Material and Energy Balances
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Lecture - 46
Estimating Latent Heat

Welcome to today's lecture on Estimating Latent Heat. In the last lecture we talked about the different aspects and fundamentals related to phase change process. During that time, we looked at some of the latent heat or heat of vaporization and heat of fusion and so on. We used values which were directly obtained from the tables. However, in some cases such data might not be readily available what do we do then.

We need to estimate these latent heat using different correlations and in today's lecture we will actually talk about what correlations can be used and how to apply them and what values you would be getting that.

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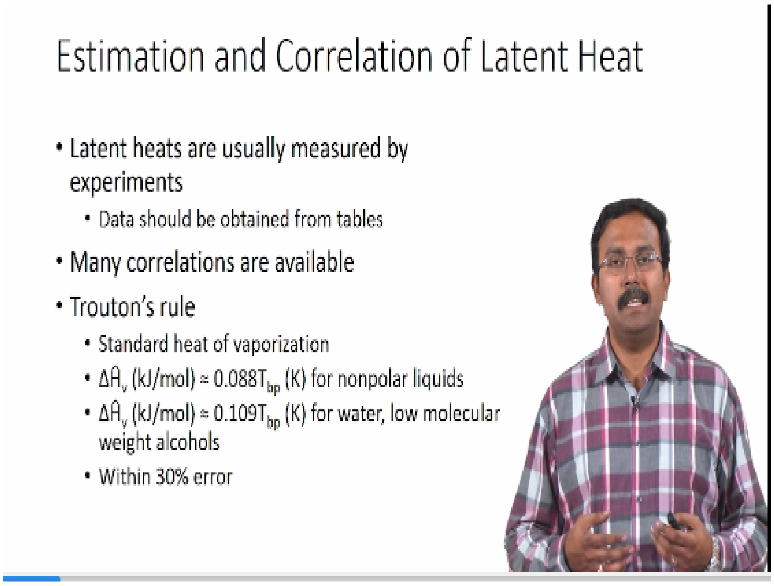

Estimation and Correlation of Latent Heat

- Latent heats are usually measured by experiments
  - Data should be obtained from tables
- Many correlations are available
- Trouton's rule
  - Standard heat of vaporization
  - $\Delta \hat{H}_v$ (kJ/mol) ≈ $0.088T_{bp}$ (K) for nonpolar liquids
  - $\Delta \hat{H}_v$ (kJ/mol) ≈ $0.109T_{bp}$ (K) for water, low molecular weight alcohols
  - Within 30% error

So latent heat is usually measured by experiments. The data usually is obtained from tables. However, as I said in many cases such value is not readily available. When data is not readily available in tables you would have to use many correlations that are available. So you will look at some of the correlations which can be commonly applied. So the first and the simplest correlation that can be used is the Trouton's rule.

This is used for estimating the standard heat of vaporization. Heat of vaporization for non polar liquids can be given as 0.88 times boiling points and for water and lower molecular weight alcohol it can be calculated as 0.109 times boiling point. Here the temperature for the boiling point has to be used in Kelvin and this will give you the heat of vaporization within about 30% error.

So this is not the most accurate method however it is this simplest thing to use.

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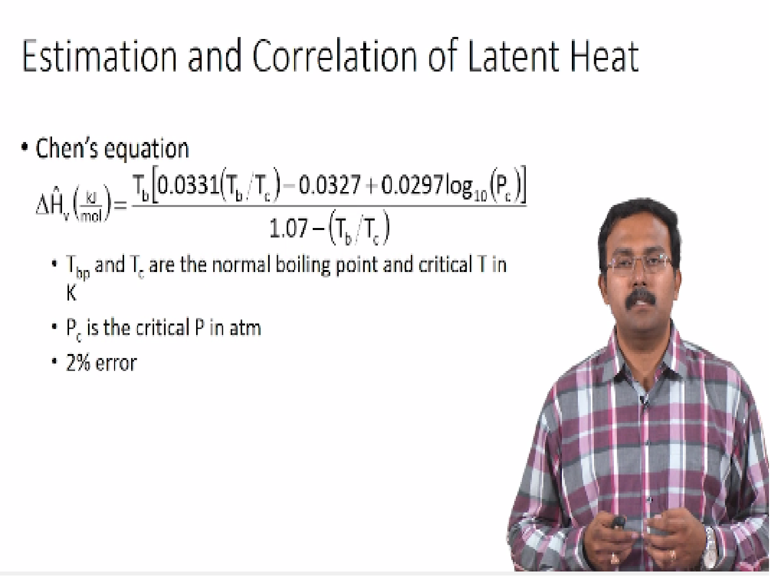

