

FUNDAMENTALS OF GAS LAWS

John Chisholm

Texas A&M University — Kingsville
Chemical & Natural Gas Engineering
Kingsville, TX 78363

INTRODUCTION

In the gas industry a standard unit of measure is required. In the English system it is the standard cubic foot. In the metric, it is the standard cubic meter. This standard unit is the basis of all exchange in the gas industry. When the unit of purchase is the energy content (BTU) we achieve it by multiplying the BTU content of a standard cubic foot times the number of cubic feet delivered to the customer. So we must obtain standard cubic feet or meters.

A standard cubic foot is defined as one cubic foot of gas at a pressure and temperature agreed upon by the buyer and seller. Common standard conditions are 14.73 psia and 60° Fahrenheit. The gas passing through a meter is rarely at standard conditions. It is necessary to convert the gas in the meter from the metered conditions to standard cubic feet. The tools we have for relating volume to pressure and temperature are *Equations of State* or, simply, the *Gas Laws*.

The Gas Laws serve two purposes. They allow the conversion of a gas stream from metered conditions to standard conditions. They also provide an understanding of what the gas is doing and why. This paper will briefly present the Gas Laws and the physical properties of gas which the Gas Laws describe.

ABSOLUTE UNITS

The very first thing you need to know is that all calculations using the Gas Laws are in *Absolute Units*. Absolute pressure starts at zero psia, an absolute vacuum. Absolute temperature starts at zero degrees Rankine, approximately -460°F, where theoretically no molecular motion exists. It is an error to perform calculations using psig or °F.

COMPOSITION OF NATURAL GAS

Matter can exist in three phases, solid, liquid, and vapor. The phase of a pure substance such as water is controlled by the energy of the molecules. For example, water at low energy forms a crystalline solid, ice. At higher energy, it is liquid water. The molecules have too much energy to remain bound in a crystalline structure, but the attractive forces between the molecules cause them to assume a minimum volume. Liquids will conform to the shape of the lowest parts of a vessel, but maintain the same volume.

As the energy increases the vibration of the molecules overcomes the attractive forces and the water boils. The

steam molecules completely fill the confining vessel. In normal measurement conditions natural gas is always in the vapor phase.

The phase of a pure substance is determined by the temperature and pressure. Figure 1 is a phase diagram of a pure substance such as ethane. At low temperatures the material exists as a liquid and will occupy a specific volume at the base of its container. As a pure substance changes from liquid to vapor there is a sudden change of volume as the liquid changes from its minimum volume to the volume of the confining vessel. As the temperature increased across the line on Figure 1 the material changes from liquid to vapor and this sudden change of volume can be observed. However, there is a pressure above which no sudden change of volume is observed. The "liquid" completely filled the vessel and then the "vapor" completely filled the vessel. So, an observer cannot tell whether the material is a liquid or a vapor. However, as the material completely fills the vessel, we can treat it as a vapor either way. This *critical pressure*, P_c , is specific to a given material. There also exists a *critical temperature*, T_c , above which only one phase can exist. The critical temperature and pressure become important in the determination of the compressibility factor, z , which will be discussed later.

Natural gas is not a pure substance. Figures 2 and 3 are phase diagrams for hydrocarbon mixtures. Whenever a mixture of gases exists at intermediate energy levels, two phases, liquid and vapor, can exist at the same temperature and pressure. The shape of the two phase region depends on the composition of the mixture. If the confining vessel is transparent, an obvious liquid phase will occupy the bottom of the vessel and the remainder of the vessel will be filled with the vapor phase. As the energy is increased, the mixture eventually goes to pure vapor completely filling the vessel as a single phase. There exists a temperature and pressure at which an observer watching as the mixture reaches that point would report that the mixture went to a single phase occupying the entire volume of the containing vessel. The unique aspect of that temperature and pressure is that the moment before, any combination of liquid and vapor may have existed in the chamber. This is the point where all the lines in the two phase region come together. For example, if the mixture were 75% liquid and 25% vapor, the observer would announce that the mixture suddenly became single phase occupying the entire volume. Whether the material is now 100% liquid or 100% vapor, the observer would be unable to tell. (Given which side of the two phase region this point is on, one might hazard a guess.) However, as

