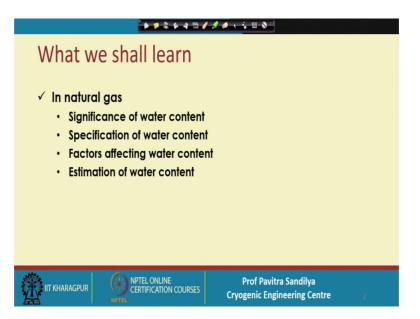
# Upstream LNG Technology Prof. Pavitra Sandilya Department of Cryogenic Engineering Centre Indian Institute of Technology, Kharagpur

# Lecture – 35 Estimation of water content in natural gas

Welcome, when we talk of the natural gas purification or natural gas separation, we have to take out the various types of impurities present and water is one of the main impurities in natural gas, and for that we need to know the water content in the natural gas so that we can design how to dehydrate the water.

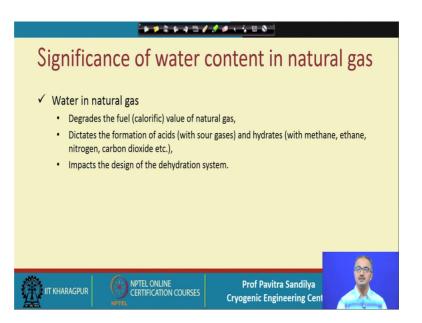
So, today's lecture, we will be concerning about the estimation of water content in natural gas.

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In this, what we shall learn that what is the significance of water content in natural gas, how to specify the water content, then what are the factors which affect the water content and lastly, what are the various estimated methods to for the water content. Here, we will be talking about only a few representative methods because there are exhaustive methods depending on the various types of natural gases.

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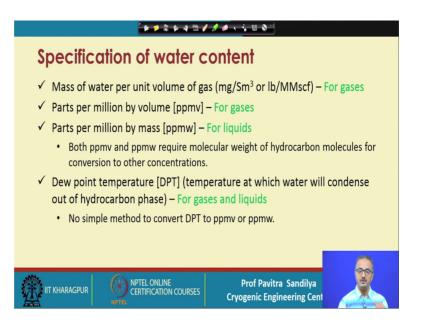


So, first let us see the significance of water content in natural gas. Water in natural gas; it has some bad effects that first, it degrades the fuel value of the natural gas that is the natural gas with lots of water will be having less calorific value. So, we shall not be able to derive much thermal energy, by burning this kind of natural gas with high amount of water, then water also dictates the formation of some acid because when in natural gas generally we have carbon dioxide and hydrogen sulfide which may react with water and form weak acids which may corrode the pipelines and the equipment.

And water also forms hydrates with some of the gases like carbon dioxide, methane, etcetera, it can form hydrates and these hydrates as we know that they are solid particles and they may get deposited inside the pipelines or in the equipment and heat exchangers. So, that they will either produce some lot generate pressure drop by they will impede the flow of the gas or they can make skills on the heat surfaces so that the heat transfer efficiency will also get reduced.

And that is how we will find that; it will affect the dehydration system so that is why we have to understand the water content in the natural gas. Now there are various ways of specifying the a water content.

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First is the in terms of mass of water per unit volume of the gas and this is given generally in terms of milligram per standard meter cube or pounds for million standard cubic feet and this is generally used for gases another way is pounds per million by volume, it is also used for gases and then we have parts per million by mass ppmw that is for liquids and both ppmv and ppmw required molecular weight of hydrocarbon molecules for conversion to the other units.

And then lastly, we have the dew point temperature because when depending on the amount of water in any gas, the gas will be having different dew points. So, dew point is an indication of the water content and this is used for both gases and liquids and generally there is no simple method to convert the dew point temperature that is DPT into ppmv or ppmw. So, now, we shall see that how to do some kind of basic conversion among these particular representations.

