# FUNDAMENTALS OF GAS MEASUREMENT I

Class 1140

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## INTRODUCTION

To truly understand gas measurement, a person must understand gas measurement fundamentals. This includes the units of measurement, the behavior of the gas molecule, the property of gases, the gas laws, and the methods and means of measuring gas. Since the quality of gas is often the responsibility of the gas measurement technician, it is important that they have an understanding of natural gas chemistry.

## NATURAL GAS CHEMISTRY

It is believed that the word gas was derived from the Greek work "chaos". If this is true, then it is an applicable word. The molecules of gas are indeed in a chaotic state. But what is a gas molecule? To understand this, let us first examine matter.

Matter is anything that possessed mass and occupies space. It is made up of elements and compounds of elements.

Types of Matter:

Element **-** An element is the simplest form of matter. An element is matter that cannot be further decomposed by ordinary means and thus is the simplest form in which matter can exist. The universe is made of elements or combinations of elements. New elements are discovered by scientist from time to time. You may ask, what is different about each of the elements other than the fact that some exist at standard temperature and pressure as gas, a liquid or as a solid. What is the basic distinguishing feature of each element? The thing that differentiates elements is the structure of their atom. Table 1 shows the most abundant elements found in the earth's crust.

TABLE 1

| **Element** | **Percent** |
|---|---|
| Oxygen | 49.2 |
| Silicon | 25.7 |
| Aluminum | 7.5 |
| Iron | 4.7 |
| Calcium | 3.3 |
| Sodium | 2.6 |
| Potassium | 2.4 |
| Magnesium | 1.9 |
| Hydrogen | 0.9 |
| Titanium | 0.6 |
| All Others | 1.2 |

Atom **-** An atom is the smallest part of an element which can be divided and still retain all the properties of that element. The atom is the smallest unit of matter, which can enter into combination with itself, or atoms of other elements.

An atom consists of three basic particles: electrons, protons and neutrons. The proton is a particle consisting of a positive (+) electrical charge located in the nucleus of the atom. Also located in the nucleus is the neutron, which is a particle with no electrical charge. The electron is a particle consisting of a negative (-) electrical charge located in various orbits and rotating around the nucleus of the atom. The proton and neutron have essentially the same weight. The electron is much smaller, weighing approximately 1/1848 times as much as the proton. Although the electron is smaller in mass than the proton, it exerts an equal but opposite electrical charge.

The atom has three important characteristics:

1. All atoms contain the same number of electrons as they have protons; therefore, all atoms are electrically neutral.

2. Each element has an atomic number, which indicates the number of protons as well as the number of electrons in the atom.

3. Each atom has an atomic weight, which approximates the number of protons plus the number of neutrons in the atom. The electron can be considered weightless as compared to the other two particles. Nearly all the weight of the atom is concentrated in the nucleus. Atomic weights are relative weights of one atom to another. For example, oxygen, with an atomic weight of 16, is four times heavier than helium, with an atomic weight of 4, and is about one-half the weight of sulfur which has an atomic weight of 32.

All of the elements have different atomic structures. What makes the atomic structures different is the varying numbers of protons and neutrons in the nucleus and the electrons orbiting the nucleus. For example, carbon has six protons and six neutrons in the nucleus. It has six electrons orbiting the nucleus with two electrons in the first orbit and four in the second orbit. Nitrogen has just one more of each particle in its atomic structure, namely, seven electrons, seven protons, and seven neutrons, but carbon is a solid while nitrogen, under normal pressure and temperature conditions, is a gas.

Molecule - A molecule is the smallest portion or unit of matter formed by the combination of atoms. This can be a combination of two atoms of the same element such as the diatomic molecules oxygen and nitrogen.

Compound - A compound, which is a more complex form of matter, is made up of chemically combined elements. The molecules of compounds are identical to each other in composition and properties. Typical compounds are methane, carbon dioxide, sodium chloride (salt) and water.

Mixture - Mixtures are two or more elements or compounds that are combined physically but still maintain their chemical identity. There is no chemical reaction involved. A mixture can always be physically separated into its component parts. Examples of common mixtures are natural gas, air, oil, coal, brass or any alloy.

VALENCE OF ELEMENTS

Elements form compounds through sharing of electrons in their outer orbit. The number of electrons of an element involved in forming a compound is the valence number. Elements have a tendency to lose or gain electrons in the outer orbit of their atom to form ions. An ion is an electrically charged particle of an atom. When the atom gains or loses electrons in an outer orbit and becomes an ion, it changes its properties it possessed as an atom. Those atoms that lose one, two, or three electrons (usually metallic elements) become positively charged or form positive ions. Those atoms that gain one, two, or three (usually non-metals) become negatively charged or form negative ions. The atoms with four electrons can gain, lose or share their electrons.

