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FUNDAMENTALS OF GAS MEASUREMENT III
Class 1160

Joseph J. Bauer
Spectra Energy
5400 Westheimer Ct.
Houston, TX 77056

INTRODUCTION

To become proficient in all phases of gas measurement, one must fully understand what natural gas is and the theory of its properties. The theories about natural gas properties are the gas laws, and their application is essential to gas measurement. Quantities of natural gas for custody transfer are stated in terms of standard cubic feet. To arrive at standard cubic feet from actual flowing conditions requires application of correction factors that are defined by the gas laws.

NATURAL GAS PROPERTIES

Composition of Natural Gas - A gas is composed of matter. Matter is defined as anything that contains mass and occupies space. Matter is composed of elements, the simplest form of matter that can exist. These elements combine to form molecules of all existing matter.

Matter exists in three physical states which are solid, liquid, and gas. These states can be defined as follows:

1) Solid - a solid material is somewhat rigid and is bound internally in all dimensions. Solids do not require a container for retention of shape. Most elements and materials we deal with are in a solid state.

2) Liquid - a liquid is bound by one internal boundary which is the surface. A liquid can fill a container below this surface in the shape of the container. Typical liquid elements are bromine and mercury.

3) Gas - a gas has no internal boundaries. It will expand to fill a container or a confining wall. Typical gases are air and natural gas. Natural gas is composed of molecules of hydrocarbon gases, primarily methane but containing some ethane, propane, butanes, pentanes, and hexanes. Measuring problems involving quality control are associated with non-hydrocarbons which may exist in natural gas, such as carbon dioxide, oxygen, hydrogen sulfide and water vapor.

Behavior of Gas Molecules - To better understand the gas laws and the fundamentals of gas measurement, it is necessary to understand the behavior of the gas molecule. Natural gas is made up of a mixture of gas molecules consisting essentially of methane and with varying amounts of other hydrocarbon and diluent gases. A cubic centimeter of any gas at standard temperature and pressure conditions contains about twenty-six billion molecules. Although this small volume contains a very large number of gas 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 negligible. The gas molecule itself is not compressible. Compression of gas is accomplished by bringing the gas molecules closer together in this relatively large empty space occupied by the gas.

Gas molecules are in continuous 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.

Exerted Pressure - The pressure exerted by gas depends on how hard and how often the molecules collide with the confining walls. The fewer number of gas molecules in a confined chamber, the fewer collisions there will be between the molecules and the confining wall; thus the lower the exerted pressure. As the number of gas molecules in a confined space increases there are more molecular collisions.   Thus a greater exerted pressure is produced in the confining space.

Ideal Gas - An ideal gas may be defined as gas molecules which have mass and velocity, but exhibit no attractive or repulsive forces among themselves or with other matter. An ideal gas, under ideal conditions has a direct relationship between the number of collisions by a given number of gas molecules with the confining wall and the exerted pressure. To increase pressure, the number of gas molecules must be increased in a confined space, such as in a section of pipe, or the number of molecules can be held constant while the confined space is reduced, as happens in the piston chamber of a reciprocating engine. To reduce pressure in a confined chamber, gas molecules must be removed or the size of the confined chamber increased for a constant number of molecules.

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 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 caused by an attractive force between molecules, the other by a repulsive force between the same molecules.

Attractive Force - The attractive force between molecules opposes the kinetic pressure translated by the collision of the molecules with the confining walls. This force tends to reduce the momentum of the molecules, which 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 deviation force will be larger and therefore the actual pressure exerted will be less than the ideal. To maintain a given actual pressure, more molecules of gas will be required in a confined volume than indicated under ideal conditions.

The attractive force between molecules can best be demonstrated by observing liquids 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 higher gas pressures.

Repulsive Force - The repulsive force between molecules is opposite to the attractive force. As gas pressure increases with the larger number of gas molecules in a confined chamber, 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, each molecule exerts a repulsive force. The space available for the molecules to move in is greatly reduced. The repulsive force thus adds a positive increment to the dynamic or deviation pressure by restricting molecular movement and impact. 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.

Effect of Temperature - Temperature also affects the behavior of gas molecules. The higher the temperature, the faster the gas molecules move. This causes more collisions between the molecules and thus more collisions within a confined space create a proportional increase in pressure. Under constant volume conditions, pressure increases as temperature increases. The lower the temperature, the slower the gas molecules move, thus causing fewer collisions between the molecules and the confining walls. Under constant volume, pressure decreases as temperature decreases.