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Conversion of ppmv to $mg/m^3$
✓ ppmv is same as ppm on molar basis 1 ppmv = $10^{-6} \frac{\text{kmol species } i}{\text{kmol gas mixture}}$
$= 10^{-6}  imes M_i rac{ m kg}{ m kmol \ of \ gas \ mixture}$
$= M_i \frac{\text{mg species } i}{\text{kmol of gas mixture}}$ Where $M_i$ is Molecular weight of species $i$ (in kg/kmol) $\checkmark$ Applying ideal gas law, $V = n \frac{RT}{P} \text{ m}^3 \left[ R \text{ in } \frac{\text{kJ}}{\text{kmol K}}, T \text{ in Kand } P \text{ in kPa} \right]$ $1 \text{ppmv} = \frac{M_i P}{RT} \frac{\text{mg species}}{\text{m}^3 \text{ of gas mixture}}$
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Now first we see that; how we can convert ppmv to milligram per meter cube. Now one ppmv is defined like 10 to the power minus 6 kilomole of species i to kilomole of gas mixture that is how much 1 ppmv means 1 part per million and million represents 10 to the power 6. So, 1 kilomole of species i in 10 to the power 6 kilomole of the gaseous mixture and that is how we are getting 10 to the power minus 6 in the numerator.

And then to convert the kilomole into the mass; what we do we multiply weight with the molecular weight. So, we now get mi in milligram the species of the, of i that is milligram means kg into 10 to the power minus 6 gives us 1 milligram. So, milligram of species i per kilomole of the gas mixture and then we use for ideal gas flow, if we can use we find that by using ideal gas we can write v equal to n RT by P and in this, we are putting everything in terms of the si units.

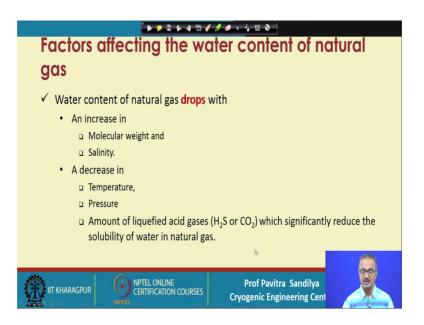
So, these are if we put all these units temperature in Kelvin pressure in kilopascal and universal gas constant in kilo joule per kilomole per Kelvin, then we get that 1 ppmv is equal to this particular thing molecular weight into pressure divided by R into T and this is the milligram species per cubic meter of the gas mixture. So, that is how we can convert ppmv to milligram per meter cube.

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<mark>*************************************</mark>	
Conversion of ppmw to n	ng/m <sup>3</sup>
$1 \text{ppmw} = 10^{-6} \frac{\text{kg species } i}{\text{kg liquid mixture}}$	$1 \text{ppmw} = 10^{-6} \frac{\text{kg species } i}{\text{kg gas mixture}}$
$=\frac{1}{\rho_{\rm avg}}\frac{\rm mgspeciesi}{\rm m^3liquidmixture}$ Where $\rho_{\rm avg}$ is in kg/m <sup>3</sup> .	$= M_{\rm avg} \frac{{\rm mgspecies}i}{{\rm kmolgasmixture}}$
	$= \frac{PM_{\rm avg}}{RT} \frac{\rm mgspeciesi}{\rm m^3 ofgasmixture}$
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Next we come to ppmw to milligram per meter cube, in this, first we see that if you are using liquid, then we have this 10 to the power minus 6 kilogram of species i per kg of liquid mixture because for liquids, we are talking in terms of mass not in terms of mole. So, we have then what we do that we if we divide by the average density, then what we find that we are getting milligram of the species i per cubic meter of the liquid mixture and in this case, the density is given in terms of kg per meter cube, this ppmw may also be used for gas, in that case we, if we put this kgs, then what we do that it is very simple that we are simply having the molecular weight to convert this gas mixture into kilomole and we get by the ideal gas law we put PM by RT to get milligram species per meter cube of the yan by the ideal gas law we are doing this inter conversions of the various units.

