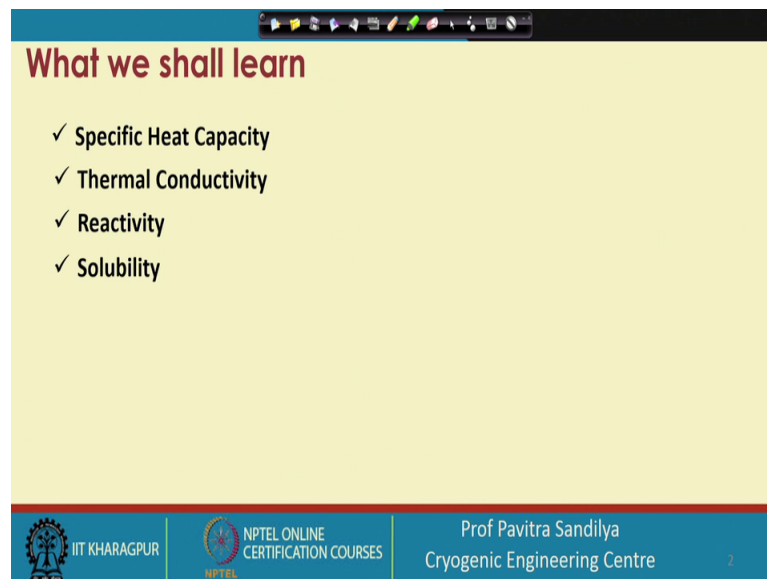


Upstream LNG Technology
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Lecture – 12
Thermodynamic and Chemical Properties

Welcome back, today in this lecture, we are going to learn about the Thermodynamic and Chemical Properties of natural gas. We already learnt some other properties some of physical properties like density, viscosity, etcetera. Now lastly in this, we shall be looking into some of the important thermodynamic properties. What we mean by thermodynamic as I told you earlier that, these properties are necessary to understand the various processes related to any kind of heat exchange and then we have also just have a glimpse of the chemical properties which are important for the processing of the natural gas.

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The slide is titled "What we shall learn" and lists four properties with checkmarks:

- ✓ Specific Heat Capacity
- ✓ Thermal Conductivity
- ✓ Reactivity
- ✓ Solubility

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So, in this lecture, we shall be looking at these 4 properties. First, we specific heat capacity, then thermal conductivity reactivity and solubility, first two related to relate to the thermodynamic property, whereas, the last two related to the chemical property of any substance.

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Specific heat capacity

- ✓ Quantity of heat required to raise the temperature of a unit mass of the natural gas by one degree
 - Heat energy is evolved or absorbed when the temperature of natural gas changes
- ✓ Needed to design intercooler of the multi-stage compressors during transfer of natural gas through pipelines
- ✓ Two types of specific heat capacity:
 - Isobaric C_p
 - Isochoric C_v
 - Specific heat ratio, $\gamma = \frac{C_p}{C_v}$

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Now, specific heat capacity, this perhaps all of you are aware that for any kind of substance whenever we are trying to heat it up, it will undergo some changes and one of them is that its temperature will start increasing. So, if I am heating it, it will start increasing and if I am cooling it, it will start decreasing.

So, how much heat is needed to change the temperature of a substance that is important for us because that determines the cost of energy. So, specific heat means that it is the amount of heat energy that is needed to raise the temperature, a particular mass unit mass of a substance by a unit degree; that means, how much amount of heat energy is needed to change by 1 degree per unit mass of the substance.

And as I said that increase of natural gas changes, then heat may evolve or heat may be absorbed by the natural gas and this heat capacity knowledge is needed for designing of the various types of equipment like the intercooler for the multi stage compressor and these compressors are needed as I told you in the processing lecture that needed to compress the outlet natural gas.

There are 2 types of heat capacities, we know that one is the isobaric heat capacity; that means, when the heating or cooling is done at constant pressure and the other which is determined represented by C_p and another we have the isochoric heat capacity that is means when the heating or cooling is done at constant volume.

And then we define something called specific heat ratio that is denoted by gamma and the ratio is the ratio of the specific heat capacity at constant pressure to the specific capacity at constant volume. So, if I know C_p and if I know gamma then I can find the value of C_v .

