In order to understand the chemistry of natural gas, it is important to be familiar with some basic concepts of general chemistry. Here are some definitions you should know:

**Matter** - anything that has mass and occupies space.

**Energy** - the capacity to do work or transfer heat.

**Elements** - substances that cannot be decomposed into simpler substances by chemical changes. There are approximately 112 known elements. Examples: carbon, oxygen, and nitrogen.

**Atom** - the smallest unit in which an element can exist. Atoms are composed of electrons, protons, and neutrons.

**Compounds** - pure substances consisting of two or more different elements in a fixed ratio. Examples: water and methane.

**Molecule** - the smallest unit in which a compound can exist or the normal form in which an element exists. Example: One molecule of water consist of two hydrogen atoms and one oxygen atom. One molecule of nitrogen consist of two atoms of nitrogen.

**Mixture** - combination of two or more pure substances in which each substance maintains its own composition and properties. Examples: natural gas, gasoline, and air.

**Bonds**

The attractive forces that hold atoms together in compounds are called chemical bonds. There are two major classes of bonds--ionic bonds and covalent bonds. Most of the bonds involved in natural gas components are single covalent bonds. A single covalent bond consists of a pair of electrons shared by two atoms. A double bond is two pair of electrons shared between two atoms. Some minor components of natural gas may contain both single and double bonds. Aromatic molecules, such as benzene, contain covalent bonds where multiple electrons are shared among more than two atoms.

**States of Matter**

Matter exists mainly in three physical states--gas, liquid, and solid. Solids are rigid and have definite shapes. The volume a solid occupies does not vary much with changes in temperature and pressure. In liquids, the individual particles are confined to a given volume. A liquid flows and assumes the shape of its container. Liquids cannot be easily compressed. Gases are much less dense than liquids and solids. They occupy all parts of any vessel in which they are confined. Gases are capable of infinite expansion and are easily compressed. They consist primarily of empty space because the individual particles are so far apart.

**Units of Measurement**

Quantities of matter can be expressed in a variety of ways depending on the nature of the substance being measured. For example, solids are generally measured by weight while liquids are measured by volume or weight. Gas is most commonly measured in units of volume but can also be measured by weight. The standard unit of volume used in natural gas measurement is a cubic foot corrected to a standard (stated) pressure and temperature. Large volumes of natural gas are usually expressed in units of one thousand cubic feet (Mcf). A million cubic feet is indicated by MMcf. However, when a gas sample is analyzed, the composition is usually expressed in mole percent--the percent (by number) of moles of the particular substance out of the total molecules of the gas. This is roughly equivalent to volume percent. A mole is defined as the amount of a substance that contains the same number of units as the number of atoms in 12 grams of Carbon12 which is 6.022 x 10^23, otherwise known as Avogadro’s number. Therefore, a mole of any element or compound is simply the molecular weight of that substance in grams. For example, the molecular weight of water is 18, so a mole of water is 18 grams and contains 6.022 x 10^23 molecules. Moles are often used in chemistry because they make it easier to keep track of quantities of substances involved in chemical reactions. One mole of oxygen will react with 2 moles of hydrogen to form one mole of water. However, there would be an excess of hydrogen if one gram of oxygen were reacted with 2 grams of hydrogen.
Natural Gas

Natural gas is a mixture of many compounds which can be classified into three major groups—hydrocarbons, inerts, and miscellaneous trace compounds. Hydrocarbons are compounds which contain hydrogen and carbon. Most of the hydrocarbons in natural gas are saturated, meaning that each carbon atom is bonded to four other atoms while each hydrogen atom is bonded to only one carbon atom. This group of compounds is also known as alkanes, paraffins, and aliphatics. The most abundant alkane in natural gas is methane, commonly referred to as C1 because it contains one carbon atom. Next is ethane (C2) with two carbons, followed by propane (C3), iso-butane and normal butane (C4), iso-pentane and normal pentane (C5), and hexanes and heavier hydrocarbons (C6+). The C6+ fraction can contain up to 100 or more compounds including aromatics such as benzene, toluene, ethylbenzene and xylenes (BTEX).

