Chemical Principles II

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Module 3

Lecture 17

Joule-Thomson Effect (For Van der Waals gas)

Calculate the Joule's coefficient and Joules Thomson coefficient for Vander Waals gas. We have done that for Joule coefficient for Vander Waal's gas now let us do for Joule Thomson coefficient.

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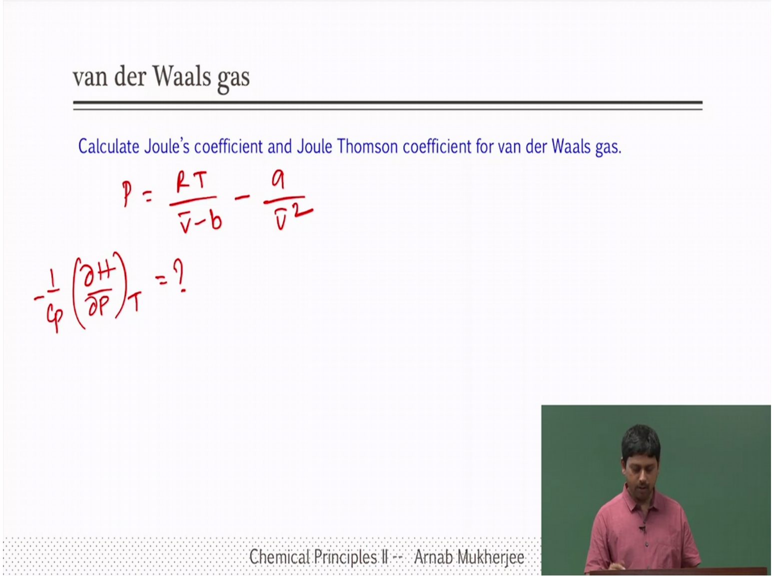

van der Waals gas

Calculate Joule's coefficient and Joule Thomson coefficient for van der Waals gas.

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$$-\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T = ?$$

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So again P equal to R T by V – b – a by V square, this is our starting point and we need to calculate del H by del P at a constant temperature. In fact, if I have to calculate the Joule Thomson coefficient, I have to divide by -1 by C p. So that means we have to redo the whole thing back again right, so and I do not have the marking with me right now but we are going to I have to do that quickly so I will just do that once more, so we have to calculate del H by del P at a constant temperature, this is what we are going to calculate right.

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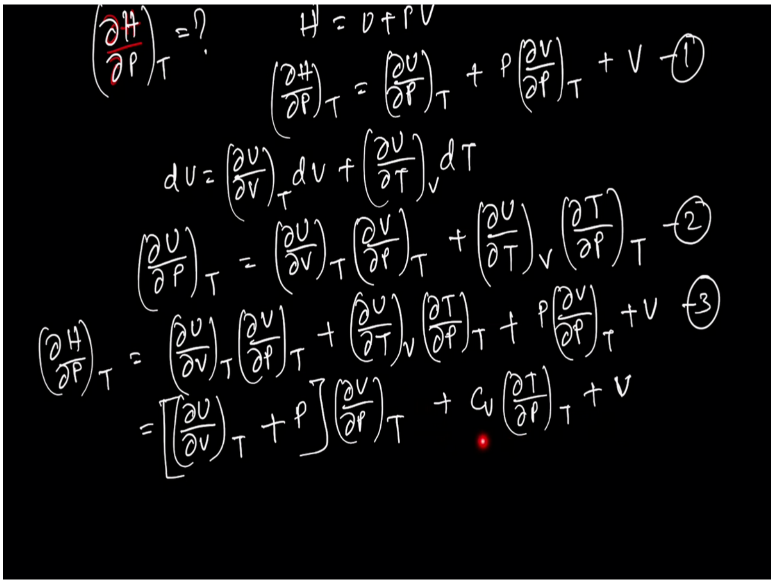

$$\left(\frac{\partial H}{\partial P}\right)_T = ? \qquad H = U + PV$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V \quad ①$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_T \quad ②$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V \quad ③$$

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + C_v\left(\frac{\partial T}{\partial P}\right)_T + V$$

