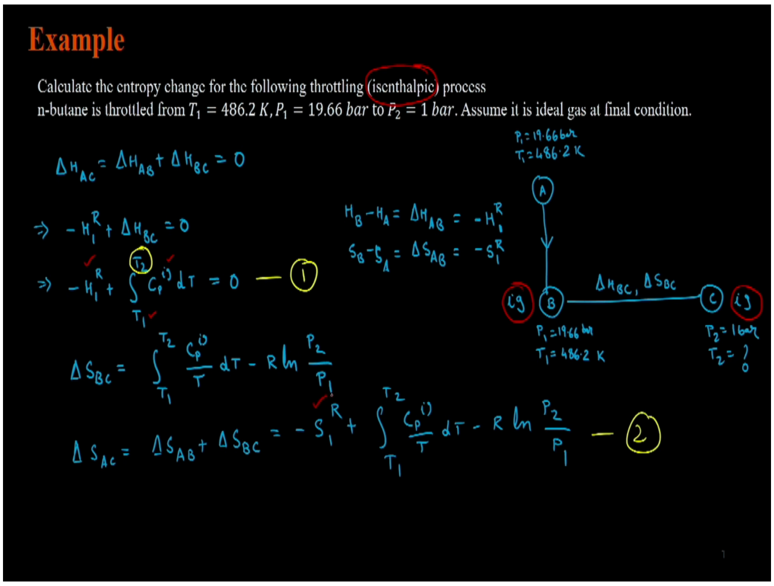
# Chemical Engineering Thermodynamics
Dr. Sasidhar Gumma
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

## Lecture – 19
## Process Involving Phase Changes

(Refer Slide Time: 00:27)



**Example**

Calculate the entropy change for the following throttling (isenthalpic) process
n-butane is throttled from $T_1 = 486.2\ K, P_1 = 19.66\ bar$ to $P_2 = 1\ bar$. Assume it is ideal gas at final condition.

$$\Delta H_{AC} = \Delta H_{AB} + \Delta H_{BC} = 0$$

$$\Rightarrow -H_1^R + \Delta H_{BC} = 0$$

$$\Rightarrow -H_1^R + \int_{T_1}^{\boxed{T_2}} C_p^{ig}\, dT = 0 \quad — ①$$

$$H_B - H_A = \Delta H_{AB} = -H_1^R$$

$$S_B - S_A = \Delta S_{AB} = -S_1^R$$

$$\Delta S_{BC} = \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT - R \ln \frac{P_2}{P_1}$$

$$\Delta S_{AC} = \Delta S_{AB} + \Delta S_{BC} = -S_1^R + \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT - R \ln \frac{P_2}{P_1} \quad — ②$$

Let us look at another example. In this example we want to find the change in entropy, when a gas is throttled from a high pressure P 1 about 19.66 bar to a low pressure atmospheric pressure at about 1 bar. The initial temperature of this gas is 486.2 Kelvin and the gas happens to be n butane. So, we have n butane at some temperature and a high pressure, which is being throttled to a lower pressure.

And throttling processes are usually isenthalpic meaning that there is no change in enthalpy for the process and what we are interested in calculating is entropy change for such a process alright let us see how we can solve this problem. So, for this particular process let me see if I can sketch a schematic of these steps we can use, to calculate the changes in enthalpy and entropy.

So, initially I am at a temperature of T 1 and P 1. So, let us call this as A and my final condition is P 2 equal to 1 bar I do not know the temperature, but what I do know that is that it is an ideal gas all right. We are going to break this into a series of steps right going from step A to B, we start with the initial condition and take you to an ideal gas at the same condition and from B to C we are going to go from ideal gas at the initial condition to the ideal gas at the final condition. And over each one of these steps along each one of these steps we should be able to easily calculate the enthalpy and entropy changes which is what we are interested in for this particular example. So, if you recall from going from A to B the change is what we call as H R or the residual enthalpy right. In fact, it is negative of residual enthalpy because the direction is going from A to B.