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Isobaric heat capacity of natural gas
 Jarrahan et al. (2014) correlation:
 Validity: $0.1 < P < 40$ MPa, $250 < T < 414$ K

$$C_p = C_{DL}^{corr} \left[a \frac{T}{b} \left(\frac{d^2\beta}{dT^2} \right) \ln \left(\frac{Z+B}{Z} \right) + \frac{R(M-N)^2}{M^2 - A(2Z+B)} - R \right] + C_p^\circ \left[\frac{\text{J}}{\text{mol K}} \right]$$

T in K, P in MPa

$$C_p^\circ = A_1 + A_2 T_{pr} + A_3 T_{pr}^2 + \frac{A_4}{\gamma_g} + \frac{A_5}{\gamma_g^2}$$

$$\frac{d\beta}{dT} = \frac{2\beta_3 T_{pc}}{T^2} - \frac{2\beta_5 T_{pc}}{T^3} - \frac{\beta_6 \ln(P_{pr}) T_{pc}}{T^2}$$

$$\frac{d^2\beta}{dT^2} = \frac{2\beta_3 T_{pc}}{T^3} + \frac{6\beta_5 T_{pc}}{T^4} + \frac{2\beta_6 \ln(P_{pr}) T_{pc}}{T^3}$$

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Now, in the literature there are many correlations available to estimate the values of the heat capacities and again, this correlations may change depending on the type of natural gas and depending on the operating conditions, here I have shown one of the latest correlations from proposed by Jarrahan at in 2014, and this correlation is valid for this pressure range and this temperature range.

So, these are quite broad ranges of pressure temperature these researchers have considered and accordingly they put this particular correlation, these correlations as I told you or obtained may be in a semi empirical manner and they considered many of the experimental data, in the literature from that without going into detail of the derivation, we just understand that these are the correlations and these correlation need not be remembered, they are just available, you should be aware of the sources of the correlation that is why I have given the thing given the source.

So, we just be should be aware the Ts, there are correlations available using those correlations, we can estimate the value of the specific heat and we will find that all these expressions used in the correlation have been given in this equations.

So, and there are many parameters involved in this like a capital B are etcetera, etcetera, all these parameters involved an use see that all these correlations involved. The temperature the pseudo reduced temperature, then the specific gas heat ratio. So, all these things are there and this Cp 0 is the ideal gas heat capacity.

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Isobaric heat capacity of natural gas

$$\beta = \beta_1 + \beta_2 \ln(P_{pr}) + \frac{\beta_3}{T_{pr}} + B_4 [\ln(P_{pr})]^2 + \frac{\beta_5}{T_{pr}^2} + \frac{\beta_5 \ln(P_{pr})}{T_{pr}}$$

$$C_{DL}^{corr} = B_1 + B_2 \ln(T_{pr}) + B_3 P_{pr} + B_4 [\ln(T_{pr})]^2 + B_5 P_{pr} \ln(T_{pr})$$

$$P_{pc} = \frac{K^2}{J^2} \quad T_{pc} = \frac{K^2}{J}$$

$$J = J_1 + J_2 y_{H_2S} + J_3 y_{CO_2} + J_4 y_{N_2} + J_5 y_{H_2} + J_6 y_{H_2O} + J_7 \gamma_{gMix} + J_8 \gamma_{gMix}^2$$

$$K = K_1 + K_2 y_{H_2S} + K_3 y_{CO_2} + K_4 y_{N_2} + K_5 y_{H_2} + K_6 y_{H_2O} + K_7 \gamma_{gMix} + K_8 \gamma_{gMix}^2$$

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So, all these host of equations associated with the determination of the heat capacity for the natural gas are given in this equations, and then plugging in the appropriate values you can estimate the specific heat capacity.