Estimation and Correlation of Latent Heat

- Chen's equation

$$\Delta\hat{H}_v\left(\frac{kJ}{mol}\right)=\frac{T_b\left[0.0331\left(T_b/T_c\right)-0.0327+0.0297\log_{10}\left(P_c\right)\right]}{1.07-\left(T_b/T_c\right)}$$

  - T_{bp} and T_c are the normal boiling point and critical T in K
  - P_c is the critical P in atm
  - 2% error

If you are looking for calculating the heat of vaporization to more accurate level, then you should use the Chen's equation. As you see the Chen's equation is a lot more cumbersome. It uses the boiling point and critical temperature in Kelvin and critical pressure in atmosphere Tc is the critical temperature Pc is the critical pressure and Tb is the boiling point. This gives the value for heat of vaporization in a more accurate fashion.

There is only about 2% error when Chen's equation is used. So this is a good correlation to use however you need information not just about the boiling point, but also about the critical temperature and critical pressure for the liquid you are looking at.

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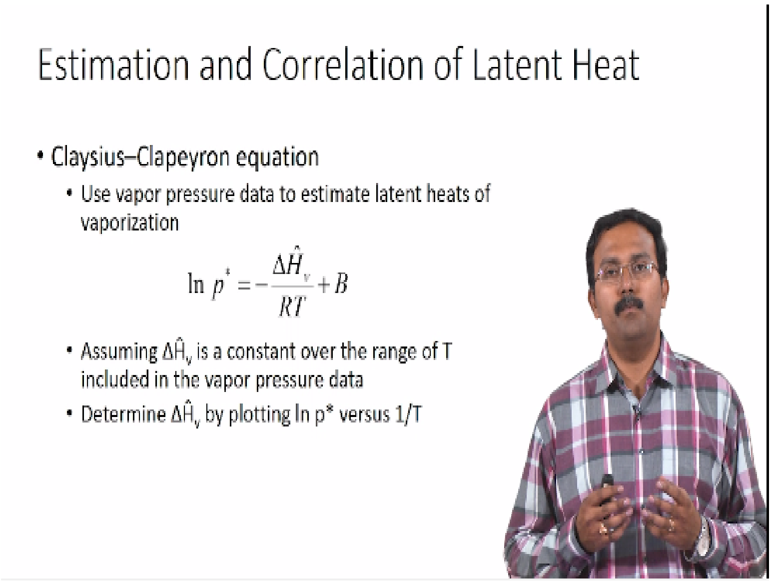

Estimation and Correlation of Latent Heat

- Claysius–Clapeyron equation
  - Use vapor pressure data to estimate latent heats of vaporization

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

  - Assuming $\Delta\hat{H}_v$ is a constant over the range of T included in the vapor pressure data
  - Determine $\Delta\hat{H}_v$ by plotting ln p* versus 1/T

Claysius-Clapeyron Equation is another equation which can be used to measure the estimate the heat of vaporization. So this uses the vapor pressure data to estimate the latent heat of vaporization lawn of p *= -delta H v/ RT+ B. Assuming delta H cap v is a constant over a range of temperature including in the vapor pressure data given you can estimate the data H cap value by plotting lawn p* versus 1/T.

So this would give you delta H cap v/RT as the slope. So from there you can calculate delta H cap v which is the heat of vaporization.

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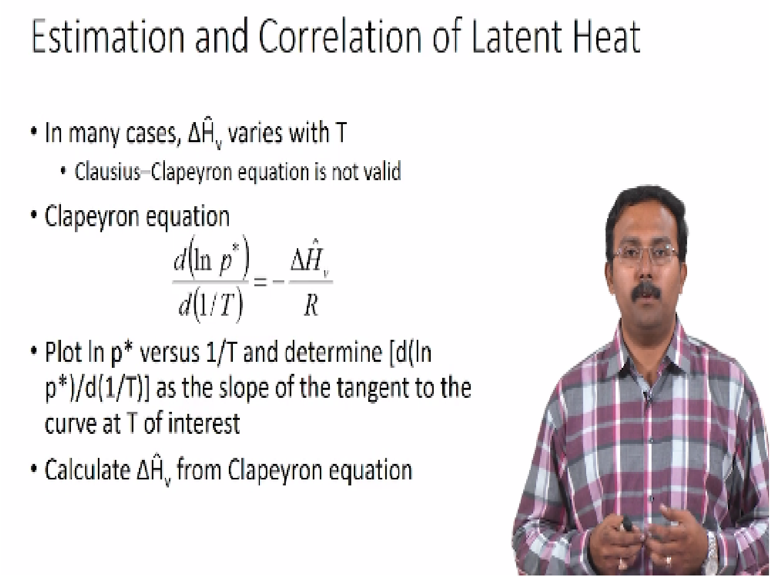