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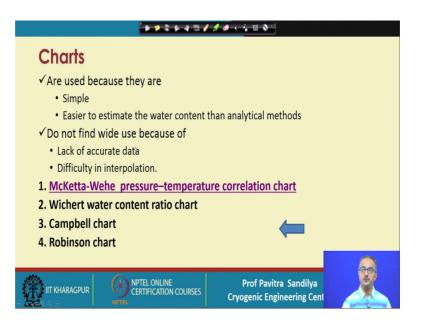
Then the various factors which affect the water content in the natural gas are like this that when we the water content will drop with an increase in the molecular weight and in increase in the salinity that is the presence of the salts, and it can decrease also with a decrease in the temperature decrease in the pressure and a decrease in the amount of the liquefied acid gases which significantly reduce the solubility of water in natural gas.

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	<b>**</b> *****	<u># @ </u>
	Estimation of wate	er content in natural gas
	<u>Charts</u>	Analytical models
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Now, here we have the various charts and analytical models to estimate the water content in natural gas, first let us look into the charts.

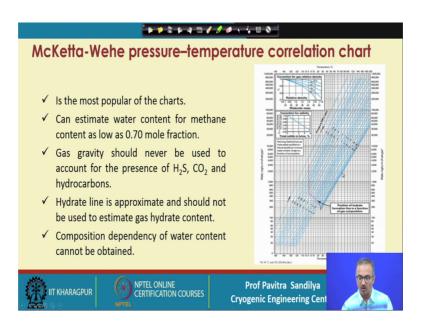
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Now, we have various types of charts in the literature because there are so many varieties of natural gas and people are still working all over the world to get generate such kinds of charts for different types of natural gas, here, we have just taken named a few of them, first, let us see that a charts are used for there because as simple and easy to estimate the water content, then an analytical methods because we do not need to solve any equation we have chart and we can read out the values.

On the other hand, they have some drawbacks that we cannot have one particular chart which will represent all sorts of natural gases and also, it is very difficult to interpolate the chart charts and these charts are not much useful when we talk of any kind of theoretical analysis through coding and modeling. So, these are some drawbacks, but for quick estimation we can use these charts and here we I have given a few of the charts which are available in the literature and one of them the popular one is the McKetta Wehe pressure temperature correlation chart I we shall be talking about only this particular chart.

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So, let us see how this particular chart looks like that it is among the most popular of the charts it can estimate the water content for methane content as low as 0.70 mole fraction. So, for this small amount of mole fraction also, it can give the water content and gas gravity is not used to in the presence of the H 2 S and CO 2 and other hydrocarbons and in this chart, we shall see that there is a hydrate line, which tells us that whether there will be hydrate formation or not due to the water.

So, this graph is just indicative it should not be used to know the exactly the hydrate content, it can just tell us the demarcation that or the point below which the hydrate reformed and this composition dependency of on the on the water content cannot be ascertained from this kind of a chart. So, here is a typical chart of this proposed way McKetta and Wehe, we find that on the y axis, we have the water content on the x axis, we have temperatures and all these lines represent the various pressures and here, we have some correction factors for the salinity for the gas relative density and here we find that by the red line it is the position where the hydrate may be formed.

So, it is just a qualitative indication that above which there could be hydrate formation, but it should not be used to find out the amount of hydrate in the natural gas after this we come to some analytical techniques.

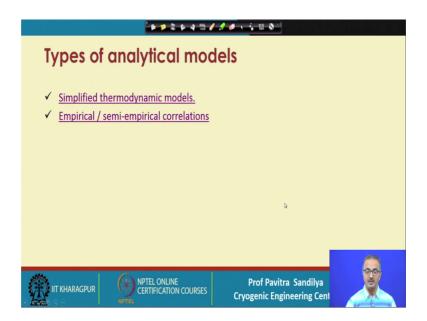
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Ana	lytical models		
	Advantages	Disadvantages	
	<ul><li>Accurate</li><li>Quick</li><li>Convenient</li><li>Easy to program</li></ul>	<ul> <li>Non-robust</li> <li>Not available for every type of natural gas</li> <li>Not unique for any given natural gas.</li> </ul>	
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And these analytical models have the advantage that, they are quite accurate and they are quick, they are very convenient and easy to program.