So, this is negative of residual enthalpy at 1 similarly negative entropy at 1. So, delta H going from A to B is negative H 1 R delta s A to B is negative S 1 R right. This is because delta H A to B is H B minus H A that is the ideal gas value minus the real gas value which is by definition negative of the residual thermodynamics property.

So, if I can calculate the residual thermodynamic property at the initial condition then I know what a has 1 rr and hence the change along the path A to B. And from B to C it is pretty straightforward because all I am interested in is just the change for an ideal gas going from B to C and for an ideal gas if you recall it is pretty easy to calculate enthalpy and entropy changes given the specific heat capacity.

So, let us call this as delta H B C and delta S B C. However, if I have to calculate delta H B C what I need are the initial and the final temperatures and the initial temperature we know it is 486.2 at B, but I do not know the final temperature T 2 is unknown what I do know is that the final pressure is 1 bar, but then for an ideal gas pressure does not affect the enthalpy. So, I still have to figure a way out to calculate the final temperature and to be able to do that what we will do is, use the information given to us about the process.

So, let us highlight a few key things here right this is an ideal gas like condition, this is an ideal gas like condition and we are also given that the whole process itself is isentropic what; that means, is that delta H from A to C which is delta H from A to B plus delta H from B to C equals 0 that is because the process is isentropic right. So, what this means then is negative of H 1 R plus delta H B to C is 0 and the other H B to C is the enthalpy change for an ideal gas.

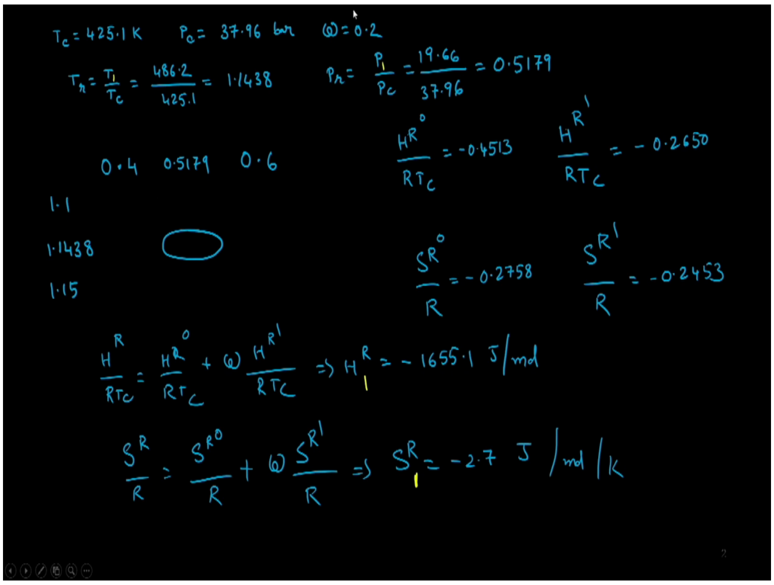
So, that is in terms of the specific heat capacities it is T 1 to T 2 C p i g d T this equals 0. Now in this I can use any convenient method to calculate H 1 R; similarly I know the initial temperature T 1 I know the ideal gas heat capacities from any handbook C p ig.

So, all I do not know in this equation is T 2. So, because I know everything else, I can use this equation to calculate T 2. And once I have T 2 I know the initial and final temperatures and pressures. So, I should be able to calculate the change in entropy for the ideal gas like condition delta S B to C and because I know S 1 R I should be able to calculate the overall entropy change going from a to c let us write that out as well. Delta S B to C is the entropy change for an ideal gas and if you recall for an ideal gas this is given as C p ig by T d T minus R ln P 2 over P 1.

So, delta S A to C is delta s A to B plus delta S B to C which is negative S 1 R plus integral T 1 to T 2 C p ig by T d T minus R ln P 2 over P 1. Now if you look at this equation for delta S A to C I can calculate the residual property at condition 1 using any convenient equation of state or correlations Lee Kesler tables for example, and if I know Cp i g and the final temperature which I will find by solving equation 1 here right if I solve equation 1 I will get T 2 and if I use that T 2 in equation 2 I know the initial and final pressure.