Deposits of natural gas are usually found with petroleum deposits. Most of the natural gas and petroleum being produced today was formed by the decay of plants and animals buried deep within the earth millions of years ago. A small fraction of natural gas is also being produced by the decomposition of residential and commercial waste in landfills.

Petroleum products are complex mixtures of aliphatic and aromatic compounds including sulfur and nitrogen compounds. Some of the most common refined petroleum products include methane gas, natural gas liquid or NGL (the ethane and heavier gas components), liquefied petroleum gas or LPG (mostly propane and butane), gasoline (C5-C10), kerosene (C11-C12), diesel fuel (C13-C17), heating oil (C18-C25), and lubricants (C26-C38). Heavier residues of refining are referred to as asphalts.

In addition to hydrocarbons, natural gas components include the inerts, nitrogen and carbon dioxide, which do not combust. Therefore, they do not contribute to the heating value of the gas, making them undesirable. Trace components commonly include hydrogen sulfide, water vapor, and helium. Hydrogen sulfide is highly toxic and is characterized by a very strong foul odor. It is also referred to as sour gas. Helium is a true inert gas that is nonreactive with other compounds. Most of the nation’s helium production comes from natural gas deposits in Texas. Other less common trace components include oxygen, hydrogen, and carbon monoxide.

Physical Properties

Physical properties are those that can be observed without causing any change in the chemical composition of the specimen. One of the most important physical properties used in the petroleum industry is density. Density is the mass (weight) per unit volume of a substance and may be expressed as specific gravity or relative density. In liquids, the specific gravity is the ratio of the density of the liquid to the density of water. In gases, it is the ratio of the density of the gas to the density of air. The specific gravity of natural gas varies from less than .600 for gas containing mostly methane to greater than 1.000 for gas containing a high percentage of heavy end components.

Other important physical properties of gases include boiling point, hydrocarbon dew point, odor, toxicity, and thermal conductivity. Boiling point is the temperature at which the vapor pressure of a liquid equals the atmospheric pressure. Hydrocarbon dew point is the temperature at which hydrocarbons start to condense from a gas stream. This is important in gas production and transmission because condensation in a natural gas line will lower the capacity of the line to carry gas. Consequently, there will be problems with compressors, dehydrators, and other processing equipment. More importantly, liquids in a gas line make it impossible to accurately measure the gas. The dew point also allows the heavier gases to be liquefied by processing. They are generally more valuable as liquids than gas.

Odorizing is important in gas processing and transportation as a relatively inexpensive way of determining the location of leaks. Unless it contains high concentrations of hydrogen sulfide or other contaminants, natural gas is normally odorless and nontoxic when it comes out of the ground. Nontoxic odorants, such as mercaptans, are added during processing to make it detectable by sense of smell.

Thermal conductivity is the property that enables the detector on a chromatograph to quantify the amount of each component in a gas mixture. Simply stated, it is the ability of a substance to conduct heat. Thermal conductivity usually decreases with increasing particle size. For this reason, helium makes a good carrier gas for gas chromatographs. Its molecules are very small, allowing it to effectively draw heat away from the detector.

Heating Value

The Btu, or British thermal unit, is a measure of the energy produced by burning natural gas. A Btu is equal to the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit at 62° F. The Btu may be expressed as dry, wet, or as delivered. The dry Btu calculation assumes that there is no water vapor in the gas. As might be expected, the wet Btu is calculated on the assumption that the gas is saturated with water vapor at standard conditions (60° F and atmospheric pressure). Hence, the wet Btu is less than the dry Btu. The as delivered or actual Btu is calculated by accounting for the actual amount of water in the gas based on delivery conditions. The Btu factors of the individual components in natural gas increase with the number of carbon atoms. The table in Figure 1 illustrates the Btu of the most common components in natural gas.
The inerts commonly found in gas, carbon dioxide and nitrogen, do not participate in combustion and contribute no heating value or Btu to a gas.

Water vapor, though it does not burn, has a heating value as defined by this industry. Water vapor has a heating value of 50.4 Btu per standard cubic foot.

**Compressibility**

Compressibility is a measure of a real gas’s deviation from ideal gas behavior. Real gases behave like ideal gases at low pressures and high temperatures. Because they deviate significantly at high pressures and low temperatures, the deviation should be accounted for when calculating Btu.