the single phase fills the entire volume of the vessel it can be treated as a gas. These values of temperature and pressure are called the *pseudo-critical* temperature and pressure, pT_c and pP_c . The word *pseudo* is from the Greek and means false, counterfeit, or lie. However it has the property that it resembles the genuine. The pseudo-critical point is the point where all combinations of phases can exist simultaneously. The pseudo-critical properties can be determined for any mixture of gases and are used to determine the compressibility factor.

Natural gas consists of molecules of hydrocarbons. Usually this is predominantly methane. Other gases may be present as *contaminants* such as water, oxygen, nitrogen, carbon dioxide, and hydrogen sulfide.

THE IDEAL AND REAL GAS LAWS

The ideal gas law is given as

$$PV = nRT$$

and the real gas law as

$$PV = znRT$$

where P = pressure, psia

V = volume, cubic feet

z = compressibility factor, dimensionless

n = number of moles of gas, lb mol

T = temperature °R

R = 10.732 psia ft³/(lb mol °R) for this system of units. (The value of R will change depending on the system of units.)

The difference between the ideal and the real gas law is the compressibility factor, z . The ideal gas law assumes that the molecules of gas have no volume and there are no attractive or repulsive forces acting between the molecules. At very low pressures $z \cong 1.0$ and gases behave as if they are ideal gases. At higher pressures the attractive and repulsive forces (often called the dynamic pressure) are significant and the behavior of gases deviates from the ideal. The compressibility factor is often called the gas deviation factor or, simply, the z -factor.

Early experiments were conducted at low pressures and the gases tested acted as ideal gases. Boyle's Law states that at a constant temperature the product of the pressure and the volume is a constant, so any two conditions, 1 and 2, of a gas were related by

$$P_1V_1 = P_2V_2$$

Charles' Law states the ratio of volume to temperature is constant at constant pressure,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

These can be combined into one of the most common expressions of the ideal gas law.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The real gas law simply includes the compressibility factors.

$$\frac{P_1V_1}{z_1T_1} = \frac{P_2V_2}{z_2T_2}$$

Solving this equation for V_2 yields

$$V_2 = V_1 \frac{P_1 T_2 z_2}{P_2 T_1 z_1}$$

This equation is widely used to convert between two conditions as in the calculation of line pack, for example, and to convert flowing conditions to standard conditions.

PRESSURE AND THE KINETIC THEORY OF GASES

Pressure is the force per unit area. The force on the wall of a container containing gas is the number of impacts of gas molecules on the wall. So, anything that increases the number of impacts or the velocity of the impacts will increase the force, and, hence, the pressure.

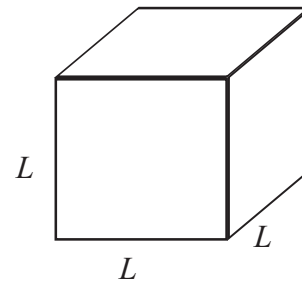
The *Kinetic Theory of Gases* states that the kinetic energy (KE) of a molecule is directly proportional to its temperature.

$$KE(T) = \frac{1}{2}mv^2 = cT$$

Where m is the mass of the molecule, v is the molecule's velocity, and c is a constant.

The Ideal Gas Law can be derived using the Kinetic Theory. And the derivation explains a great deal about what pressure is and how gases react.

Consider a cubic container with sides of length L ,



In a container of fixed volume, the velocity controls how long it will take a molecule to travel from one side of the container to the other and back again.