So, everything in equation 2 can be readily calculated or known and so, I should be able to find delta S A to C. So, that is the approach we are going to use to solve this particular problem. So, let us start working with each 1 at a time the first thing is to be able to calculate the residual enthalpy and of course, if you are calculating residual enthalpy let us also attempt to calculate residual entropy S 1 R and H 1 R right

(Refer Slide Time: 08:37)



$T_c = 425.1\ K \quad P_c = 37.96\ bar \quad \omega = 0.2$

$T_r = \frac{T_1}{T_c} = \frac{486.2}{425.1} = 1.1438 \qquad P_r = \frac{P_1}{P_c} = \frac{19.66}{37.96} = 0.5179$

0.4 0.5179 0.6

1.1

1.1438

1.15

$\frac{H^{R^0}}{RT_c} = -0.4513 \qquad \frac{H^{R^1}}{RT_c} = -0.2650$

$\frac{S^{R^0}}{R} = -0.2758 \qquad \frac{S^{R^1}}{R} = -0.2453$

$\frac{H^R}{RT_c} = \frac{H^{R^0}}{RT_c} + \omega \frac{H^{R^1}}{RT_c} \Rightarrow H_1^R = -1655.1\ J/mol$

$\frac{S^R}{R} = \frac{S^{R^0}}{R} + \omega \frac{S^{R^1}}{R} \Rightarrow S_1^R = -2.7\ J/mol/K$

Let us get some numbers from a suitable reference a handbook or the back of your textbook for n butane it turns out that T c is 425.1 Kelvin and pc is a 37.96 bar and the eccentric factor omega is 0.2. At these T c and P c values T r is going to be T over T c and from the given temperature which is 486.2 or T c is 425.1 I get a T r of 1.1438 and similarly P r is P over Pc.

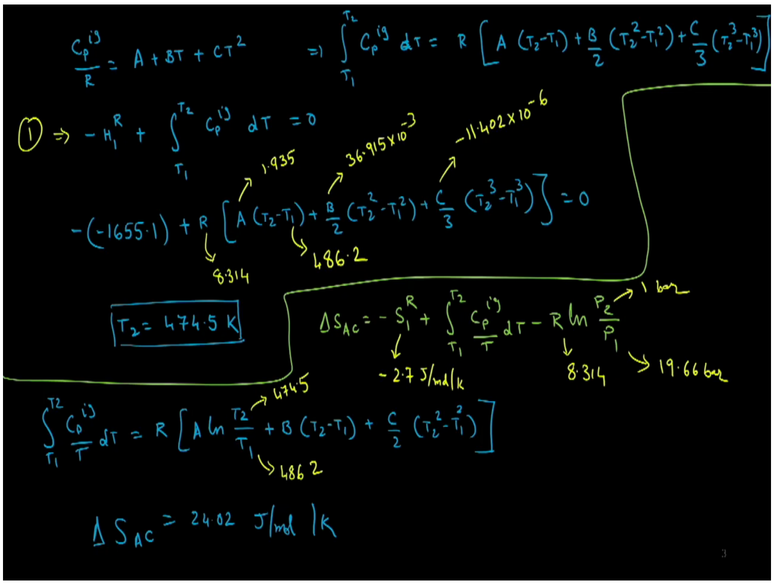
So, that is 19.66 bar over 37.96 bar. So, that is a P r of about 0.5179. At is T r and P r n butane is probably going to be in the vapor phase you can look at any of the correlations I used Lee Kesler tables to find the state of the system it turns out to be in the vapor phase, and if you recall the liquid phase is highlighted differently in the Lee Kesler tables from the vapor phase.

So, you can look at the Lee Kesler tables identify the phase of the system in this case it turns out to be in the vapor phase, and I can use these Lee Kesler tables do a double linear interpolation for P between 0.4 and.6 as well as T between 1.1 and 1.15. And using that double linear interpolation I will get the value of H naught over RT c and H 1 over RT c S naught over R and S 1 over R at the condition of my interest which is T r of 1.1438 and P r of 0.5179.