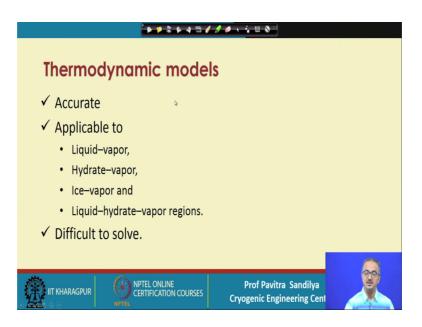
On the other hand, they are not robust in the sense that they are not universally applicable there are various analytical models already reported and are being developed and these are not available for all type of natural gases because different depending on the type of natural gas the source of natural gas the compositions will change. So, we may not be able to use one particular model for all kinds of natural gases then they are not unique even for any given natural gas.

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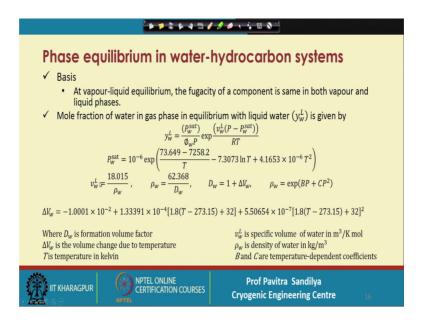
Despite them, they are finding quite amount of applications and again, we have different types of models with the 2 broad classifications. One was simplified thermodynamic models and some are empirical or semi empirical correlations.

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So, first let us see again thermodynamic model, they are quite accurate and they are applicable to all kinds of phase combinations like a liquid vapor, hydrate vapor, ice vapor and liquid hydrate vapor region, there is a possibility of ice formation in natural gas depending on the temperature and pressure due to the water content.

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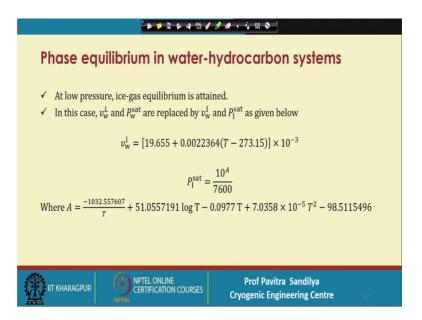


But these thermodynamic models are difficult to solve. So, here we put one of the models in which the basis is this at the vapor liquid equilibrium the fugacity of a component is same in both the vapor and the liquid phases. So, with this these a thermodynamic condition. So, when we are equating the fugacity of a component in both the liquid and the vapor phases, we get this kind of an equation and then we find that these are the various parameter that is the this w is the water these, this is the vapor pressure of water and this is given by this particular equation and we see that this changes for the temperature, then we have the fugacity of water and we have this partial volume of water in the liquid.

So, this is given by this expression and in this, we need the density of water which is given by this and in this, we have another Dw, this is given in terms of some delta Vw which is given by this particular expression and we find that this is a function of the temperature and then we have the rho w that is a function of pressure and this B and C are some temperature dependent functions.

So, ultimately what we find this Vw is a function of both temperature and pressure and here we have temperature T and pressure P. So, here the various notations are there that Dw is some formation volume factor and delta Vw is the change in the volume due to temperature. So, by using if we know these all these parameter values, then we can find out the mole fraction of water in the natural gas.

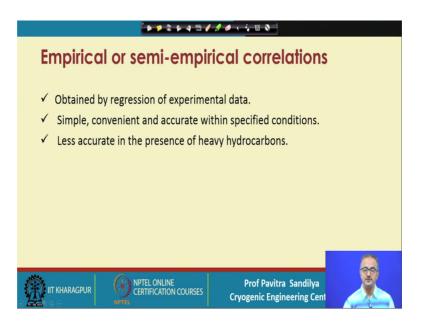
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Now, if there is a ice formation in that case we have this water in the ice. So, this is given by this particular expression and is a function of the temperature and here, we find the vapor pressure of the ice is given by this expression and in this expression, there is a parameter a which is given in terms of temperature. So, what we what we see that in this way, we are able to estimate the amount of water both in the ice phase if it is formed and also in the vapor phase.

So, these expressions may be used please understand that these expressions need not be memorized, you can refer to the various references given in this lecture to look into these expressions and find out the various values. Now we go to some empirical or semi empirical correlations.