Estimation and Correlation of Latent Heat

- In many cases, $\Delta\hat{H}_v$ varies with T
  - Clausius–Clapeyron equation is not valid
- Clapeyron equation

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta \hat{H}_v}{R}$$

- Plot ln p* versus 1/T and determine [d(ln p*)/d(1/T)] as the slope of the tangent to the curve at T of interest
- Calculate $\Delta\hat{H}_v$ from Clapeyron equation

In many cases heat of vaporization is not a constant for range of temperature it varies with temperature. So in such scenarios the Claysius-Clapeyron equation which we just saw is not directly valid. So instead you can use something called as the Clapeyron equation which is the differential form of the Clasius-Claypeyron equation. So d of lawn p * by d of 1/T equals –delta H cap v/r. So you are expected to plot lawn p* versus 1/T.

And you would be determining d lawn p*/ d 1/T as the slope of the tangent to the slope at the temperature of interest. So as the slope changes the delta H cap v will would change indicating the change in heat of vaporization as a function of temperature. So this delta H cap v can be calculated using the Clapeyron equation by plotting this curve and finding the slope of the tangent.

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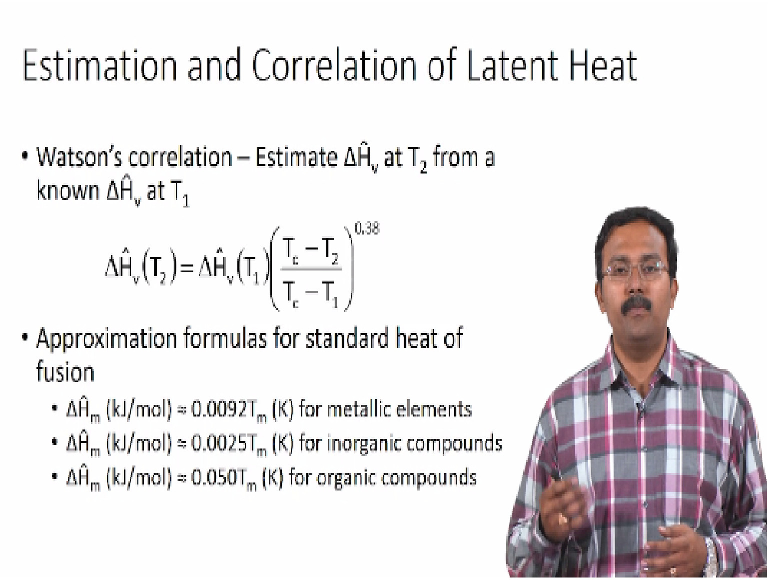

Estimation and Correlation of Latent Heat

- Watson's correlation – Estimate $\Delta\hat{H}_v$ at T_2 from a known $\Delta\hat{H}_v$ at T_1

$$\Delta\hat{H}_v(T_2)=\Delta\hat{H}_v(T_1)\left(\frac{T_c-T_2}{T_c-T_1}\right)^{0.38}$$

- Approximation formulas for standard heat of fusion
  - $\Delta\hat{H}_m$ (kJ/mol) ≈ $0.0092T_m$ (K) for metallic elements
  - $\Delta\hat{H}_m$ (kJ/mol) ≈ $0.0025T_m$ (K) for inorganic compounds
  - $\Delta\hat{H}_m$ (kJ/mol) ≈ $0.050T_m$ (K) for organic compounds

Watson's Correlation is another correlation that is used for estimating the heat of vaporization at a temperature different from the temperature for which you already have the heat of vaporization. If you have the heat of vaporization at temperature T1 you can calculate the heat of vaporization at a different temperature using the Watson's correlation which is given here.

Again you would need to know the critical temperature which is for the component involved. So you can also have approximate formulas for estimating standard heat of fusion. So you have standard heat of fusion for metallic elements as 0.0092 times melting point and for inorganic compounds as 0.0025 times melting point and for organic compounds as 0.050 times melting point. So all the melting point used should be in terms of Kelvin.