So I am going to do it little bit faster now, so am I doing it correctly till now? So I have got equation number 1 in which I have this and then I have equation number 2 which I have to put in a question number 1 so without doing any this thing I will just put that. So del U by del V T del V by del P T + del U by del T V del T by del P T that is just this one + P del V by del P T + V. Can I take anything common? Del V by del P I can take common so del U by del V T and del V by del P I can take common so + P + C v, is it going in the right direction. So let me see whether we are doing it rightly or not so U + P V so del U by del P T + P del V + del P T + V this is correct and now we are coming here and then we write this, del U by del V, del V by del P, del P by del P T correct.

Now when I write that, del U by del V T, and del V by del P T that is correct, that is correct, okay. So now del V by del P I have taken common that is also fine and del U by del V P T + P that is fine, V I have and del U by del T V C v, I think it is fine okay. Now we have to evaluate this, it just looks big but you see in the derivation there was no ambiguity that is the most important thing, you can make it bigger or whatever but there should not be any ambiguity. Now as I said that in order to write del U by del V we used that trick right that trick we have to use again, let me erase this part very carefully, only thing is that we do not want to remember anything we want to do it from scratch, so this is our final expression so I can just remove this line also.

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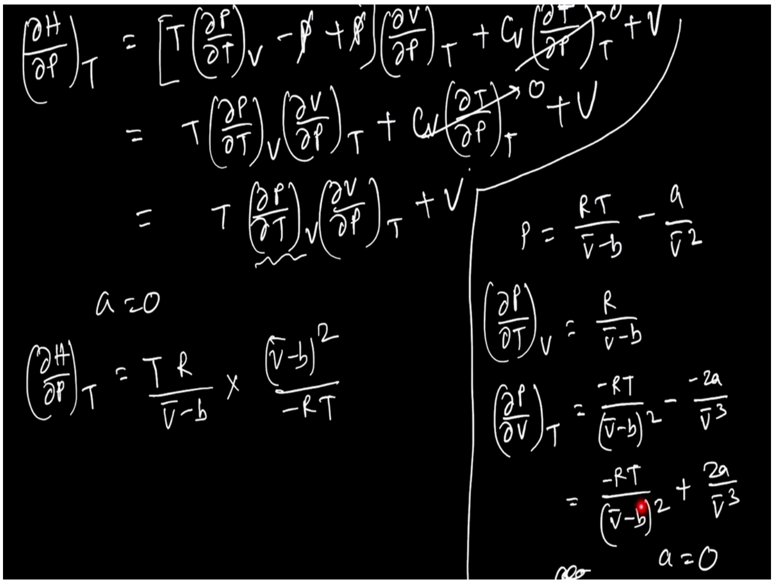

Now, del U by del V T can be written as T del P by del T V - P, which we will learn later. Now this equation 1, now I am denoting that equation 1 and equation 2 so I am going to put equation 2 in equation 1 and derive it again. Del H by del P, I am going to put equation 2 in equation 1 so I am going to write T del P del T V - P here so + I am replacing the whole thing here into this + del V del T P + C v del T del P T + V, now one P cancels P that is a good thing. Now giving us T del P Del T V del V del P T + C v del T del P oh so why I was writing all that all along, this quantity is 0 + V you see that was just writing for because I did not notice that it was at a constant temperature you understand?

So now I have this thing so now I am going to delete this portion now, now I am more or less handle on the situation. Now it is giving me this quantity, T del P del T V del V del P T + V, now nice looking small expression. Now we are going to go back and derive this quantity for ideal gas for Vander Waal gas equation and we know how to do that now. P equal to R T by v – b – a by v square so I am going to take derivative with respect to P now at a constant volume, which means I am to get R by v - b, this quantity. Now del V del P, del V del P will not going to be so easy yeah so if I want to do del V del P how do I write it? We have to take the derivative of V with respect to P we can take P with V and then invert it ok.