An ideal gas is one that obeys the Ideal Gas Law -- it occupies half its initial volume at twice the initial pressure and twice its volume at twice its (absolute) temperature.

**Reactions and Processes Involving Natural Gas**

Under normal conditions, the hydrocarbon components in natural gas are unreactive because saturated carbons form chemically stable molecules. However, at high temperatures and in the presence of oxygen, alkanes will undergo combustion, giving off heat in the process. This capacity to produce heat, otherwise known as heating value, is what makes natural gas and crude oil two of the most precious energy sources in the world. The two major by-products of combustion, water vapor and carbon dioxide, also occur naturally as individual compounds.

Other reactions and processes include corrosion, hydrate formation, and condensation. Corrosion is the process in which metals are oxidized in the presence of moisture or some other corrosive agent such as carbon dioxide or hydrogen sulfide. The degree of corrosion in pipelines can be significantly reduced by removing these components from the gas during production. The removal of water vapor (dehydration) is commonly accomplished by bubbling the gas stream through a vessel containing a chemical, such as glycol, which has an affinity for water. Similarly, carbon dioxide and hydrogen sulfide are removed by passing the gas through chemicals, such as amine, that have an affinity for each of them.

Natural gas hydrates are solids that form from natural gas molecules and water. The water molecules form a honeycombed structure with a molecule of one of the natural gas components occupying each void. Because these solids are denser than water ice, their formation is favored at higher pressures. They are favored so much to the extent that natural gas hydrates may form at temperatures up to 70º F. Like liquids, they interfere with the flow of gas and cause operational problems. One of the places hydrates often form is in the sensing lines to the orifice recorder. When formed in these lines, hydrates cause incorrect recording of the differential pressure. This is what is often called meter freeze and is a major cause of measurement errors.

**Gas Laws**

Accurate measurement of natural gas must take into account a variety of gas laws involving relationships between temperature, pressure, and volume. Pressure is defined as force per unit and is commonly expressed in a variety of ways including psi, atmospheres, bars, mm of Hg, inches of water, and pascals. The quantitative relationship between volume and pressure is summarized by Boyle’s Law which states that the volume of a sample of gas varies inversely with the pressure under which it is measured, given a constant temperature. If the pressure is doubled, the volume is reduced by half. If the pressure is cut in half, the volume is doubled. Charles’ Law states that the volume of a sample of gas varies directly with the absolute temperature, given a constant pressure. Absolute temperature is measured in degrees Kelvin and starts with absolute zero, representing a complete absence of heat. Thus, on the Kelvin scale, the freezing point of water is 273ºK and on the Celsius scale, absolute zero is -273ºC. If the absolute temperature of a gas is doubled, its volume will double. Combining Boyle’s Law and Charles’ Law results in a single expression known as the Combined Gas Law Equation:

Boyle’s Law \[ P_1V_1 = P_2V_2 \]

Charles’ Law \[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]

Combined Gas Law \[ P_1V_1/T_1 = P_2V_2/T_2 \]

Based on Avogadro’s Law, equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. A standard molar volume of an ideal gas is 22.4 liters per mole at STP (standard temperature and pressure, 0ºC and 1 atm.).

According to the kinetic theory, gas pressure is caused by molecular collisions with the walls of the container. Therefore, the larger the number of molecules per unit volume, the greater the number of collisions and the higher the pressure. The average kinetic energy of the molecules is also proportional to the absolute temperature.

While the molecules are at rest at absolute zero, at high temperatures, the molecules move at increasing speeds resulting in higher pressures. Combining these concepts into one equation produces what is known as the ideal gas equation:

\[ PV = nRT \]

where \( P \) = pressure (atmospheres)
\( V \) = volume (liters)
\( N \) = number of moles
\( R \) = the ideal gas constant (0.08206 liter atm/K mol)
\( T \) = temperature (degrees Kelvin)
**Conclusion**

Natural gas measurement and processing is based largely upon the fundamental principles of chemistry and physics. The intent of this presentation was to bring forth some of the basic concepts helpful to personnel involved in the industry.

**Figure 1**

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Name</th>
<th>Btu @14.696 psia and 60°F</th>
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<td>Methane</td>
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<td>Ethane</td>
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