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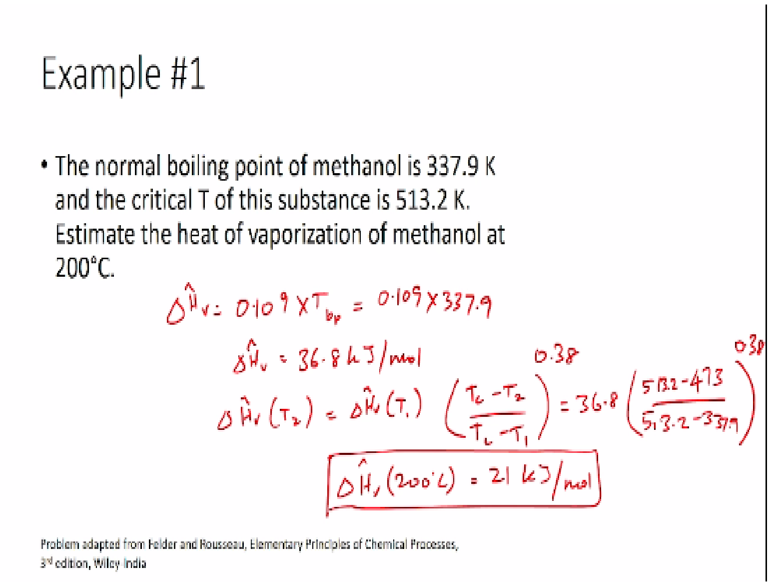

Example #1

- The normal boiling point of methanol is 337.9 K and the critical T of this substance is 513.2 K. Estimate the heat of vaporization of methanol at 200°C.

$$\Delta \hat{H}_v = 0.109 \times T_{bp} = 0.109 \times 337.9$$

$$\Delta \hat{H}_v = 36.8 \text{ kJ/mol}$$

$$\Delta \hat{H}_v(T_2) = \Delta \hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38} = 36.8\left(\frac{513.2 - 473}{513.2 - 337.9}\right)^{0.38}$$

$$\boxed{\Delta \hat{H}_v(200^\circ C) = 21 \text{ kJ/mol}}$$

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley India

So here are a couple of example problems where we will try and apply these equations to calculate the heat of vaporization or the heat of melting. The first example is the normal boiling point of methanol is 337.9 Kelvin and the critical temperature for this substance is 513.2 Kelvin. Estimate the heat of vaporization of methanol at 200 degree Celsius. Now what we have is the boiling point in the critical temperature only.

And we have been asked to calculate a heat of vaporization at some temperature which is 200 degree Celsius. So this means we first need to identify and quantify the standard heat of vaporization for methanol which would be at its regular boiling point which is the boiling point has been identified as 337.9 Kelvin. So this can be obtained either using Trouton's rule or Chen's equation.

For Chen's equation we need critical temperature and critical pressure. However critical pressure has not been given to us in this problem. So using Trouton's rule would be the simplest thing to do to get the heat of vaporization although it is not the most accurate way to get the value. If we have the critical pressure value, we could have used Chen's equation to get a more accurate value for heat of vaporization.

Let us now perform the calculation for heat of vaporization using the Trouton's rule. So Trouton's rule had multiple equations. We had one equation for so if you see these equations for Trouton's rule you have 2 different equations. One for non polar liquid and the other for water and low molecular weight alcohols. So here in this example we have to measure the heat of vaporization for methanol which is a low molecular weight alcohol.

So we would use the second equation which is delta H cap v = 0.109 times boiling times. So here the boiling point is 337.9 so it is 0.109 times 337.9 giving us delta H cap v as 36.8 kilo joules per mol. So now we have the heat of vaporization at its normal boiling point. However, we have been asked to calculate the heat of vaporization of methanol at 200 degree Celsius.

For doing this we would have to use the Watson's correlation. So Watson's correlation was delta H cap v at temperature T2 would be= delta H cap v at temperature T1 times critical temperature- temperature of interest/ critical temperature- temperature at which the heat of vaporization is known to the power of 0.38. So this would be 36.8 times 513.2-473 / 513.2-337.9 to the power of 0.38.

So using this we would be able to calculate the heat of vaporization for methanol at 200 degree Celsius as 21 kilo joules per mol. So performing the calculation themselves is not too difficult here. What is crucial is to identify which equations to use and use them appropriately.