An atom such as sodium can lose its single electron in the outer orbit of its atom, thus forming a positive ion. While sodium loses its electron, another atom must gain this electron. For example, a chlorine atom, which has seven electrons in its outer orbit, can gain the electron that sodium loses, thus becoming a negative ion. The positively charged sodium ion and the negatively charged chlorine ion attract each other to form the compound, sodium chloride or salt. This union of atoms is formed by a polar or electrovalent reaction, which is one method of forming compounds. Electrovalent unions form most compounds in nature. It is interesting to note that atomic sodium or molecular chlorine are toxic elements. In the compound form of $NaCl$ (salt), it is commonly a non-toxic food additive.

Another method of forming compounds is a covalent or a non-polar reaction in which the atoms share electrons, thus forming nonpolar or covalent unions. A classic example of a covalent reaction is when carbon, which has four electrons in its outer orbit, shares each of its electrons with four hydrogen atoms, each of which have one electron.

This satisfies the carbon atom, which is seeking four electrons, and the four hydrogen atoms, each of which are seeking one electron to complete its outer orbit. This union of one carbon and four hydrogen atoms forms the compound methane ($CH_4$). Most atoms, such as hydrogen, oxygen, nitrogen, chlorine, etc. share their electrons with a similar atom to form elemental gases of hydrogen ($H_2$), oxygen ($O_2$), nitrogen ($N_2$) and chlorine ($Cl_2$).

## STATE OF MATTER

Matter exists in three physical states. These are as a solid, liquid or gas. Temperature and pressure are factors that influence the physical state of matter. For example, water can exist at normal atmospheric pressure in each of these forms. Other compounds such as carbon dioxide exist as a gas in nature but also can take the form of a solid known as dry ice.

Solid - A solid is rigid and bounds itself internally in all dimensions. Solids do not require a container for retention of their shape. Copper is an example of element that exists naturally as a solid.

Liquid - Liquids are bound by one internal boundary, which is the surface. A liquid fills a container below its surface in the shape of the container. Bromine and mercury are examples of elements that are liquids.

Gas - Gases have no internal boundaries. They will expand to fill a container or a confining wall. Oxygen and Nitrogen are examples of elements that typically exist as gases in our atmosphere.

## HYDROCARBONS

Hydrocarbons - Hydrocarbons are compounds made up of carbon and hydrogen and typically exist as either gases or liquids at atmospheric conditions. The most common type of hydrocarbons are those present in oil and natural gas. This family of hydrocarbons is known as the saturated or paraffin series.

The paraffin hydrocarbons are characterized by their carbon to carbon single bond. Methane ($CH_4$) has a molecular weight of 16 and is the lightest member of this family and is the main component of natural gas. The next heaviest paraffin is ethane ($C_2H_6$) which has two single bonded carbon atoms. Additional carbon atoms bond to form heavier compounds such as propane, normal butane, iso-butane, normal pentane, iso-pentane, hexanes, heptanes, octanes and heavier hydrocarbons such as waxes. In natural gas the propane and butanes are typically called the LPGs and the pentanes and heavier the GPM (gallons per thousand) gasoline fraction.

Gas Quality - Often the terms hydrocarbon dew point or water vapor content are used to describe the pipeline quality of a gas mixture. The hydrocarbon dew point or water vapor dew point is the pressure and temperature at which the gas begins to form liquids. The dew point of a gas mixture is dependent on its molecular composition, pressure and temperature and can change with operating conditions. Under certain operating conditions hydrates may form in operating equipment. Hydrates are frozen mixtures of hydrocarbons and water and can plug up gathering systems and pipelines. In addition, oil or gas production may contain naturally occurring contaminants such as carbon dioxide, nitrogen, sulfur, hydrogen sulfide, paraffin, water or metals.

## THE KINETIC THEORY OF GAS

Behavior of the Gas Molecules - To better understand the gas laws and the fundamentals of gas measurement, a person should understand the behavior of the gas molecule. Air is made up of a mixture of gas molecules consisting essentially of nitrogen and oxygen which is everywhere in the earth's atmosphere. Gas molecules are all around us. A cubic centimeter of air or any gas at standard temperature and pressure conditions contains about twenty-six billion billion molecules; there is a large amount of frictionless empty space around each molecule. At low pressures the relative size of the space surrounding the molecule is so great that the actual volume occupied by the molecule itself is minimal. The gas molecule is incompressible. Compression of gas is accomplished by bringing the gas molecules closer together in a relatively large empty space occupied by the gas. This is done by adding more molecules or reducing the space occupied by the gas.