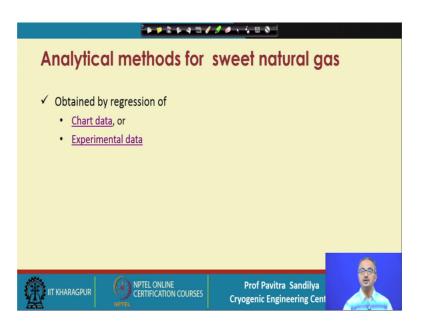
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In this, first we see that this these empirical or semi empirical relations are obtained by regression of the experimental data, they were quite simple and very convenient and very accurate within the specified conditions because outside the specified conditions, they may not be giving good results because they have the regression is valid only within some specified range, but there less accurate in presence of heavy hydrocarbons.

So, but still they are quite popular. Now in this, we have now some analytical methods for this.

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So, we find first for the sweet natural gas sweet natural gas means we have almost no sulfur content in it. So, again for the sweet natural gas there are some expressions which have been obtained by regressing the chart data the chart data, we have shown already McKetta Wehe is one of them and then we have some experimental data.

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<b>●●●</b> ◆◆◆●● <b>●</b> ◆●
Ning et al. method
✓ Based on the McKetta-Wehe chart
$\checkmark$ Water content for sweet natural gas is found as
$W_{\rm H_{2}0,sweet} = (714.855 + 1.1T + 369.673d - 1.42Td) \times (1 - 0.02247S) \times \exp(a_0 + a_1T + a_2T^2)$
Where $d = \sum \frac{M_i y_i}{28,966}$
S: Mole fraction of brine in water,
$M_i$ and $y_i$ are the molecular mass and mole fraction of component $i$ in gas.
✓ The coefficients can be estimated from this <u>table</u>
✓ This correlation is valid for 0.1 MPa≤ $P \le 100$ Mpa
Reference :Ning, Y.N., Zhang, H., Zhou, G., 2000. Mathematical simulation and program for water content chart of natural gas. Chem.Eng. Oil Gas 29, 75–77
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So, let us see that what kind of chart data like Ning et al proposed one correlation, they use the McKetta Wehe chart and this is a reference from which this has been taken and in this we find that the water content is given by this particular expression which is a function of temperature and this D factor is there which is given by this expression.

And here we have 1 S, this S is the mole fraction of the brine in water; that means this particular expression is able to also make the correction for the salinity and D is taking care of the specific gravity. Now there various correlations are there this a 0, a 1, a 2, etcetera and these parameters may be obtained from this particular table.

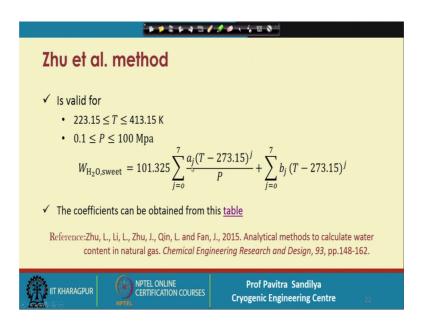
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P/MPa	ao	a <sub>1</sub>	a2	P/MPa	ao	aı	a2
0.1	-30.0672	0.1634	$-1.7452 \times 10^{-4}$	5	-26.8976	0.1232	-1.1618 × 10
0.2	-27.5786	0.1435	$-1.4347 \times 10^{-4}$	6	-25.1163	0.1128	$-1.0264 \times 10^{-1}$
).3	-27.8357	0.1425	$-1.4216 \times 10^{-4}$	8	-26.0341	0.1172	$-1.0912 \times 10^{-1}$
).4	-27.3193	0.1383	$-1.3668 \times 10^{-4}$	10	-25.4407	0.1133	$-1.0425 \times 10^{-1}$
).5	-26.2146	0.1309	$-1.2643 \times 10^{-4}$	15	-22.6263	0.0973	$-8.4136 \times 10^{-1}$
0.6	-25.7488	0.1261	$-1.1875 \times 10^{-4}$	20	-22.1364	0.0946	-8.1751 × 10°
0.8	-27.2133	0.1334	$-1.2884 \times 10^{-4}$	30	-20.4434	0.0851	-7.0353 × 10
L.O	-26.2406	0.1268	$-1.1991 \times 10^{-4}$	40	-21.1259	0.0881	-7.4510 × 10
1.5	-26.1290	0.1237	$-1.1534 \times 10^{-4}$	50	-20.2527	0.0834	$-6.9094 \times 10^{-1}$
2	-24.5786	0.1133	$-1.0108 \times 10^{-4}$	60	-19.1174	0.0773	$-6.1641 \times 10^{-1}$
3	-24.7653	0.1128	$-1.0113 \times 10^{-4}$	70 Þ	-20.5002	0.0845	$-7.1151 \times 10^{-1}$
1	-24.7175	0.1120	$-1.0085 \times 10^{-4}$	100	-20.4974	0.0838	$-7.0494 \times 10^{-1}$
	-24.5786 -24.7653	0.1133 0.1128	$\begin{array}{c} -1.0108 \times 10^{-4} \\ -1.0113 \times 10^{-4} \end{array}$	60 70 ₽	-19.1174 -20.5002	0.0773 0.0845	-6.1641 -7.1151