Length of a round trip = $2L$

The number of impacts on a given wall is then:

$$\text{Number of impacts per unit time} = \frac{v}{2L}$$

where v is the average velocity of the molecule. Each molecule of gas hits the wall at v and rebounds at $-v$. The

momentum of a molecule is its mass times its velocity, so the change of momentum at the wall is given by:

$$\Delta \text{ momentum} = m'v - m'(-v) = 2m'v$$

where m' is the mass of each molecule and the Δ stands for "change". Consider a ball thrown at a wall. The wall must first stop the ball's momentum ($m'v$) and then send it away again with momentum $m'v$. So from the point of view of the wall it had to impart to the ball $2m'v$, half just to stop it and half to send it away.

The change in momentum of a molecule per unit time is given by:

$$2m'v * \frac{v}{2L} = m' \frac{v^2}{L}$$

Only a third of the molecules, $\frac{n'}{3}$ in the box are hitting each wall.

The force acting on a wall is the number of molecules times the change in momentum per unit time.

$$F = \frac{n'}{3} \frac{m'v^2}{L}$$

And pressure is the force per unit area.

$$P = \frac{n' m' v^2}{3} \frac{1}{L^2} = \frac{n' m' v^2}{3L^3}$$

Now, $L^3 = V$, the volume of the cube, so:

$$P = \frac{n' m' v^2}{3V} \text{ or } PV = \frac{n' m' v^2}{3}$$

The beginning assumption was that the kinetic energy was a function of temperature alone.

Then,

$$m' v^2 = 2cT \text{ and } PV = \frac{n'}{3} 2cT$$

where c is a constant.

Before completing the derivation, consider some consequences of the equation above. If the temperature is held constant, then $PV = a$ constant, which is Boyle's

Law. If pressure is held constant, then $\frac{V}{T} = a$ constant, which is Charles' Law.

If we set $A =$ Avogadro's number, the number of molecules in one mole, then

$$PV = \frac{n'}{A} \left(\frac{2}{3} cA \right) T$$

Now

$$\frac{n'}{A} = n \quad \text{and we set} \quad \frac{2}{3} cA = R$$

Then,

$$PV = nRT$$

which is the ideal gas law.

The Kinetic Theory shows that each impact contributes to the pressure. If the temperature increases, the velocity increases, the round trip time goes down, and the number of impacts goes up, hence, more pressure. If the number of molecules in the container increases, the number of impacts increase and the pressure increases. Finally, if the volume of the container is reduced, it takes less time for the molecules to travel back and forth, so each molecule makes more impacts in a unit of time. More impacts produced more pressure. The reverse of each of these events produces less pressure.

Both Charles' and Boyle's Laws have been derived from the Kinetic Theory. Some other very useful laws can be derived from the Kinetic Theory. (For the record, the Laws were determined experimentally before the Kinetic Theory was developed.) Avogadro's Law states that, at the same temperature and pressure, equal volumes of an ideal gas contains the same number of molecules. Also the volume containing one molecular weight of a given gas will be equivalent to the volume containing one molecular weight of another gas at the same temperature and pressure. There are 2.73×10^{26} molecules per pound mole of an ideal gas.

When the Kinetic Theory is extended to mixtures of gases, Dalton's Law of Partial Pressures can be found. Dalton's Law states that the pressure on a surface by a gas is the sum of the pressures that would be exerted by each component in the gas if it were alone,

$$P_{total} = P_A + P_B + P_C + \dots$$

and that the partial pressures are proportional to the mole fractions of each component. The partial pressures become especially important if liquid water is in contact with the gas. The partial pressures can be used to determine what fraction of each gas is in solution in the liquid. If significant quantities of CO_2 or H_2S are present, they will produce corrosive acids in solution with water.

THE DYNAMIC PRESSURE AND THE Z-FACTOR

The Kinetic Theory assumes no attractive or repulsive forces are acting in the gas. This allows the Kinetic Theory to derive the ideal gas law. However, these forces do exist and at higher pressures cause gases to deviate from ideal behavior significantly. These forces are called the dynamic pressure. The gas deviation factor is just the ratio of the actual volume of a gas to that which would be predicted by the ideal gas law.

$$Z = \frac{V_{ACTUAL}}{V_{IDEAL}}$$

As the pressure increases from near atmospheric, the molecules are pushed closer together. Both gravitational and electrical attractions cause the molecules to pull towards one another with the result that the volume occupied by the gas is less than that predicted by the gas law. The z-factor becomes less than one.

