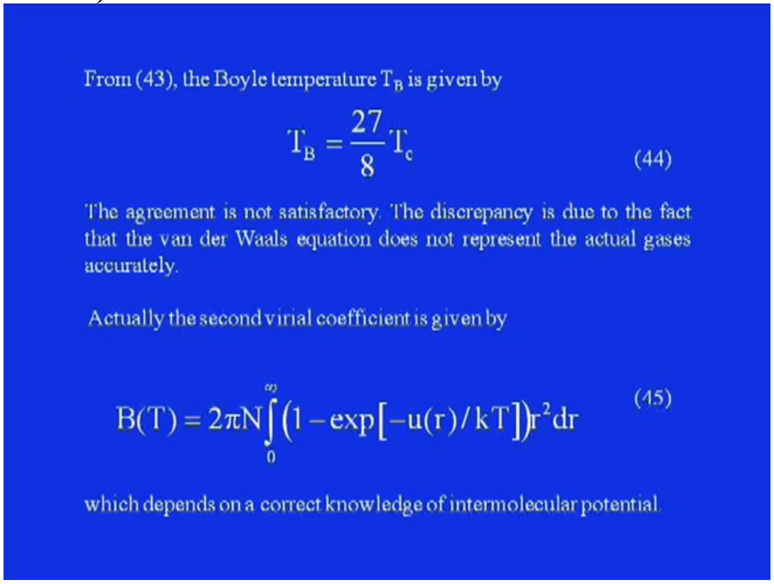

From (43), the Boyle temperature T_B is given by

$$T_B = \frac{27}{8} T_c \qquad (44)$$

The agreement is not satisfactory. The discrepancy is due to the fact that the van der Waals equation does not represent the actual gases accurately.

Actually the second virial coefficient is given by

$$B(T) = 2\pi N \int_0^\infty \left(1 - \exp\left[-u(r)/kT\right]\right) r^2 dr \qquad (45)$$

which depends on a correct knowledge of intermolecular potential.

As I already told you which is infinity when r less than sigma and it, so this form if you write it then another if it is u naught r when r greater than sigma if you will substitute that form of ur from equation in 18a. So, BT could be written as 2 Pi N 1 by 3 sigma cube – summed over I = 1 to N 1 by I – 1 by KT to the power I sigma to infinity u of r to the power I r square dr, so these indicates that equation 38. Let me show you what we are trying to say, so this equation 38.

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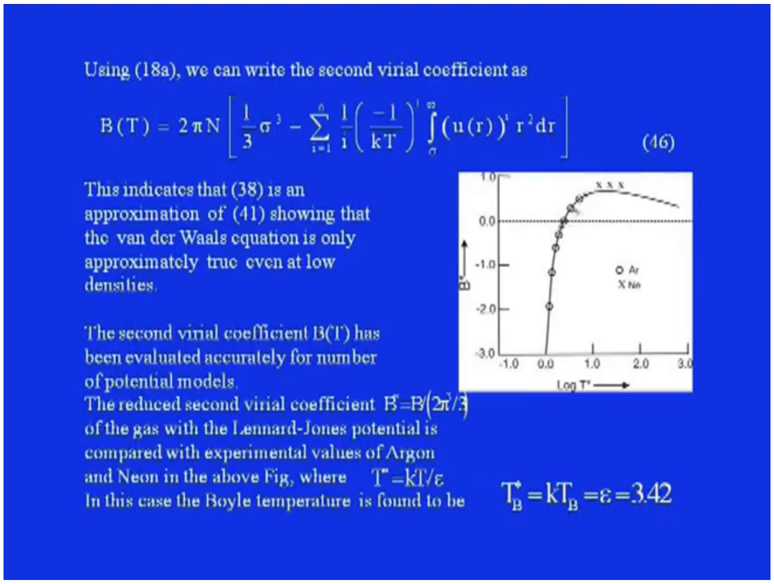

Using (18a), we can write the second virial coefficient as

$$B(T) = 2\pi N\left[\frac{1}{3}\sigma^3 - \sum_{i=1}^{n}\frac{1}{i}\left(\frac{-1}{kT}\right)^i\int_{\sigma}^{\infty}(u(r))^i r^2 dr\right] \qquad (46)$$

This indicates that (38) is an approximation of (41) showing that the van der Waals equation is only approximately true even at low densities.

The second virial coefficient B(T) has been evaluated accurately for number of potential models.
The reduced second virial coefficient $B^*=B/(2\pi^3/3)$ of the gas with the Lennard-Jones potential is compared with experimental values of Argon and Neon in the above Fig, where $T^*=kT/\varepsilon$
In this case the Boyle temperature is found to be $T_B^* = kT_B = \varepsilon = 3.42$

This equation reduced equation of state for Vanderwaal's this reduced equation 38 is an approximation of 41 showing that the Vanderwaal's equation is only approximately true at low density. The second virial coefficient BT has been evaluated accurately for number of potential models means they are people have assumed some different kind of potential different kind of inter molecular potential.

And put the different form of intermolecular potential in the expression for Tc's and people have calculated numerically or analytically the values of BT, so, then they are plotted with respect to temperature. So, they reduced second virial coefficient B star = B by 2 Pi cube by 3 of the gas with the Lenard Jones potential is compared to the experimental values of organ and neon in this figure.

So in this circle represents the organ gas and cross represent the neon gas, so they have plotted with the experimental values of organ and neon it is shown in the above figure with T star is modified reduced temperature with KT by epsilon in this case the Boyle temperature is found to be a TV star = K times Tv which is nothing but the 3.42. So, that means we are trying to; we have been able to understand why there will be a deviation and try to estimate the deviation from the deal gas allocation of state.

So, finally although we have told many times, finally the validity of Vanderwaal's equation of state, so above the critical temperature the Vanderwaal's equation is the improvement of the ideal gas and for lower temperature the equation is also qualitatively reasonable for the liquid state and low pressure gaseous state. However the Vanderwaal's model is not appropriate for rigorous quantitative calculation remaining useful only for teaching and qualitative purposes.

So, as we have already told you that in the first order phase transition state of P, V, T the liquid and gas phases are equilibrium so as you know that the first order phase transition is defined as where the liquid and the gas phase which are in equilibrium. So, it does not exhibit the empirical fact that each constant function for a given temperature.

Although this behavior can be easily inserted into the Vanderwaal's model the result is which is nothing but a Maxwell's correction result is no longer a simple analytical model and others such as those based on the principle of corresponding states as if a better state with roughly with same work ok, thank you.