Learning Objectives

This section will cover the following learning objective:

✓ Estimate the water content of sweet and sour natural gas
Operational Concerns

Water in natural gas is a concern because:

- Liquid water aides in corrosion.
- Liquid water may cause hydrates to form at room temperature (hydrates can be thought of as dirty ice that burns).
- Liquid water can freeze to ice at cold temperatures.

Water Content of Sweet Natural Gas

- The saturated water content of natural gas depends on temperature (T), pressure (P) and composition.
- Generalized pressure-temperature correlations can be used for sweet, lean natural gas.
  - Chart accuracy is between 6% and 10%, which is probably more accurate than the underlying data used to develop the correlation.
Water Content of Sweet, Lean Natural Gas (SI Units)

Constant Pressure Curves
Water Content

Is water content more sensitive to changes in temperature or pressure? Let's work this together by filling in the following Table in SI units:

<table>
<thead>
<tr>
<th></th>
<th>5 MPa (725 psia)</th>
<th>10 MPa (1450 psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 C (86 F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 C (104 F)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water Content

- Water content is very sensitive to temperature
- The effect of pressure on water is much less

<table>
<thead>
<tr>
<th></th>
<th>5 MPa (725 psia)</th>
<th>10 MPa (1450 psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 C (86 F)</td>
<td>800</td>
<td>500</td>
</tr>
<tr>
<td>40 C (104 F)</td>
<td>1300</td>
<td>840</td>
</tr>
</tbody>
</table>
Learning Objectives

This section has covered the following learning objective:

☑ Estimate the water content of sweet natural gas
What Are Hydrates and How They Are Formed

Learning Objectives

This section will cover the following learning objective:

☑ Describe what are hydrates and how they are formed
  - System temperature
  - System pressure
  - The presence of water-saturated gas
  - The composition of the gas stream
Hydrate Formation

- Hydrates are composed of light hydrocarbon molecules (plus CO₂, H₂S and N₂) and water.
- Hydrates can form at temperatures well above the freezing point of water.
- Hydrate formation temperature depends on the gas composition and pressure.
- Hydrates typically form when liquid water is present in the system however this is not a requirement.
- The gas must be water saturated to form hydrates.

Hydrate Formation

- Hydrates consists of a lattice that traps molecules.
- The lattice is formed by water molecules, which are connected by hydrogen bonds.
- The molecules that build the lattice are called "host" molecules.
- The cage structures in the lattice are occupied or filled by "guest" molecules.
- The molecules that fill the lattice are primarily light hydrocarbons.
- Hydrates can form at temperatures well above the freezing point of water and can block the flow through pipelines and process equipment.
Schematic of Natural Gas Hydrate Lattices

Structure I (8 gas molecules + 46 water molecules)
- Radius \( \approx 4.3 \text{ Å} \)

Hydrate Features:
- \( \text{N}_2 \)
- \( \text{CO}_2 \)
- \( \text{H}_2\text{S} \)
- \( \text{CH}_4 \)
- \( \text{C}_2\text{H}_6 \)
- \( \text{C}_3\text{H}_8 \)
- \( \text{tC}_4\text{H}_{10} \)
- \( \text{nC}_4\text{H}_{10} \)
- \( \text{C}_7\text{H}_{16}^* \) (Nonane)
- \( \text{C}_8\text{H}_{18}^* \) (Cyclooctane)

Stabilized by:
- Methane
- Ethane
- Carbon dioxide
- Hydrogen sulfide

Structure II (24 gas molecules + 136 water molecules)
- Radius \( \approx 4.7 \text{ Å} \)

Structure H (6 gas molecules + 34 water molecules)
- Radius \( \approx 5.7 \text{ Å} \)

*Form structure H only
Schematic of Natural Gas Hydrate Lattices

- Stabilized by:
  - Methane
  - Hydrogen sulfide
  - Propane
  - Iso-butane

Structure I (8 gas molecules)

Structure II (24 gas molecules + 136 water molecules)

Structure H (6 gas molecules + 34 water molecules)

Hydrate Features:

- N₂
- CO₂
- H₂S
- CH₄
- C₅H₁₂
- C₆H₁₄
- nC₆H₁₄
- C₇H₁₆
- Cyclohexane
- Cycloheptane

Radius

Structure I: Radius ≈ 4.3 Å
Structure II: Radius ≈ 5.7 Å
Structure H: Radius = 5.7 Å

*Form structure H only
Gas Hydrates

- Potential Hydrate Deposition Locations
  - Pipelines / Flowlines
  - Wellbores
  - Process piping
  - Heat exchangers
  - Expansion devices
    - Valves, expanders
  - Separator internals
Hydrate Forming Conditions for Natural Gas Components

Phase Behavior of Propane Water System
This section will cover the following learning objectives:

- Describe what are hydrates and how they are formed
  - System temperature
  - System pressure
  - The presence of water-saturated gas
  - The composition of the gas stream
Hydrate Formation Temperature

This section will cover the following learning objectives:

- Estimate the hydrate formation temperature of a natural gas stream

Note:

- The methods discussed in this lesson are based on the measurement of the hydrate melting point.
- The hydrate melting point is also called the hydrate dissociation point.
- The actual hydrate formation temperature will be lower than the hydrate dissociation temperature.
- The accuracy of all these correlations, including computer simulations, is at best +/- 1°C (2°F).
Estimating the Hydrate Formation Temperature

- Hydrate Formation Temperature (HFT) as a function of pressure and relative density
- Empirical Correlations (developed based on empirical data)
  - Katz Method
  - Treckell-Campbell Method
  - The McLeod-Campbell Method
- Equation of State (EOS) correlations
- The Baille and Wichert Method

Conditions for Formation of Natural Gas Hydrates
Guided Exercise

- Estimate the hydrate formation temperature of a sweet, lean natural gas with a relative density of 0.7 at 6.9 Mpa (1000 psia).

Solution (In SI Units)

Conditions for Formation of Natural Gas Hydrates

ROT: The HFT of a typical natural gas stream at 69 bar [1000 psia] is 18 °C [65 °F]
Solution (In FPS Units)

Conditions for Formation of Natural Gas Hydrates

ROT: The HFT of a typical natural gas stream at 69 bar [1000 psia] is 18°C [65°F]

The Impact of N₂, Acid Gases and Light Hydrocarbons on the Sweet Gas Hydrate Formation Curve

Temperature, °C

Pressure, kPa

Component | N₂ | CO₂ | H₂S | CH₄ | C₂H₆ | C₃H₈ | IC₄ | nC₄ | IC₅ | nC₅ | C₆ | C₇ | H₂O | Total
--- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | ---
Mol % | 0.031 | 0.000 | 0.000 | 85.620 | 7.886 | 3.758 | 0.595 | 0.785 | 0.372 | 0.220 | 0.127 | 0.486 | 0.121 | 100.0

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Learning Objectives

This section has covered the following learning objective:

✓ Estimate the hydrate formation temperature of a natural gas stream
This section will cover the following learning objectives:

- Hydrates can only form when the gas is saturated with water
- Injecting chemicals can inhibit hydrate formation
- Chemical inhibitors:
  - Thermodynamic inhibitors
  - Low Dosage Hydrate Inhibitors (LDHI)
Hydrate Prevention Options

- Dehydrate the gas.
- Maintain gas temperature above the hydrate formation temperature.
- Maintain the gas pressure below the hydrate formation pressure.
- Inject chemical inhibitors.
  - Thermodynamic (equilibrium) inhibitors
    - Monoethylene glycol (MEG)
    - Methanol (MeOH)
  - Low Dosage Hydrate Inhibitors (LDHIs)
    - Kinetic
    - Anti-agglomerate

Thermodynamic Inhibitors in Pipelines

- Lower hydrate formation temperature
- Does not lower hydrate formation temperature
General Hydrate Formation Characteristics of a Gas Mixture

- **P<sub>op</sub>** vs. **T<sub>cold</sub>**
- **Hydrate Curve**
- **Hydrocarbon Bubble Point Line**
- **Hydrocarbon Dewpoint Line**
- **Water Dewpoint Line**