So, for various pressures, these have been listed out here. So, the pressure is from 0.1 MPa, 200 MPa that is about 1 bar 2000 bar.

So, from this table, we can get these values of the various parameters and then we can estimate the water content in sweet natural gas and this correlation is valid for this 1 bar 2000 bar. Now we come to another type of expression which have been obtained from the experimental data here, we have an method given by Zhu et al and we find that this is applicable within this temperature range and within this pressure range.

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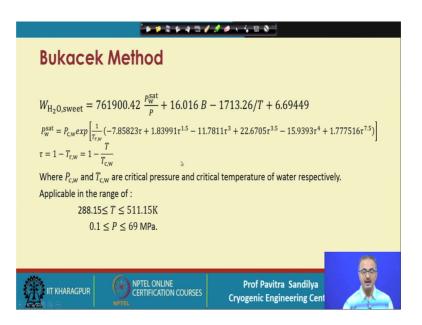
And here is the expression for the water content in the sweet natural gas and if you go into the literature and on this in these papers, you will find the validity of these particular correlations and their mutual comparisons also. So, here we find again we have many parameters aj and bj which may be obtained from this particular table given by the authors.

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				180 - 1			
Coef	Coefficients of Zhu et al. correlation						
a <sub>0</sub> 4.65925	a <sub>1</sub> 3.37802 × 10-1	a <sub>2</sub> 1.11426 × 10 <sup>-2</sup>	a3 2.04372 × 10-4	a₄ 1.91021×10− <sup>6</sup>	a5 1.56275 × 10 <sup>-8</sup>	a <sub>6</sub> 1.99046 × 10 <sup>-10</sup>	a7 -1.23039 × 10 <sup>-12</sup>
bo							
4.67351 × 10 <sup>1</sup>	4.60019	8.68387 × 10-3	-4.65719×10 <sup>-3</sup>	9.32789×10 <sup>-5</sup>	2.06031 × 10 <sup>-6</sup>	-4.78943×10 <sup>-8</sup>	2.37537 × 10 <sup>-10</sup>
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So, using these a and b values, we can get the water content in sweet natural gas and this is the reference.

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Now, there is another method Bukacek, this is also quite popular method and here we have these in this method, we have this various expressions and here, we are generally not using any kind of parameters, they are coming basically from the reduced temperature with respect to the critical temperature of water. So, this tau is defined as 1 minus T r w that is a reduced temperature with respect to the critical temperature of temperature pressure of water and we are using the only the critical temperature of temperature pressure of water and water.

So, this is again the range of validity for temperature pressure for this Bukacek method. Now after learning about the sweet natural gas, we go to the sour natural gas.