To maintain constant pressure in a confined space as the temperature increases, gas molecules must be released. To maintain constant pressure as temperature decreases, gas molecules must be introduced.

GAS LAWS

Avogadro's Law - Avogadro's Law states that equal volumes of gases measured at the same temperature and pressure conditions contain the same number of molecules. One mol-volume or molecular weight expressed in pounds at $60^{o}F$ and 14.73 psia occupies a volume of 378.9 cubic feet. Under these standard conditions, one

cubic foot of gas contains 7.61 X 10 to the 23rd power 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 cubic meters, and the rates in cubic feet or cubic meters per unit of time.   (Diagram 1)

Kinetic Energy of Translation - We discussed the behavior of gas molecules in a confined space. We have learned that the gas molecules are in rapid motion, and 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.

$$K. E. = 1/2 \, mv^2$$

Where: K. E.   = kinetic energy of translation
        m   = mass of the molecule
        v   = velocity of the molecule

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 lighter 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 a greater numbers of collisions due to their higher velocity, but each impact creates less force.

Boyle's Law - If a given quantity of gas is compressed at constant temperature, the volume of gas will decrease, or if the gas is expanded under constant temperature, the volume of gas will increase. The English scientist, Robert Boyle, studied this phenomenon and discovered that at a constant temperature, the volume occupied by a gas varies inversely with the pressure. (Diagram 2) This is known as Boyle's Law and expressed as:

$$P = K \frac{1}{V} \text{ or } PV = K$$

Where: P = absolute pressure
        V = volume
        K = a constant

Since at a given temperature the product of the absolute pressure and the volume is a constant, then the following is true:

$$P_1 V_1 = K = P_2 V_2 \text{ or } P_1 V_1 = P_2 V_2$$

Where: P_1 = original pressure of gas (absolute)

       V_1 = original volume of gas

       P_2 = new pressure of gas (absolute)

       V_2 = new volume of gas

Charles Law - About a hundred years following the discovery of Boyle's Law a French scientist, Jacques A. Charles, discovered a relationship between temperature an the volume of gas. Charles' Law states that at a constant pressure, the volume occupied by gas varies directly or is directly proportional to the absolute temperature of the gas. (Diagram 3) (Diagram 4) Stated as an equation:

$$V = KT$$

Where: V = volume

       T = absolute temperature of gas

K = a constant

Charles' Law states that at a constant pressure the ratio of the volume to the absolute temperature is a constant, and then the following is true:

V_1/T_1 = K = V_2/T_2 or V_1/T_1 = V_2/T_2

Similar to the above relationship, another form of Charles' Law can be written:

P_1/T_1 = K = P_2/T_2 or P_1/T_1 = P_2/T_2

Where: V_1 = original volume

P_1 = original absolute pressure

T_1 = original absolute temperature

V_2 = new volume

P_2 = new absolute pressure

T_2 = new absolute temperature

Ideal Gas Law - Boyle's and Charles Law can be combined into an ideal gas law as follows:

P_1V_1/T_1 = K = P_2V_2/T_2 or $P_1V_1/T_1 = P_2V_2/T_2$

A derivation of this equation can be used to solve for a new volume of gas when the new conditions and the original volume with the original conditions are known. (Diagram 5)

$V_2 = V_1 \times P_1/P_2 \times T_2/T_1$

Real Gas Law - Gas deviates from ideal gas laws because of the attractive and repulsive forces between molecules, the dynamic pressure. To correct for the deviation, a compressibility factor "Z" is introduced into the ideal gas laws which compensates for the effect of dynamic pressure on the kinetic or ideal pressure. (Diagram 6) The real gas laws can thus be written:

$PV = ZnRT$

or by mathematically rearranging

$\dfrac{PV}{ZT} = nR$ = constant

where: n = 1 mole of gas
Z = compressibility
P = pressure
V = volume
T = temperature

therefore the combined real gas equation becomes:

P_1V_1/Z_1T_1 = P_2V_2/Z_2T_2

or by solving for V_2

$V_2 = (V_1) (P_1/P_2) (T_2/T_1) (Z_2/Z_1)$

<u>Supercompressibility Effect</u> - Natural gas does not follow the ideal gas laws because of the attractive and repulsive forces between the molecules. To compensate for this deviation from the ideal gas laws a compressibility factor "Z" is introduced. In orifice measurement the factor appears as:

$$(1/Z)^{1/2}$$ and this factor is termed the Supercompressibility Factor F_{pv}

AGA Gas Measurement Report No. 3, 8 and NX-19 have tables for the determination of the Supercompressibility factors.