And at these conditions the numbers I get negative 0.4513 and this is negative 0.2650 and for S this is negative 0.2758 and this is negative 0.2453. Using these I can calculate H R I am sorry these need to be H R naught right naught H naught I should have written it as H R naught and H R 1 SRnaught and S R 1.

So, H R is H R naught plus omega H R 1 over R T c right and from this I get a H R value of negative 1655.1 Joule per mole and similarly S R over R is S R naught over R plus omega times S R 1 over R. So, I get an S R of negative 2.7 Joule per Kelvin. So, these are the H R and S R values at the initial condition right and my initial condition happens to be 1. So, these are H R 1 and S R 1 right because all through I have used the condition 1 in these calculations. So, now, I have H R 1 and S R 1 values. If you look at this equation 1 I know H 1 R what I do not know is the temperature T 2 I want to solve this equation to get the temperature T 2 like we discussedSo, to be able to do that I need a Cp i g value.

(Refer Slide Time: 12:50)



$$\frac{C_p^{ig}}{R} = A + BT + CT^2 \Rightarrow \int_{T_1}^{T_2} C_p^{ig}\, dT = R\left[A(T_2-T_1) + \frac{B}{2}(T_2^2-T_1^2) + \frac{C}{3}(T_2^3-T_1^3)\right]$$

① $\Rightarrow -H_1^R + \int_{T_1}^{T_2} C_p^{ig}\, dT = 0$

$$-(-1655.1) + \underset{8.314}{R}\left[\overset{1.935}{A}(T_2-\underset{486.2}{T_1}) + \frac{\overset{36.915\times10^{-3}}{B}}{2}(T_2^2-T_1^2) + \frac{\overset{-11.402\times10^{-6}}{C}}{3}(T_2^3-T_1^3)\right] = 0$$

$$\boxed{T_2 = 474.5\ K}$$

$$\Delta S_{AC} = -\underset{-2.7\ J/mol/K}{S_1^R} + \int_{T_1}^{T_2} \frac{C_p^{ig}}{T}\, dT - \underset{8.314}{R}\ln\frac{\overset{1\ bar}{P_2}}{\underset{19.66\ bar}{P_1}}$$

$$\int_{T_1}^{T2} \frac{C_p^{ig}}{T}\, dT = R\left[A\ln\frac{\overset{474.5}{T2}}{\underset{486\ 2}{T_1}} + B(T_2-T_1) + \frac{C}{2}(T_2^2-T_1^2)\right]$$

$$\Delta S_{AC} = 24.02\ J/mol/K$$

It turns out for n butane Cp i g is a function of temperature in this form A plus BT plus CT square this is one of the correlations I have found in the textbook for n butane or the ideal gas like heat capacity for n butane the temperature dependency for that. And I am going to use this and if I rewrite equation 1 it reads negative of H 1 R plus integral T 1 to T 2 C p i g d T equals 0. So, what I am interested in is first writing an expression for C p i g d T or integral of that value.

So, from the given relation or temperature dependency C p ig or integral of that T 1 to T 2, d T will be r times A T 2 minus T 1 plus B by 2 T 2 square minus T 1 square plus C by 3 T 2 cube minus T 1 cube all right. So, then equation 1 reads negative 1655.1 that was the value of H 1 R H 1 R was negative 16.51 0.1. So, negative of that will be positive plus integral T 1 which is 486.2 to T 2 C p i g d T well let us write the expression we have; R times A T 2 minus T 1 plus B by 2 T 2 square minus T 1 squared plus C by 3 T 2 cube minus T 1 cube equals 0.

From the handbook the values of A B and C can be readily found for this particular case A happens to B of n butane a happens to be 1.935 B happens to be 36.915 10 power negative 3 and C happens to be negative 11.402 times 10 power negative 6. And remember T 1 was the initial temperature which is 486.2, I can make all these substitutions along with the value for R 8.314 Joules per mole per Kelvin. Now everything in equation 1 is known except T 2.

So, I can solve this equation any suitable software you could easily do it in excel for example, and it turns out the value of T 2 you will get by solving this equation is 474.5 Kelvin. So, when you throttle n butane from high pressure to a lower pressure, the temperature is going to reduce its going to reduce by about 11 to 12 Kelvin right this is my final temperature.