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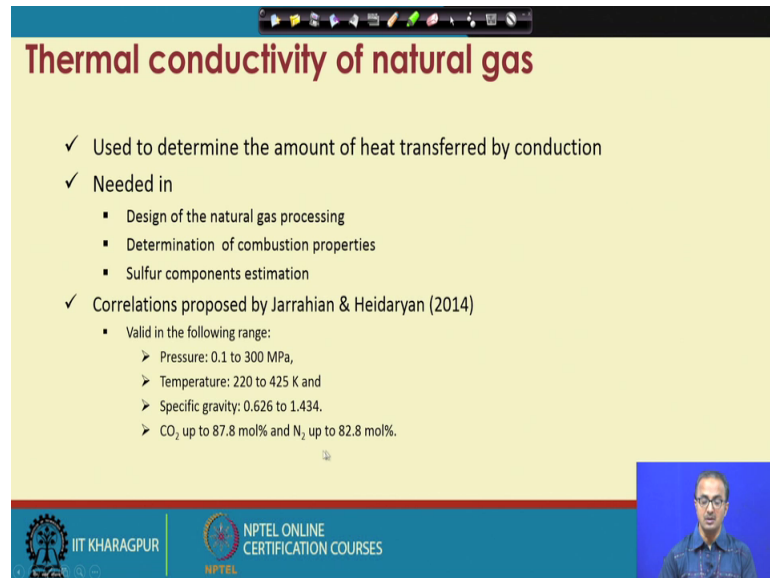
Coefficient values for Jarrhian et al. correlation

i	J _i	K _i	b _i	A _i	B _i
1	1.1925 e-1	3.7548	2.3824 e-1	4.5947 e+1	5.5763 e-1
2	-2.8740 e-1	-3.4047	-3.5155 e-2	9.9075	6.3484 e-1
3	-4.8994 e-1	-9.7700	6.2046 e-1	4.1793 e-1	-2.6822 e-2
4	-2.3645 e-1	-9.4707	-5.7451 e-3	7.0950 e-1	7.8386 e-2
5	1.5539	1.3586 e+1	-1.1838 e-1	-9.0246	-1.1171 e-3
6	-1.3885 e-1	-8.9443 e-1	8.1836 e-2	-	-
7	7.3025 e-1	1.9677 e+1	-	-	-
8	-1.1842 e-1	-2.9918	-	-	-

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And the authors have also listed out the values of the various parameters that associated with this type of correlation. So, again this things will be available to you, you have to select them properly and get this things get the values.

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Thermal conductivity of natural gas

- ✓ Used to determine the amount of heat transferred by conduction
- ✓ Needed in
 - Design of the natural gas processing
 - Determination of combustion properties
 - Sulfur components estimation
- ✓ Correlations proposed by Jarrahan & Heidaryan (2014)
 - Valid in the following range:
 - Pressure: 0.1 to 300 MPa,
 - Temperature: 220 to 425 K and
 - Specific gravity: 0.626 to 1.434.
 - CO₂ up to 87.8 mol% and N₂ up to 82.8 mol%.

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Then we have thermal conductivity of natural gas in this case also, we know that what is conductivity; conductivity determines the efficacy of heat transfer by conduction in a. So, how suppose, I have we are heating something at one point in the of them system, then how that heat is getting propagated to other places around that point.

So, that is determine by the thermal conductivity and these are needed in the design of the various natural gas processing the determine the combustion properties, then even sulfur component estimation, again there are many many correlations available in the literature of natural gas, I have put one of them which is the also reported recently and this particular correlation is valid for this pressure and temperature ranges and this specific gravity range.

So, and in this case, we can also this correlation also considers the presence of the acid gases by carbon dioxide the about this particular percentage and nitrogen of about this percentage. So, this is quite a generalized correlation accounting for the some of the impurities in the natural gas, we have to understand that because as the compositions of the natural gas change quite broadly very broadly. So, it becomes impossible to make one correlation for everything.

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Jarrahian & Heidaryan correlation

$$\lambda = \lambda_{1 atm} \left[1 + \frac{A_9}{T_{pr}^5} \left(\frac{P_{pr}^4}{T_{pr}^{20} + P_{pr}^4} \right) + A_{10} \left(\frac{P_{pr}}{T_{pr}} \right)^2 + A_{11} \left(\frac{P_{pr}}{T_{pr}} \right) \right]$$
$$\lambda_{1 atm} = \lambda_{1 atm}^{uncorrected} + \Delta\lambda_{N_2} + \Delta\lambda_{CO_2} + \Delta\lambda_{H_2S}$$
$$\lambda_{1 atm}^{uncorrected} = A_{1atm} \gamma_{gMix}^{A_2} (T - 459.67) + A_3 + A_4 \log(\gamma_{gMix})$$
$$\Delta\lambda_{N_2} = \gamma_{N_2} [A_5 \log(\gamma_{gMix}) + A_6]$$
$$\Delta\lambda_{CO_2} = \gamma_{CO_2} [A_7 \log(\gamma_{gMix}) + A_8]$$