As the pressure continues to increase, the molecules, which have a real volume and velocity, begin to interfere with the other molecules in the gas. Personifying the gas, one can think of each molecule fighting for its own space. This results in repulsive forces. So the z-factor begins to increase and returns to and then exceeds 1.0, so that at high pressures the gas will occupy more volume than that predicted by the ideal gas law.

As many pure gases and mixtures of gases were tested it was observed that their behavior matched that described above. Although the z-factors for methane followed the same trends as that of ethane, the z-factors were by no means identical. To unify these relations all the tests were related to the reduced temperature and pressure.

$$Tr = \frac{T}{T_c} \text{ and } Pr = \frac{P}{P_c}$$

For mixtures, the pseudo-critical properties can be used in these calculations. When plotted for each and every hydrocarbon gas the z-factor lines now tracked together. This discovery is commonly called the *Law of Corresponding States*. This allowed a generalized compressibility factor chart to be developed.

Many mathematical correlations have been developed to calculate z-factors. The current methodology in AGA 8 should be used unless another method is specified in a gas contract.

The pseudo-critical properties can be calculated using

$$P_c T_c = \sum y_j T_{c_j} \text{ and } P_c = \sum y_j P_{c_j}$$

where y_j is the mass fraction of each component of the mixture. Values of y_j are obtained from gas chromatograph readings.

The density and specific gravity of a gas can be calculated using

$$\rho_g = \frac{P MW_g}{zRT} \text{ and } SG_g = \frac{\rho_g}{\rho_{air}} = \frac{MW_g}{MW_{air}}$$

where MW_g is the molecular weight of the gas and ρ_g is the density of the gas. Values of the critical properties

and molecular weights of the individual gases are available from any gas handbook.

EXAMPLE 1 – A turbine meter indicates that 4,000 macf of gas passed through it in one day. The line pressure and temperature were 500 psia and 122°F. The gas stream was 85% methane, 9% ethane, 4% propane, and 2% butane+. What volume of gas in mscf was delivered that day?

The calculation of the critical properties of this gas is given in Table 1.

$$122^\circ F + 460 = 582^\circ R$$

$$P_r T_r = 582^\circ R / 384.5^\circ R = 1.51$$

$$P_r = 500 \text{ psia} / 664.2 \text{ psia} = 0.75$$

$$z = 0.925$$

$$V_{sc} = V_{line} \frac{P_{line} T_{sc} z_{sc}}{P_{sc} T_{line} z_{line}}$$

$$V_{sc} = 4,000 \text{ macf} \frac{500 \text{ psia } 520^\circ R \ 1.0}{14.7 \text{ psia } 582^\circ R \ 0.925}$$

$$V_{sc} = 131,417 \text{ mscf}$$

EXAMPLE 2 – LINE PACK

Each day a pipeline must be balanced as to receipts and deliveries. A pipeline also represents a large storage unit for gas. At a constant temperature, if the pressure of the pipeline is different at the end of the day than at the beginning, then the receipts and deliveries will not balance because the amount of gas stored in the pipeline has changed. Determining the amount of that change is often called a line pack calculation.

Consider the gas of Example 1. The pipeline runs 39 miles of 8 inch pipe with a total enclosed volume of 70,000 cubic feet. If we start the day with an average pressure of 500 psia and 122EF and end it at 600 psia and 122EF, how much additional gas is in the pipeline?

Initial gas in the pipeline:

$$V_{sc} = V_{pipe} \frac{P_{pipe} T_{sc} z_{sc}}{P_{sc} T_{pipe} z_{pipe}}$$

Table 1. Pseudo-Property Calculation for Example 1.