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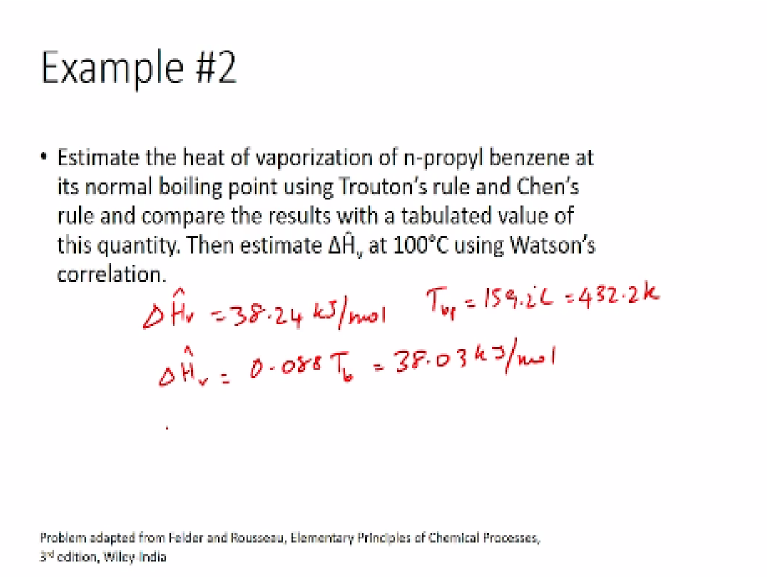

Example #2

- Estimate the heat of vaporization of n-propyl benzene at its normal boiling point using Trouton's rule and Chen's rule and compare the results with a tabulated value of this quantity. Then estimate $\Delta\hat{H}_v$ at 100°C using Watson's correlation.

$\Delta\hat{H}_v = 38.24$ kJ/mol $T_{bp} = 159.2C = 432.2k$

$\Delta\hat{H}_v = 0.088\, T_b = 38.03$ kJ/mol

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley India

We will look at another example problem to illustrate how to use the appropriate equations. We are again asking to estimate the heat of vaporization for n-propyl benzene at its normal boiling rule using Trouton's rule and Chen's rule and you are asked to compare the results with tabulated value for this quantity. You are then asked to estimate the heat of vaporization at 100 degree Celsius using Watson's correlation.

No information has been provided to us. So we would have to use some handbooks or textbooks to get the values to get the values for critical temperature, critical pressure and boiling point for n-propyl benzene so that we can use Trouton's rule and Chen's rule. So the tabulated value for heat of vaporization should also be looked at so that we can look at how the errors are for these equations are.

Looking up the table we can get the standard heat of vaporization for n propyl benzene as 38.24 kilo joules per mol. So Trouton's rule can be used so here it would be 0.088 times boiling point. The boiling point for n propyl benzene can also be looked up the table and the value is 159.2 degree Celsius which is= 432.2 Kelvin. So using this value we can get heat of vaporization from Trouton's rule as 38.03 kilo joules per mol.

So for this particular case Trouton's rule seems to fit very well you get very small errors and this is as good as it gets. It is actually < 1% error. So even Chen's rules might not have this accurate data. So the Chen's rule can be used for calculating the heat of vaporization using the boiling point, critical temperature and critical pressure.

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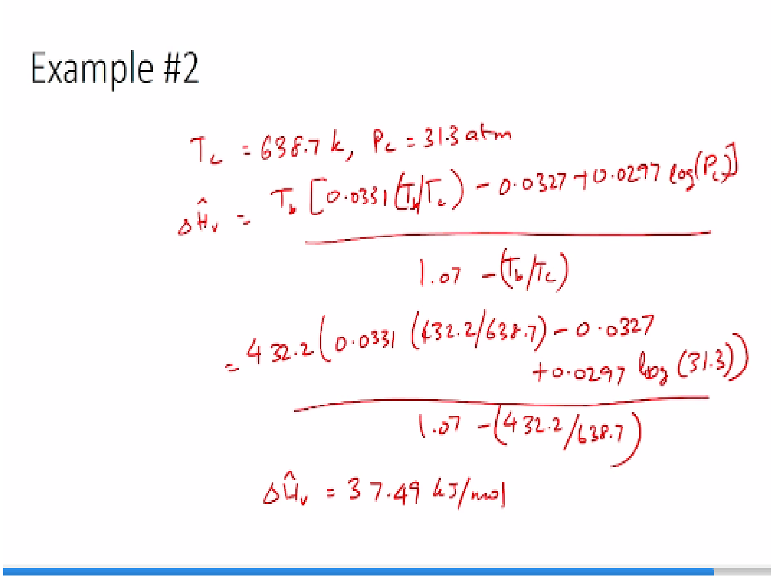