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Analytical methods for sour natural gas
<ul> <li>✓ <u>Maddox's component contribution model</u></li> <li>✓ Correlations corrected by equivalent mole fraction: <u>Robinson's H<sub>2</sub>S model</u></li> </ul>
<ul> <li>Correlations incorporating acid gas effect on the physical properties</li> <li>Based on the calculation of phase equilibrium in water-hydrocarbon- acid gas system</li> </ul>
<ul> <li>Do not require the estimation of the water content in sweet natural gas in advance.</li> <li>Most commonly used :<u>Wang et al. method</u></li> </ul>
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We have to see that what kind how these things are again modified. So, first, we have again, I have given only a few popular methods, first, we use the Maddox's component contribution method.

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Maddox's component contribution model					
$\checkmark$ Assumes water content in sour natural gas as the sum of the contributions by sweet natural gas, $\rm H_2S$ and $\rm CO_2.$					
✓ Thus the water content is given by $W_{H_2O,sour} = W_{HC,sweet} + Y_{CO_2}W_{CO_2} + Y_{H_2S}W_{H_2S}$					
Where subscripts 'HC' and 'sour' refer to hydrocarbons and sour natural gas respectively.					
All $W_{ m H_{2}O}$ in mg/sm $^3$ , pressure in MPa, and temperature in K.					
✓ Also,					
$\log W_{\rm NHC} = a_0 + a_1 \log P + a_2 (\log P)^2$					
Where NHC stands for $H_2S$ and $CO_2$ .					
✓ The coefficients can be obtained from this <u>table</u>					
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In this method, we have we it is assumed that the water content in the sour natural gas as the total contribution due to the presence of the H 2 S and the CO 2, these the acid gases are present.

And then what we do that the water content is given by this expression in this HC represents the hydrocarbons and we have the CO2 and the H2S and in this the WH2O, this the water content is given in terms of milligram per standard meter cube a pressure is given in terms of the Mega Pascal and temperature in give in terms of the Kelvin whenever you are using any kind of correlation, you have to understand that you have to stick to the kind of units the correlation has been developed with.

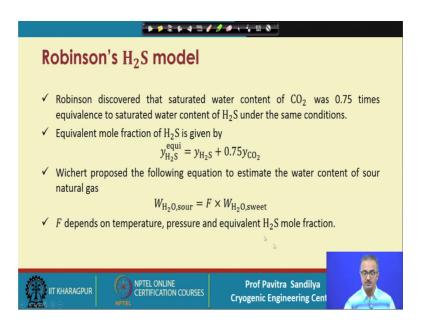
So, and this is the for the long hydrocarbon thing that this is the expression which is given in terms of the pressure.

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T/K		CO2		T/K		H <sub>2</sub> S	
	ao	aı	a2		ao	aı	a2
99.8167	2.202797	-1.058120906	0.3427	299.8167	2.314489	-0.678582201	0.3004
10.9278	2.496936	-1.036484877	0.3103	310.9278	2.544338	-0.70422576	0.3046
27.5944	2.930297	-0.990489109	0.2400	327.5944	2.890856	-0.799408896	0.3319
14.2611	3.18733	-0.924518418	0.2139	344.2611	3.241253	-0.896948037	0.3646
-	-	-	-	377.5944	3.773303	-1.030222461	0.4232
_	_	-	_	410.9278	4.277016	-1.255345485	0.4897

And from this table, we can get the values of these various parameters which are there in the particular correlation a 0, a 1, a 2 for both carbon dioxide and H2S for various types of temperatures. Now after this, the method we have another method which is the Robinson's H2S model because why this H2S1, this call because in this case, the total carbon dioxide and H2S are given in terms of H2S ok.

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So, and Robinson said that the saturated water content of CO2 is about 0.75 times of the content of the H2S under the same condition with this, what is these the equivalent H2S

mole fraction he proposed as the actual H2S mole fraction plus 0.75 of Y CO2 and then he took the Wichert proposed this kind of an expression Wichert is another chart when proposed in this sour natural gas content is given by the sweet natural gas content multiplied by some factor F and this F depends on the temperature pressure and the equivalent H2S mole fraction.