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And this correlation is given again in this terms, again, we have some value of this, this lambda is stands for the thermal conductivity and this actual lambda actual thermal conductivity depends on the thermal conductivity at one atmosphere plus these are the various other corrections for any other deviation for different pressures and temperatures. Here, we have the pseudo reduce temperature, here we have pseudo reduce pressure and may other parameters A 9, A 10, A 11, etcetera and these again have been given by this, how to find out the thermal conductivity at 1 atmosphere in terms of many other associated thermal conductivities for each of them, again, we have many other expressions which we need to use and ultimately.

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Jarrahian & Heidaryan correlation

$$P_{pc} = \frac{P_{pcMix}^{**} T_{pcMix}^{***}}{T_{pcMix}^{**} + y_{H_2S}(1 - y_{H_2S}) \left[120 \left\{ (y_{CO_2} + y_{H_2S})^{0.9} + (y_{CO_2} + y_{H_2S})^{1.6} \right\} + 15 (y_{H_2S}^{0.5} + y_{H_2S}^4) \right]}$$

$$T_{pc} = T_{pcMix}^{**} - 120 \left[(y_{CO_2} + y_{H_2S})^{0.9} + (y_{CO_2} + y_{H_2S})^{1.6} \right] + 15 (y_{H_2S}^{0.5} + y_{H_2S}^4)$$

$$P_{pcMix}^{**} = (1 - y_{N_2} - y_{CO_2} - y_{H_2S}) P_{pcHC}^{**} + y_{N_2} P_{cN_2} + y_{CO_2} P_{cCO_2} + y_{H_2S} P_{cH_2S}$$

$$T_{pcMix}^{***} = (1 - y_{N_2} - y_{CO_2} - y_{H_2S}) T_{pcHC}^{**} + y_{N_2} T_{cN_2} + y_{CO_2} T_{cCO_2} + y_{H_2S} T_{cH_2S}$$

$$P_{pc}^* = 671.1 + 14 y_{gHC} - 34.3 y_{gHC}^2 \qquad T_{pc}^* = 120.1 + 429 y_{gHC} - 62.9 y_{gHC}^2$$

$$y_{gHC} = \frac{y_{gMix} \frac{M_{N_2} y_{N_2} + M_{CO_2} y_{CO_2} + M_{H_2S} y_{H_2S}}{M_{air}}}{1 - y_{N_2} - y_{CO_2} - y_{H_2S}} \qquad y_{gMix} = \frac{1}{M_{air}} \sum y_i M_i$$

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We have you know you see that here the authors also proposed some special expressions for the pseudo critical properties these are not the ones which we learn in our previous lecture.

So, these you have to very careful about that the definition or the expression for the mixing rule, this is something like a mixing rule. So, these mixing rules may not remain the same for all types of correlations. So, in this particular correlation, we have to use this particular mixing rule to find out the pseudo critical properties and these are the pseudo critical properties for the mixer and they have considered hydrocarbon, nitrogen, carbon dioxide and hydrogen sulfide to find out the pseudo critical pressure and pseudo critical temperature and then also this expression to find out the specific gravity of the hydrocarbons and the mixtures.

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Coefficient	Value
A_1	$3.095251494612 \times 10^{-05}$
A_2	$-3.054731613002 \times 10^{-01}$
A_3	$1.205296187262 \times 10^{-02}$
A_4	$-2.155542603544 \times 10^{-02}$
A_5	$1.695938319680 \times 10^{-02}$
A_6	$1.983908703280 \times 10^{-03}$
A_7	$1.469572516483 \times 10^{-02}$
A_8	$-7.570807856000 \times 10^{-04}$
A_9	$1.854452341597 \times 10^{+00}$
A_{10}	$-1.275798197236 \times 10^{-03}$
A_{11}	$1.925784814025 \times 10^{-01}$

After plugging in these expressions and these are the values of the various coefficients involved in the estimation of the thermal conductivity. So, these coefficients have to be used properly to get the value of the thermal conductivity.