Gas molecules are in a chaotic state and continually move in violent motion. They travel in a straight line until they collide with other molecules or a confining wall. All collisions are perfectly elastic; therefore no energy is lost. When these molecules collide with each other, they are diverted in much the same manner as billiard balls when they strike each other on the billiard table.

Exerted Pressure - The pressure exerted by gas depends on how hard and how often the molecules collide with the confining walls. Each time a gas molecule collides with a confining wall it exerts a force. The sum of these forces at any given moment is the pressure exerted. The fewer number of gas molecules in a confined chamber the less will be molecular collision with the confining wall thus the lower will be the exerted pressure. The more molecules in a confined volume, the greater will be the number of molecular collisions and thus the larger will be the exerted pressure.

Under ideal conditions there is a direct relationship between the number of collisions by a given amount of gas molecules with the confining wall and the pressure exerted. To increase pressure, the number of molecular collisions must be increased. To do this, the number of gas molecules must be increased in a confined volume, such as packing a section of pipe, or the number of molecules can be held constant while the confined space is reduced, as with a piston compressing the gas in a reciprocating engine. To reduce pressure in a confined chamber, gas molecules must be removed from the chamber or the confined volume must be increased for a given number of molecules and this reduces the number of molecular collisions with the confining wall. A regulator valve reduces the number of gas molecules per unit of space in a downstream segment of pipe, thus reducing the gas pressure.

Under ideal conditions the pressure exerted is referred to as kinetic pressure. Actual pressure exerted by gas molecules is seldom the same as the ideal or kinetic pressure. The actual pressure consists of the algebraic sum of the kinetic pressure and a much smaller component called the dynamic pressure. The dynamic pressure is the sum of two deviation forces. One is caused by an attractive force between molecules and the other by a repulsive force between the same molecules. This is illustrated by the following equations:

$P = Pk + Pd$

where $Pd = Pa + Pr$

or $P = Pk + Pa + Pr$

P = Actual pressure exerted by molecules

Pk = Ideal or kinetic pressure

Pd = Dynamic or deviation pressure

Pa = Attractive force between molecules

Pr = Repulsive force between molecules

The attractive force (Pa) between molecules opposes the kinetic pressure translated by the collision of the molecules with the confining walls. This force tends to reduce slightly the momentum of the molecules, which reduces the force of impact between the molecules and confining walls. This reduces the force of impact between the molecules and confining walls. This reduces slightly the pressure that would be exerted under ideal conditions. The greater number of gas molecules in a confined volume the closer the molecules come together, thus producing a larger attractive force. Since this force has a negative effect on the kinetic pressure, with higher pressures the larger will be the deviation force and therefore the less the actual pressure the less the actual pressure exerted from the ideal. To maintain a given actual pressure, more molecules of gas will be required in a confined volume than indicated under ideal conditions. In a confined chamber and at a known absolute pressure and temperature the volume of gas normally calculated will be less than the actual volume, therefore a compressibility factor must be applied to determine the actual volume of gas in the chamber. This factor must also be applied in gas measurement to determine actual volumes of gas being measured.

The attractive force between molecules can best be demonstrated by observing a liquid such as mercury on a flat surface. The mercury tends to form droplets. When these droplets get close enough together they attract each other and combine to form a larger mass of liquid. Although this attractive force is relatively slight in gas compared to the mercury, it does become significant at very high gas pressures.

The repulsive force (Pr) between molecules acts opposite to the attractive force. As gas pressure increases with the larger number of gas molecules in a confined volume, these molecules are brought closer together.

At very high pressure, the molecules get so close together that they begin to threaten each other's occupied space. Since each molecule is compelled to remain outside the space occupied by the others, they exert a repulsive force. The space available for the molecules to move is greatly reduced. The repulsive force thus adds a positive increment to the dynamic or deviation pressure. As pressure increases by introducing more gas molecules in a confined space, the repulsive force reduces the effect of the attractive force, thus reducing the deviation effect. At high enough pressure a point is reached where the repulsive force between molecules equals the attractive force, thus producing ideal conditions where the actual pressure exerted by the molecules is the same as the kinetic pressure.

<u>Effects of Temperature</u> - The higher the temperature, the faster the gas molecules will move. This will cause more collisions between a given number of molecules and thus more collisions with the confining wall. Under constant volume conditions, the pressure will increase. The lower the temperature the slower the gas molecules will move, thus causing fewer collisions between the molecules and the confining walls. Under constant volume the pressure will decrease. An example would be automobile tire pressure changes in the winter and summer.

To maintain constant pressure in a confined space as the temperature increases, gas molecules must be released. As temperature decreases, gas molecules must be introduced to maintain constant pressure. It is interesting to note that at lower temperatures the deviation forces are more pronounced than at higher temperature where they flatten out. At high enough pressure a point is reached where the repulsive force between molecules equals the attractive force, thus producing ideal conditions. For example, at a point between 4000 and 4500 psig at $240^0$F no deviation exists and the gas behaves ideally.