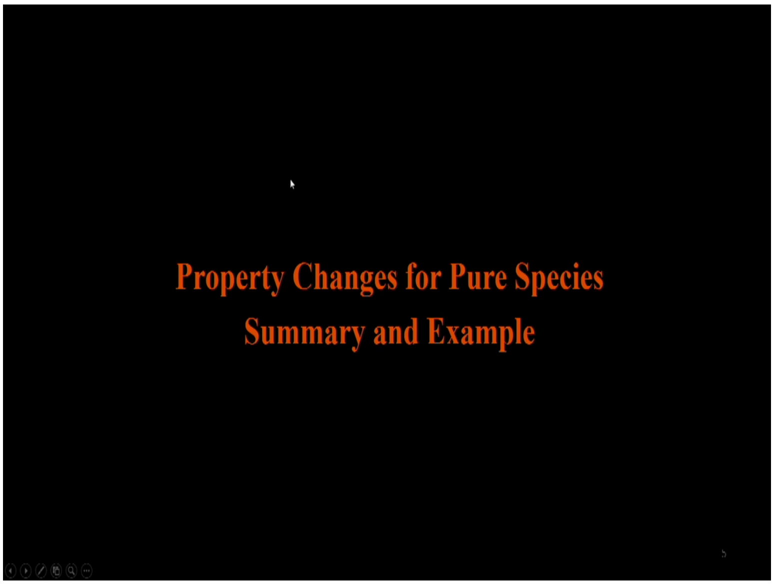
And we got this by noting that the process is isenthalpic. Now once I have the final temperature its pretty straightforward there on to calculate the entropy change delta S AC from equation 2 all you need is the residual enthalpy at initial condition and then solve those 2 integral solve that integral for C p by T d T, but we already know the values or we already have any temperature dependency for C p which I can use in equation 2 just like we did in case of enthalpy and then we should be able to solve this equation. Now I have T 1 T 2 C p i g P 1 P 2 and the initial residual enthalpy.

So, let us do that I am going to use a different color for enthalpy. So, the value or the expression for delta S A to C is negative S 1 R plus integral T 1 to T 2 C p ig by T d T minus R ln P 2 over P 1 this was equation 2. So, I am going to use this equation 2 and the to be able to write everything else in that equation. Let us first see what quantities I know S 1 R was negative 2.7 Joule per mole per Kelvin R of course, is 8.314 P 2 is 1 bar P 1 is 19.66 bar right. We have expression for C p the abc values are all the same as in case of enthalpy calculation all we need to do is integrate that expression. So, let us first do that integration integral of T 1 to T 2 C p ig by T d T is going to be R times this is A over T.

So, A ln T 2 over T 1 plus B times T 2 minus T 1 plus C over 2 times T 2 square minus T 1 square. This is the integral value again the abc values we already know I know T 1 I know T 2 T 1 is 486.2 T 2 which has got it as 474.5. So, I substitute everything in this equation to get delta S AC in the value I obtain is 24.02 Joules per mole per Kelvin this is value of delta S going from A to C. So, what we have done in this problem is considered a process where in a real gas undergoes a certain change, we know some information about the process and then we try to calculate the other thermodynamic variables including other temperature in this particular example.

So, this is how we are going to use whatever we have learned so, far to be able to perform a calculation over the process

(Refer Slide Time: 19:59)