Points:
- C
- G
- F
- H
- E

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Hydrate Depression vs. Inhibitor Concentration in Mol%, Comparison of Correlation and Data

- Pipelines typically have hydrate depression points at or below 20°C or 36°F
- The hydrate depression in a gas processing facility is often higher
- The Neilsen-Bucklin equation would provide more accurate results for hydrate depressions greater than 20°C or 36°F
Mass Flow of Inhibitor Solution

- This equation allows us to calculate the mass flow of inhibitor solution \( m_i \).
  - The mass of lean liquid inhibitor available to combine with the free water in the system.
- It does not account for losses due to vaporization or solubility in liquid hydrocarbons.

\[
m_i = m_W \left( \frac{X_R}{X_L - X_R} \right)
\]

- Mass Flow of Liquid Water in Kilograms per Day
- Rich Inhibitor Concentration in Weight Percent
- Lean Inhibitor Concentration in Weight Percent
- Mass Flow of Inhibitor Solution
Methanol Losses to Hydrocarbon Vapor Phase

- Methanol partitions to vapor phase because of its high vapor pressure compared to water
- Thermodynamic inhibitors must be in the liquid phase to depress the hydrate point

<table>
<thead>
<tr>
<th></th>
<th>Vapor Pressure at 20 °C, kPa</th>
<th>Vapor Pressure at 68 °F, psia</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>12.8</td>
<td>1.876</td>
</tr>
<tr>
<td>Water</td>
<td>2.3</td>
<td>0.33</td>
</tr>
<tr>
<td>MEG</td>
<td>0.0075</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

Summary of Results Lean and Rich Inhibitor Concentrations

<table>
<thead>
<tr>
<th></th>
<th>SL</th>
<th>X_L, wt%</th>
<th>X_R, wt%</th>
<th>m_i, kg/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>100</td>
<td>23</td>
<td></td>
<td>51.4</td>
</tr>
<tr>
<td>MEG</td>
<td>80</td>
<td>39</td>
<td></td>
<td>164</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>FPS</th>
<th>X_L, wt%</th>
<th>X_R, wt%</th>
<th>m_i, lbm/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>100</td>
<td>23</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>MEG</td>
<td>80</td>
<td>39</td>
<td></td>
<td>343</td>
</tr>
</tbody>
</table>
Summary of Results when Vapor Losses are Accounted for

### SI

<table>
<thead>
<tr>
<th></th>
<th>X_L, wt%</th>
<th>X_R, wt%</th>
<th>m_L kg/d</th>
<th>Vapor Losses kg/d</th>
<th>Total Inj. Rate Kg/d</th>
<th>m^3/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>100</td>
<td>23</td>
<td>51.4</td>
<td>98.6</td>
<td>148.2</td>
<td>0.19</td>
</tr>
<tr>
<td>MEG</td>
<td>80</td>
<td>39</td>
<td>164</td>
<td>Nil</td>
<td>164</td>
<td>0.15</td>
</tr>
</tbody>
</table>

### FPS

<table>
<thead>
<tr>
<th></th>
<th>X_L, wt%</th>
<th>X_R, wt%</th>
<th>m_L lbm/day</th>
<th>Vapor Losses lbm/day</th>
<th>Total Inj. Rate lbm/day</th>
<th>gpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>100</td>
<td>23</td>
<td>108</td>
<td>212.8</td>
<td>320.8</td>
<td>0.034</td>
</tr>
<tr>
<td>MEG</td>
<td>80</td>
<td>39</td>
<td>343</td>
<td>Nil</td>
<td>343</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Density of MEG = 1100 kg/m^3 (9.19 lbm/US gal)
Density of MeOH = 800 kg/m^3 (6.64 lbm/US gal)

Liquid-Liquid Distribution Ratios for Methanol and Hydrocarbons

Distribution of methanol between aqueous and hydrocarbon phases, data from various sources. Hydrocarbon phases includes various alkane and cycloalkane compounds. Data shows the variation of distribution with changes in the amount of toluene in the hydrocarbon phase.
Freezing Points of MEG-Water Solutions

Note: Shaded region represents range of experimental data where freezing may have been observed.
Methanol or MEG?