So you can say del P del V at a constant T is - R T by V - b square - -2 a by V cube, am I correct? Which is giving me - RT by V - b square + 2a by V cube, if you see this del P del V we need just the opposite of that so an inverse of that right. In that case of course we can invert that and we can put it and get the expression, but let us take a simple situation in which a is going to be 0. What does it mean, that particles to not have any interaction among them, all that it has is it has a finite size that means it cannot really go and bump into each other so we are taking a limiting case of a is 0 and b has a finite volume.

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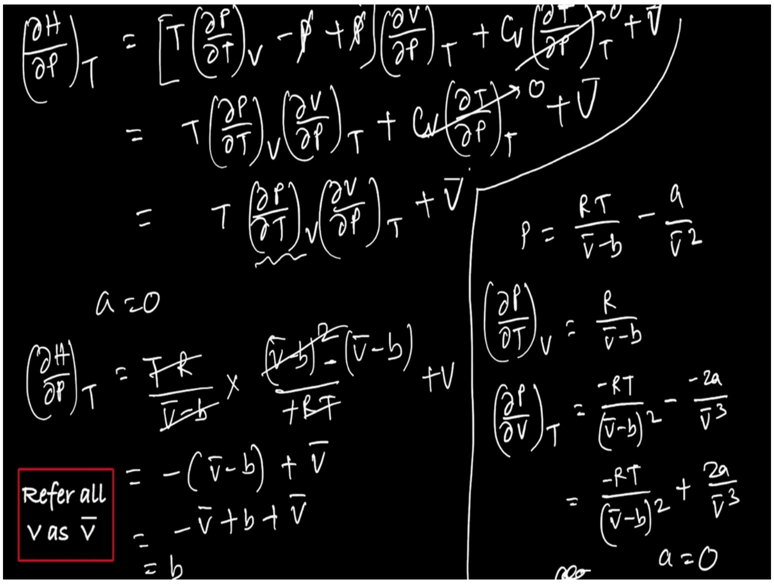

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_V \cancel{-P} \cancel{+P}\right]\left(\frac{\partial V}{\partial P}\right)_T + C_V \cancel{\left(\frac{\partial T}{\partial P}\right)_T}^{0} + \bar{V}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T + \cancel{C_V\left(\frac{\partial T}{\partial P}\right)_T} \rightarrow 0 + \bar{V}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T + \bar{V}$$

$a = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\cancel{T}R}{\cancel{\bar{V}-b}} \times \frac{\cancel{(\bar{V}-b)^2} - (\bar{V}-b)}{+\cancel{RT}} + V$$

$$= -(\bar{V}-b) + \bar{V}$$

$$= -\bar{V} + b + \bar{V}$$

$$= b$$

Refer all V as $\bar{V}$

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-b}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(\bar{V}-b)^2} - \frac{-2a}{\bar{V}^3}$$

$$= \frac{-RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3}$$

$a = 0$

Remember if b is also 0 we are going to go to the ideal gas okay, but if b is nonzero then it is not fully ideal gas although the interaction is 0 when it is not. Actually in that case the potential is up to b it is 0 and at b it is infinity ok. So now if you do that our life becomes simpler and we can get this quantity, so let us write that for a equal to 0 case del H by del P T is T into R by V - b multiplied by V - b square by - R T. You see what I did, I just took invert of that I took a equal to 0 which gave me only this quantity and since it is del P del V T, I just inverted it, did you get did you follow this particular part?

Now what I am going to do is that my RT RT cancels each other, v - b, v - b cancels each other and but there is a negative sign so and + V, so what I am going to get so this V is basically molar volume always everywhere so - v – b + v which is - V + b + v giving you b. So in case a is 0, see if a is nonzero then you should do this particular part, what you are going to do is that you know you have to simply do this particular algebra this part and then invert it and put there and you will get an expression.