Component	Mole Fraction y_j	Tc °Rankine	$y_j T_{c_j}$ °Rankine	Pc psia	$y_j P_{c_j}$ psia
C1	0.85	343.3	291.8	666.4	566.4
C2	0.09	549.9	49.5	706.5	63.6
C3	0.04	666.1	26.6	616	24.6
C4+	0.02	830.0	16.6	482	9.6
		384.5			664.2

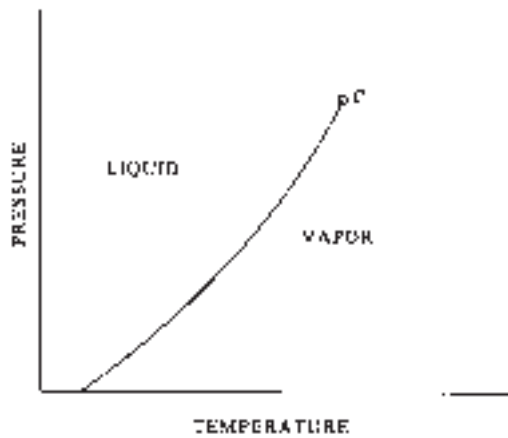


FIGURE 1. PHASE DIAGRAM OF A PURE SUBSTANCE

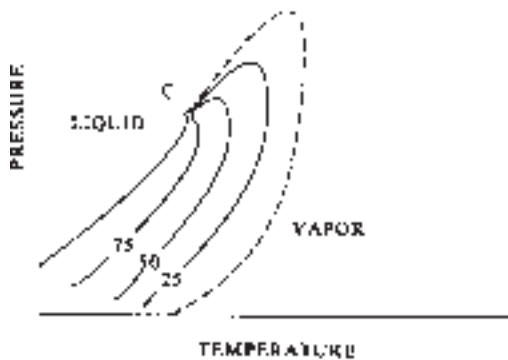


FIGURE 2. PHASE DIAGRAM OF A MIXTURE

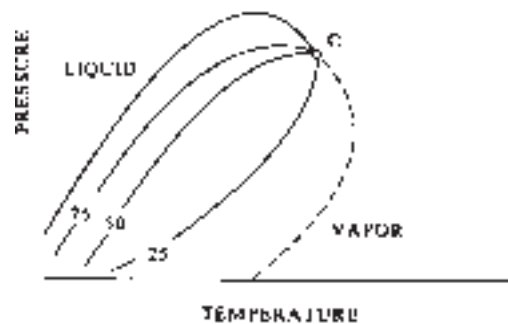


FIGURE 3. PHASE DIAGRAM OF A MIXTURE

$$V_{sc} = 70,000 \text{ acf} \frac{500 \text{ psia } 520^\circ\text{R } 1.0}{14.7 \text{ psia } 582^\circ\text{R } 0.925}$$

$$V_{sc} = 2,127,311 \text{ cubic ft} = 2,127 \text{ mscf}$$

At 600 psia, $p_r = 0.903$ and $z = 0.905$. So,

$$V_{sc} = 70,000 \text{ acf} \frac{600 \text{ psia } 520^\circ\text{R } 1.0}{14.7 \text{ psia } 582^\circ\text{R } 0.905}$$

$$V_{sc} = 2,820,744 \text{ cubic ft} = 2,821 \text{ mscf}$$

So, $2,821 - 2,127 = 694$ mscf more gas is stored in the pipeline at days end than at the beginning.

REFERENCES

McCain, William D., Jr., *The Properties of Petroleum Fluids*, Penn Well Books, Tulsa, Oklahoma, 1990.

Thompson, Roger G., "Fundamental Gas Laws," Proceedings of the 29th Annual American School of Gas Measurement Technology, Houston, Texas, September 19-22, 1994.

Gas Processors Suppliers Association, *Engineering Data Handbook*, Tulsa Oklahoma, 1972.

Standing, M.B. "Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems," SPE of AIME, Dallas, Texas, 1977.

Standing, M.B. and Katz, D.L., "Density of Natural Gases," Transactions AIME, **146**, 1942.



John Chisholm