<u>Example</u>:

From the above discussion, this example will show the use of these laws.

A meter station is flowing at a rate of 5,000 mcfd, at an absolute pressure of 700 psi and a temperature of 70 degrees F. What would be the approximate volume of gas at contract conditions? Contract conditions are a pressure of 14.73 psia and a temperature of 60 degrees F. (Supercompressibility is omitted)

Flowing conditions: Contract conditions:

T_1 = 70 + 459.67 T_2 = 60 + 459.67
  = 529.67 R   = 519.67 R
P_1 = 700 psia P_2 = 14.73 psia
V_1 = 5,000 mcfd V_2 = ?

$$P_1 V_1 / T_1 \;=\; K \;=\; P_2 V_2 / T_2$$

$$V_2 \;=\; (V_1)\,(P_1/P_2)\,(T_2/T_1)$$

Using the above equation the value of V_2 can be computed:

V_2 = (5,000)(700/14.73)(519.67/529.67)

V_2 = 233,124 mcfd

CONCLUSION

This discussion of natural gas, how its physical properties behave, and the basic gas laws governing its actions, has by no means, covered all there is to know about gas laws. However, a good understanding of the actions of gases under confinement is an excellent basis for the science of gas measurement.
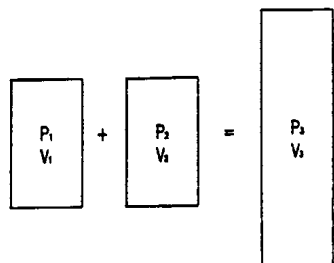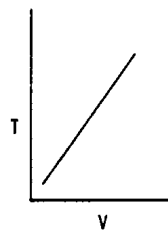
AVOCADRO'S LAW
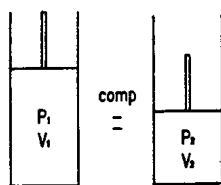$P_1=P_2,V_1=V_2,$therefore
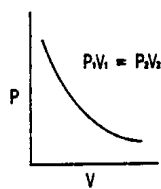$P_1V_1+P_2V_2=P_3V_3$

DIAGRAM 1
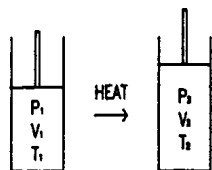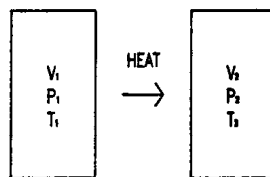
$P_1=P_2,T_2>T_1$ then $V_2>V_1$

CHARLES LAW
DIAGRAM 3

$P_2>P_1$ then $V_1>V_2$

$P_1V_1 = P_2V_2$

BOYLE'S LAW
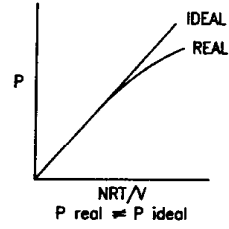DIAGRAM 2

CONSTANT VOLUME

$V_1=V_2,T_2>T_1$ then $P_2>P_1$

CHARLES LAW
DIAGRAM 4
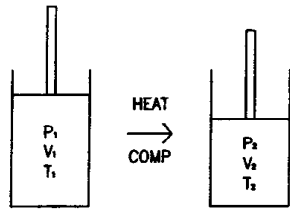
IDEAL GAS LAW
DIAGRAM 5
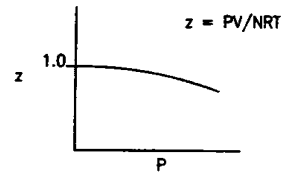
SUPERCOMPRESSIBILITY
DIAGRAM 6

References:
1. American Gas Association, Gas Measurement Manual, 1963.
2. Fundamentals of Gas Measurement, D. A. Tefankjian, 1982 International School of Hydrocarbon Measurement

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