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Reactivity

✓ To account for:

- Reaction with water under suitable conditions to produce hydrates
- Self-reactions leading to initiation by the presence of certain metals
 - Polymerization normally produces heat which accelerates the reaction
- Reaction with air to form unstable oxygen compounds which could cause an explosion
- Carbamate formation when CO_2 reacts with ammonia.
- Reactions of NG with compressor lubricating oils, resulting in blockage and damage.

Next, we come to the chemical property and in that we have to start with reactivity. Now why do we need to know reactivity and what kind of reactions are expected in the natural gas systems. So, in this first, we come to a very prominent reaction that is due to the presence of water and as I told you that water may get reacted with some of the

components in natural gas like methane like carbon dioxide, like ethane, etcetera to form hydrate. So, we need to know that, what is the rate of reaction of the natural gas with water to at that, that can lead to the formation of the hydrate.

And then natural gas because it is hydrocarbon under some you know suitable temperature pressure, then them the natural gas, ethane, methane, etcetera, they can react among themselves in the presence of some kind of metals those may catalyze this reactions to form polymers so; that means, some polymerization reactions may occur in a natural gas systems and these reactions may lead to the heat generation.

So, this heat generation may again cause some other property changes and processing may changes. So, we need to the need to know the reaction rates and reaction may also occur with air form some kind of unstable oxygen compounds that may cause explosion. So, that is that is also one important thing that we need to know the any kind of reaction kinetics or reaction rates that might be occurring in the presence of air.

And lastly that there may be carbon dioxide present in the natural gas which may react with ammonia. Ammonia is now found with the nitrogen and hydrogen. So, if the carbon dioxide reacts with ammonia then we get some carbamate formation. So, this carbamate some compounds which are need to be avoided and then we have this natural gas may also react with the compressor lubricating oils and that may result in the blockage and damage of the compressor and the other pipeline.

So, that is from this angles, we need to know what all reactions are possible in a natural gas system and if you know them we know the kinetics, then we can take measures to prevent this reactions to happen.

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Solubility

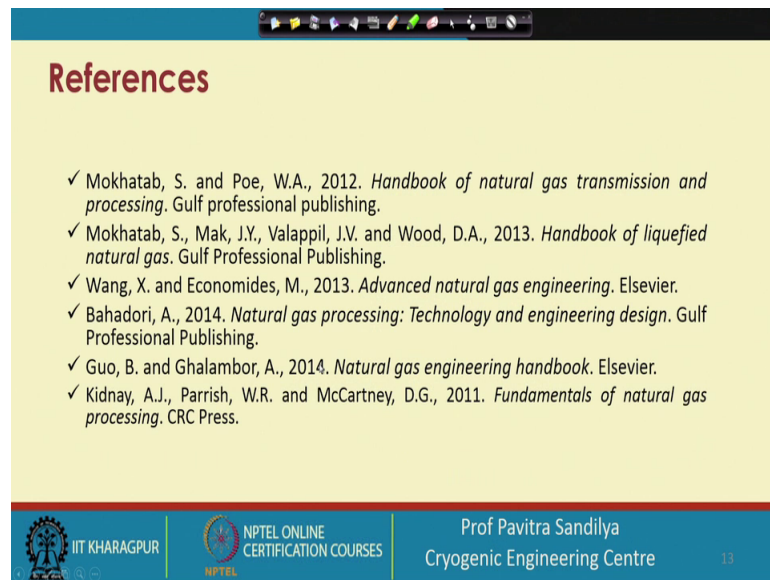
✓ Natural gas has extremely low solubility in water

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Next, in this line is the solubility and we know that natural gas as a very high solubility in water. So, this solubility can see with the solubility knowledge, we can say that how much natural gas may get lost with the water. So, that is why we need to know the solubility and to prevent the loss of natural gas to water. Again, we may take some precautionary measures and we know that solubility increases with increasing pressure and decreases with increasing temperature.

So, accordingly we can adjust the conditions. So, that the we can prevent the too much of solubilization of natural gas in water.

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So, with this, we look at the now references these are references which will help you to learn more about these properties.

Thank you.