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Robinson's H <sub>2</sub> S model		
✓ Mohammadi F-factor $F = 1 + y_{H_2S}^{equi} \left[ -0.03185 \frac{T}{T_0} - 0.01 \right]$	$538 \frac{TP}{T} + 0.0272 \frac{P}{T}$	
$T_0$ and $P_0$ are reference temperature (273.15 respectively.	-0-0	
✓ It is applicable for $310 \le T \le 420$ K and 0	0.5 < <i>P</i> < 35 MPa	
<ul> <li>To be used with McKetta-Wehe chart or n</li> </ul>	nodified ideal model.	
	<b>—</b>	
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Now, with this Mohammadi gave this expression for the F in terms of the equivalent H2S mole fraction and the some temperature pressure and T 0 P 0 are the reference temperatures given by this value 273 K that is about 0 degree centigrade and reference pressure is 0.01 Mega Pascal; that is about 0.1 bar and this is applicable for this temperature and this pressure ranges and this use the McKetta Wehe chart or the modified ideal model.

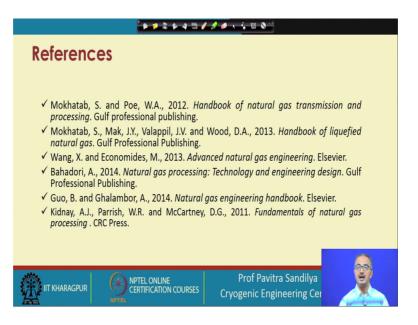
Now, lastly we this particular correlations are there that which are affected by the gas and they are based on some calculation of the water hydrocarbon acid gas system and they do not require the estimation of water content in sweet natural gas in advance. So, this is a another one, in this, we have another correlation in this in this kind of correlations we do not need to know the sweet natural gas water content as was required in case of Maddox and in Robinson, here we go to Wang method.

(Refer Slide Time: 22:30)

► > 2 + 4 = 4 3 0 + 1 = 0			
Wang et al. method			
Water content in sour natural gas(mg/Sm <sup>3</sup> ), $W_{\text{H}_2\text{O},\text{sour}} = 761900.42 \frac{(P_{\text{wsour}}^{\text{ess}} - 1-y_{\text{H}_2} - y_{\text{H}_2} - y_{\text{CO}_2})}{p - P_{\text{wsour}}^{\text{ess}} (1-y_{\text{salt}} - y_{\text{H}_2} - y_{\text{CO}_2})}$			
$P_{\rm w}^{\rm sat} = P_c \exp\left[f(T_r)\left(1 - \frac{1}{T_r}\right)\right]$			
$f(T_r) = 7.21275 + a[0.745 - T_r]^2 + b[0.745 - T_r]^c$			
Where $T_r$ is the reduced temperature of water = $\frac{T}{T_c}$			
$T_c$ is the critical temperature of water (647.3 K)			
$P_c$ is the critical pressure of water (22.12 MPa)			
If T < $T_c$ , $a = 4.33$ , $b = -185$ , $c = 5$ , else $a = 3.981$ , $b = 1.05$ , $c = 3$ .			
$P_{ m wsour}^{ m sat}$ is the saturated vapor pressure of the water in the sour natural gas			
$y_{\rm H_2O}, y_{\rm CO_2}$ and $y_{\rm salt}$ are mole fraction of $\rm H_2O$ , $\rm CO_2$ and salt in the natural gas respectively			
Reference : Wang, J.Q., 1994. The simple method of calculating water content in natural gas. Chem. Eng. Oil Gas 23, 192–193			
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And in this, we find that this is the type of correlations which is given in terms of the salt content the co two content and we have also H2O here and; that means, we have to have a iterative solution and here we have the expression for the Pw sat in terms of the critical pressure and this is the function f T r, which is there in this and this is given in terms of the reduced temperature and this critical temperature and pressure of water are given like this.

So, with this, we can use this particular expression to find out the sour the water content in the sour natural gas and these are range of applicability and whatever expressions with this in this a b and c are there. So, these are given by these values and if t is less than T c, we have one set of a, b, c and if it is more than T c, then we have another set of a, b, c and this particular reference is there which gives this particular expression. Now after this, we find that we have taken all the relationships which are necessary to know the water content for the sweet and sour natural gas. So, we have broadly looked into the two methods one is based on the chart and another based on some analytical models. (Refer Slide Time: 23:57)



And these are the references from which you can consult for further detail.

Thank you.