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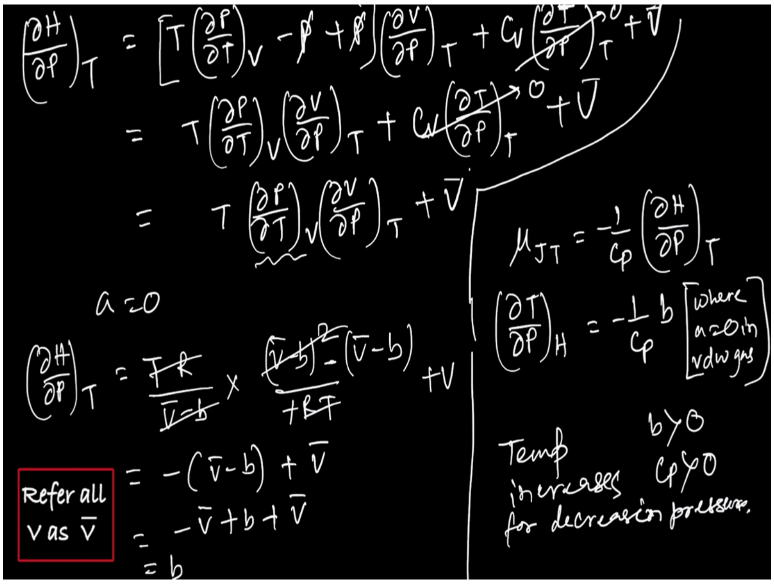

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_V - \cancel{P} + \cancel{P}\right]\left(\frac{\partial V}{\partial P}\right)_T + C_V \cancel{\left(\frac{\partial T}{\partial P}\right)_T} \to 0 + \bar{V}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + \cancel{C_V \left(\frac{\partial T}{\partial P}\right)_T} \to 0 + \bar{V}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + \bar{V}$$

$a = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\cancel{T}R}{\cancel{\bar{V}-b}} \times \frac{\cancel{(\bar{V}-b)^2}\,(\bar{V}-b)}{-\cancel{RT}} + V$$

$$= -(\bar{V}-b) + \bar{V}$$

$$= -\bar{V} + b + \bar{V}$$

$$= b$$

Refer all V as $\bar{V}$

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\, b \quad \left[\text{where } a = 0 \text{ in vdw gas}\right]$$

$b > 0$

$C_P > 0$

Temp increases for decrease in pressure.

The interesting thing that we are going to show you here is that that the joules Thomson coefficient Mu JT is 1 by C P del H by del P T right, what is joules Thomson coefficient we know, del T by del P at a constant H that was joules Thomson coefficient right, -1 by C P into b where, in the Vander Waal gas case where a equal to 0, in vdw gas. Now b is a positive quantity, C P is a positive quantity, what does it mean? When the pressure increases temperature decreases, when the pressure decreases temperature increases, so instead of becoming cooler it gets hotter. So therefore joules Thomson coefficient is not always giving you so in this particular case joules Thomson coefficient is a negative quantity so joules Thomson coefficient is not always you know going to you decrease that is what the interesting point about this particular thing that here temperature increases for decrease in pressure in this particular case ok.

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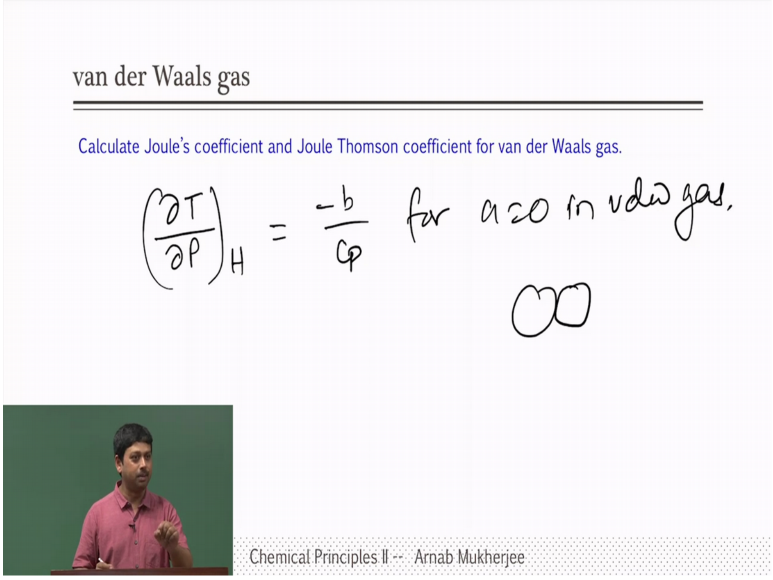

van der Waals gas

Calculate Joule's coefficient and Joule Thomson coefficient for van der Waals gas.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-b}{C_p} \text{ for } a=0 \text{ in vdw gas.}$$