- Applications that require continuous injection typically use MEG. MEG can easily be regenerated but will only inhibit down to -40°C (-40°F). Per unit volume, it is relatively expensive compared to methanol.

- Methanol is generally used in applications that have intermittent inhibition requirements, such as start-ups or shutdowns, or during periods of cold weather. It can inhibit down to -100°C (-148°F). Methanol contamination in both vapor and liquid hydrocarbon phases is becoming a significant issue.
Learning Objectives

This section has covered the following learning objective:

✓ Describe methods to prevent hydrate formation
This section will cover the following learning objective:

✓ Describe the differences between low dosage hydrate inhibitors (LDHI) and thermodynamic inhibitors
Low Dosage Hydrate Inhibitors vs. Thermodynamic Inhibitors

- LDHIs do not change the equilibrium hydrate formation temperature.
- LDHIs require much lower concentration levels compared to thermodynamic inhibitors.
- Typical concentrations for LDHIs range from 1000 to 10,000 parts per million by weight.
- Thermodynamic inhibitors typically require between 200,000 and 400,000 parts per million by weight.
- Compared to methanol and glycols, LDHI’s lower concentration levels often outweigh their higher unit cost.
- Advantages of LDHIs include lower inhibitor losses, reduced capital and operating costs, and lower toxicity.
Kinetic Hydrate Inhibitors (KHIs)

- KHIs inhibit hydrate formation by significantly reducing the rate of hydrate formation. They do not change the equilibrium hydrate formation temperature.
- KHIs are currently limited to about 15.5°C (28°C) subcooling. The amount of subcooling required to form hydrates is time dependent. KHIs are most effective in systems where the fluid residence time is short.
- KHIs are not effective in pipelines that are shut down if the pipeline temperature is below the hydrate formation temperature.
- KHIs can be used in combination with methanol or glycol. The thermodynamic inhibitor reduces the equilibrium hydrate formation temperature and the KHI provides additional hydrate suppression by increasing the subcooling.
Hydrate Prevention with Thermodynamic Inhibitor

Thermodynamic Equilibrium Inhibitors (MEG and Methanol) lower hydrate formation temperature by freezing point depression.
Antiagglomerant Inhibitors (AAs)

- Allow hydrates to form, but keep them suspended in the hydrocarbon liquid solution.
- Were developed to extend the range of subcooling beyond the capabilities of KHIs.
- May not be effective in systems that have high water cuts.
- Can perform for longer periods of non-flowing conditions compared to KHIs.
- Can achieve subcooling greater than 22 °C (40 °F).
Hydrates Prevention with LDHIs

**Advantages/Disadvantages of LDHIs**

**ADVANTAGES**
- Injection of small amount of chemical compared to thermodynamic inhibitors.
- No regeneration required.
  - Reduce CAPEX and OPEX, particularly on offshore installations

**DISADVANTAGES**
- Compatibility with other production chemicals could be an issue.
  - Corrosion inhibitors, demulsifiers, scale inhibitors, wax inhibitors
  - Must test chemical compatibility before selecting an LDHI
- High unit cost compared to thermodynamic inhibitors.
- Cannot inhibit below 0 °C (32 °F).

*Note*: Table 6.5 in the PetroCore reference book, Gas Conditioning and Processing, shows a comparison of KHIs and Aas.
This section has covered the following learning objective:

☑ Describe the differences between low dosage hydrate inhibitors (LDHI) and thermodynamic inhibitors

---

PetroAcademy™ Gas Conditioning and Processing Core

- Hydrocarbon Components and Physical Properties Core
- Introduction to Production and Gas Processing Facilities Core
- Qualitative Phase Behavior and Vapor Liquid Equilibrium Core
- **Water / Hydrocarbon Phase Behavior Core**
  - Thermodynamics and Application of Energy Balances Core
  - Fluid Flow Core
  - Relief and Flare Systems Core
  - Separation Core
  - Heat Transfer Equipment Overview Core
  - Pumps and Compressors Overview Core
  - Refrigeration, NGL Extraction and Fractionation Core
  - Gas Dehydration Core
  - Contaminant Removal (Dehydration and Sweetening) Core