Example #2

$T_c = 638.7\,k,\ P_c = 31.3\,atm$

$$\Delta\hat{H}_v = \frac{T_b\left[0.0331\left(T_b/T_c\right) - 0.0327 + 0.0297\log(P_c)\right]}{1.07 - \left(T_b/T_c\right)}$$

$$= \frac{432.2\left(0.0331\left(432.2/638.7\right) - 0.0327 + 0.0297\log(31.3)\right)}{1.07 - \left(432.2/638.7\right)}$$

$\Delta\hat{U}_v = 37.49\ kJ/mol$

So the critical temperature for n propyl benzene is 638.7 Kelvin and critical pressure is 31.3 atmosphere. So we would have to use these values in the Chen's equation which is delta H cap v= temperature of boiling point times 0.0331 times boiling point/critical temperature-0.327+ 0.0297 log of critical pressure/1.07-temperature of boiling point/critical temperature. So substituting the values we would get 432.2 times 0.331 times 432.2/638.7-0.327+ 0.297 times log of 31.3 which is the critical pressure/1.07-432.2/638.7.

So solving this equation you would get delta H cap v as 37.49 kilo joules per mol. So for this particular case we find that Trouton's rule is more accurate than Chen's equation. Chen's equation here gives still less than 2% error. So what we need to realize is although Trouton's rule is perfectly fitting for this particular scenario it can give up to 30% error. However, Chen's equation will consistently give less than 2% error.

So using Chen's equation can potential give you a higher accuracy compared to Trouton's rule in more frequent analysis. So the next step is to calculate the heat of vaporization at 100 degree Celsius. So for this we would have to use the Watson's correlation.

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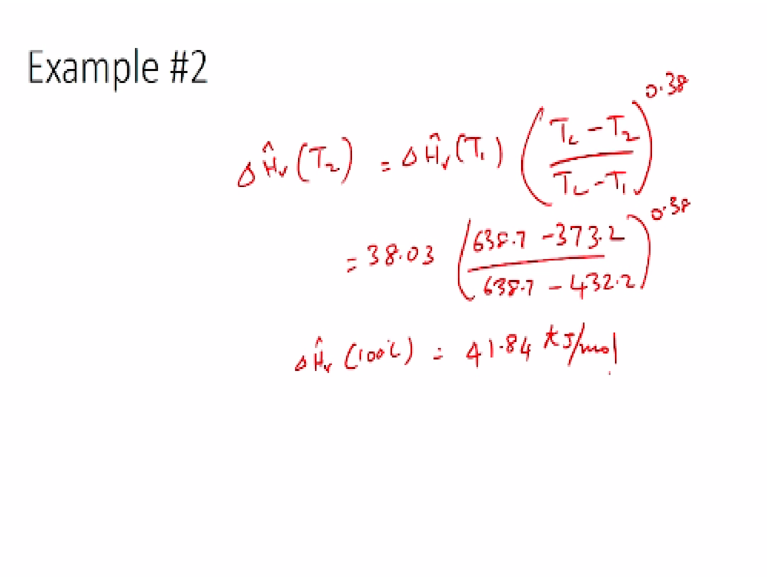

Example #2

$$\Delta \hat{H}_v(T_2) = \Delta \hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$

$$= 38.03\left(\frac{638.7 - 373.2}{638.7 - 432.2}\right)^{0.38}$$

$$\Delta \hat{H}_v(100^\circ C) = 41.84\ kJ/mol$$

So the Watson's correlation is delta H cap v at temperature T2= delta H cap v at temperature T1 times critical temperature-T2/critical temperature-T1 to the power of 0.38 substituting the values we have. We will use the more accurate value in this case which is Trouton's equation and which is 38.03 times 638.7-373.2/638.7-432.2 power 0.38. So this gives delta H cap v at 100 degree Celsius as 41.84 kilo joules per mol.

So with this we have used the different equations so again the example problem only looked at heat of vaporization. You can also do similar things with heat of fusion. So I hope you would be able to practice more problems and get yourself familiarized with these concepts. So in this case you need to estimate these heat of vaporization instead of looking up you would be able to use these correlations and actually get reasonably accurate value.

With that I would like to thank you and we will see you in the next class.