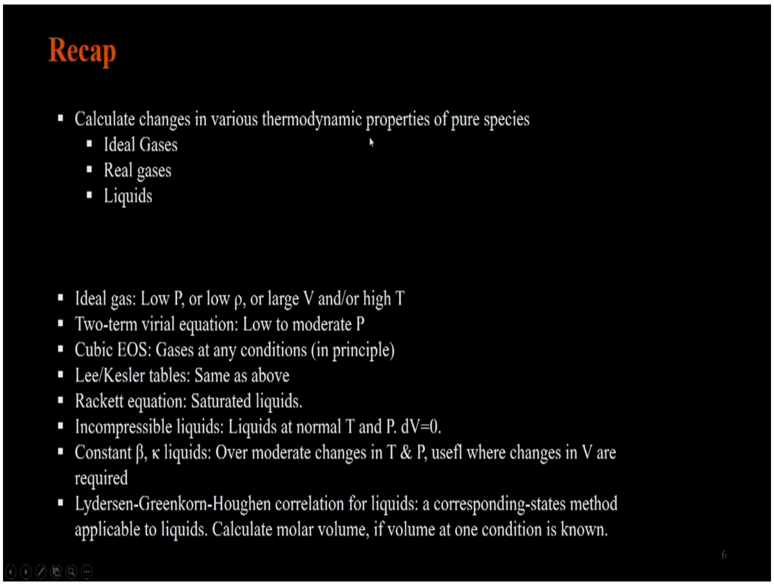


Property Changes for Pure Species

Summary and Example

So, let us quickly then summarize how we went about calculating property changes force pure species.

(Refer Slide Time: 20:04)



## Recap

- Calculate changes in various thermodynamic properties of pure species
  - Ideal Gases
  - Real gases
  - Liquids

- Ideal gas: Low P, or low ρ, or large V and/or high T
- Two-term virial equation: Low to moderate P
- Cubic EOS: Gases at any conditions (in principle)
- Lee/Kesler tables: Same as above
- Rackett equation: Saturated liquids.
- Incompressible liquids: Liquids at normal T and P. dV=0.
- Constant β, κ liquids: Over moderate changes in T & P, usefl where changes in V are required
- Lydersen-Greenkorn-Houghen correlation for liquids: a corresponding-states method applicable to liquids. Calculate molar volume, if volume at one condition is known.

Let us quickly recap what we have done so, far in terms of calculating property changes for a variety of cases. We have used ideal gas expressions that is the simplest way to calculate the property changes if of course, such a condition is applicable, otherwise we have to resort to equations that are applicable for real gases and the way we have handed real gases is using residual properties. We will come back in a minute and talk about how to calculate residual properties for various cases, and then we have developed some equations for liquids in terms of isothermal compressibility and volume expansivity.

Talking about various conditions at which several types of expressions we have used so, far are applicable the ideal gas like conditions are applicable at low densities, when the molecules are far apart at large molar volumes right which typically is the case either at low pressure or high temperature. If you want to correct for non-ideality or we want to use equations for real gases, then the easiest way we can approach that is using a virial equation of state with just the second virial coefficient. But then its applicable from low to moderate pressures right. If the pressures are slightly higher maybe if we have enough information, then we can use the third virial coefficient.

Otherwise we usually resort to cubic equations of state that are appropriate for that particular species we are using in some cases readily kuan might be more suitable, in some other cases pengrobinson might be more suitable or some other cubic equation of state right.

Depending it depends on the species we are using. Similar to cubic equations of state if we use theorem of corresponding states, then we use either we are producer correlations are the most popular ones are Lee Kesler tables. In fact, Lee Kesler tables in addition to the compressibility factors from which we can calculate the molar volumes we have Lee Kesler tables also for residual enthalpies and residual entropys. As well as liquids are concerned we can calculate the saturated liquid volume using racket equation.

We can assume that liquids are fairly incompressible at normal temperatures and pressure changes, they are fairly incompressible or the molar volume change is 0, but if there is a large change in pressure, but then if they are not incompressible, then we can make an assumption that the volume expands ability and isothermal compressibility are fairly constant which is the easiest way to handle the changes in temperature and pressure to be able to calculate the corresponding volume change for a liquid. If that is not applicable and of course, we need the temperature and pressure dependency for beta and kappa to be able to calculate the change in volume.

One of the other methods we looked at for calculating molar volume of a liquid is using what we call as Linderson correlation and to be able to use this correlation, we need molar volume at a certain condition and we can use the 2 parameters theorem of corresponding states to be able to calculate the molar volume at a different condition. So, this is a quick summary of what we have done so, far, and if you look at it in most cases it is limited only to pure species. When we come back in the next lecture, what we will do is try to extend these ideas for mixtures of liquids or gases.