<u>Thermal Energy of Gas Molecules</u> - Energy is the capacity for doing work. Energy may be stored in the form of thermal, mechanical, electrical, chemical, or nuclear energy. Energy may be transferred from one form to another. For example, if a pan of water is heated, its store of thermal energy is increased. If the pan of water is heated with a natural gas flame, the chemical energy is converted to heat or thermal energy as shown by the chemical equation for combustion of methane gas:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 + \text{heat energy}$$

If the same pan of water was heated on an electric stove, electrical energy is transferred to thermal energy. If the electricity used was generated by nuclear means, then the transfer of energy follows the sequence: nuclear to thermal, thermal to electrical and electrical to thermal.

To change the state of matter, thermal energy must be involved. To change a solid to a liquid or a liquid to a gas, thermal energy must be added to the matter involved. To change from a gaseous state to liquid or liquid to solid, thermal energy must be removed from the matter. To better understand this phenomenon, the behavior of the molecules in each of the three states is examined.

1. Gas - Molecules in the gaseous state are free to move unrestricted within a confined space. They move rapidly and in all directions, colliding with each other and the confined wall.

2. Liquid - Molecules in the liquid state are free to move within the liquid body. They do not have unrestricted motion in this confined space because of a strong attraction between molecules. The attractive force in a liquid is much stronger than the attractive force of molecules in a gas.

3. Solid - Molecules in a solid state are in motion, but are very restricted. The motion may be considered more a molecular vibration. The attractive force between molecules is very strong. To change state from solid to liquid, thermal energy is required. When heat is introduced the molecules start vibrating more rapidly in the solid. As the thermal energy increases, the molecular motion increases until a temperature is reached where the boundary walls or cohesion between molecules are broken down. The destruction of these walls requires the store of thermal energy. To change from liquid to a gas, more heat is applied until the single barrier to the molecules, which is the surface of the liquid, is destroyed and the molecules escape the attractive force of surface tension and thus are free to move unrestricted in the confined space. As was indicated earlier when a gas goes from the

gaseous state to the liquid state thermal energy is released. An example of this is when water vapor in the atmosphere is cooled forming water droplets with the release of thermal energy back into the atmosphere.

Avogadro's Law - Avogadro's Law states that equal volume of gases measured at the same temperature and pressure conditions contain the same number of molecules. One gram molecular weight of gas will occupy a volume of 22.4 liters under standard conditions. One mol-volume or molecular weight expressed in pounds at $60^0$F and 14.73 psia occupies a volume of 378.9 cubic feet. Under standard conditions 22.4 liters of any gas contains 6.023 x 1023 molecules, which is Avogadro's number. Expressed in English units, one cubic foot of gas contains 7.61 x 1023 molecules or 761,000 billion billion molecules of the gas. The measurement of gas quantity or volume could be related to the number of gas molecules in a given space or the rate of flow of the gas expressed in the number of molecules per unit of time. Obviously, due to the astronomical numbers involved, the measurement units are expressed in cubic feet or in cubic meters and the rates in cubic foot or cubic meter per unit of time.

Kinetic Energy of Translation - The Kinetic theory was discussed emphasizing the behavior of gas molecules in a confined space. We have learned that the gas molecules are in rapid motion that they collide with each other and with the confining walls. There is a relationship between the size of the gas molecule, its velocity and the kinetic energy of translation.

$$K.\ E. = \tfrac{1}{2} MV^2$$

where

K. E. = kinetic energy (Joules)

M = mass of the molecule (Kilograms)

V = velocity of the molecule (meters/second) $^2$

Under constant temperature and pressure conditions, all gas molecules will translate the same kinetic energy. The heavier gas molecules will travel at a slower velocity while the smaller molecules will travel at a greater velocity. With a given number of gas molecules, both the heavy and light molecules will exert the same pressure. While heavy molecules exert more impact force with a confining wall due to their greater mass, they will travel slower than the lighter molecule, resulting in lesser number of collisions. The lighter molecules have greater numbers of collisions due to their higher velocity, but each impact creates less force.

If the velocity of gas molecules is held constant, then the kinetic energy translated will be directly proportional to the mass of the gas. This relationship is used for determining specific gravity of gas and is the basis for mass and turbine meter measurement.

CONCLUSION

Gas measurement fundamentals are based on principles of chemistry and the physical behavior of matter. This discussion has endeavored to cover the basic principles of chemistry and physics that form the foundation for gas measurement. Knowledge of these principles is fundamental to the understanding of gas measurement.

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