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So we have calculated that so I am going to just delete this part and I do not have, okay I have the expression so I will just write it down. So del T by del P at a constant H is going to be - b by C P for a equal to 0 in vdw gas. Now why is that the case? Because here the b parameter prevents the particles from going into each other, it is a repulsive type of interaction okay. So it turns out that wherever there is repulsive type of interaction you are going to get a negative joules Thomson value such that it will get heated up rather than getting cool down, but if you had an attractive term for example, if you had that a term you will see that it will actually cool down.

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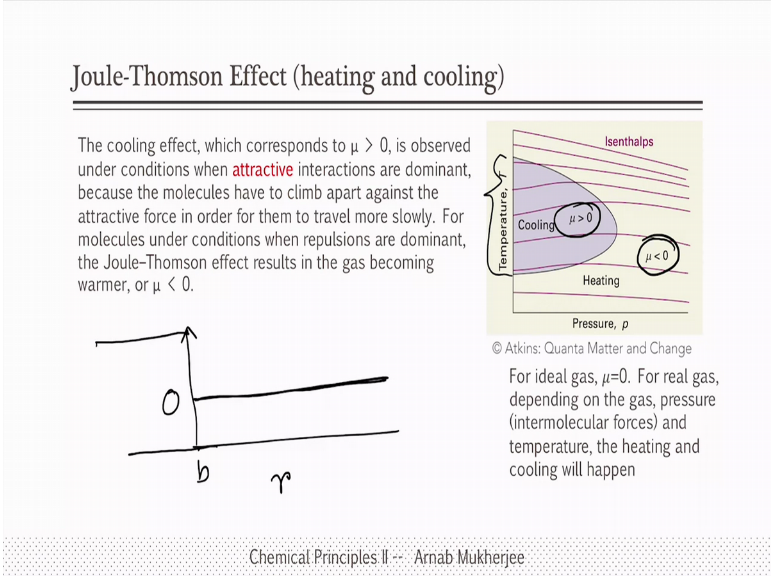

Joule-Thomson Effect (heating and cooling)

The cooling effect, which corresponds to μ > 0, is observed under conditions when attractive interactions are dominant, because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant, the Joule–Thomson effect results in the gas becoming warmer, or μ < 0.

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For ideal gas, μ=0. For real gas, depending on the gas, pressure (intermolecular forces) and temperature, the heating and cooling will happen

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And it is given by this kind of diagram in which you can see that that wherever there is Mu less than 0, you are having heating instead of cooling and wherever there is Mu greater than 0 there is a cooling. So for a real gas system a is not 0 for a real gas, real gas does have interaction. So in real gas situation you are going to get a cooling effect, typically it is used for cooling but that cooling is limited to a given range of temperature and a given rate of pressure. If you are in this region in this particular shaded region then there will be a cooling effect, however if you are in this particular region there will be heating effect.

So the cooling effect which corresponds to Mu greater than 0 is observed under the condition when attractive interactions are dominant because the molecules have to climb apart against the attractive force, as I told you the situation for joules coefficient also. For molecules under condition when repulsion are dominant, joules Thomson effect results in gas becoming more warmer or Mu less than 0, and we have shown you one example how the Mu becomes negative when attractive interactions are not there and you have only b.

Having b means as I told you having b means your potential is 0 everywhere except so this is a distance okay, your potential is 0 till everywhere except below b where it is infinity, it is called Harts fear potential, it cannot get b or below the value that is the volume occupied by the particle so it is a repulsive interaction. So I have just shown you that anything below this value and at the value b it will be infinity okay, so and we see that that is the repulsive potential at the value of b and that is that is giving us heating.