CHAPTER 3
PROPERTIES OF NATURAL GASES

The behavior of natural gas, whether pure methane or a mixture of volatile hydrocarbons and the non-hydrocarbons nitrogen, carbon dioxide, and hydrogen sulfide, must be understood by the engineer designing and operating equipment for its production, processing, and transportation. The constituents of natural gas are most likely to be found in the gaseous state but can occur as liquids and solids.

3.1 MOLECULAR THEORY OF GASES AND LIQUIDS

Gases and liquids are made up of molecules and may be treated on a molecular basis. The nature of the molecules and the forces existing between them control the properties of the fluid. The kinetic theory of gases treats a gas as crowd of molecules each moving on its own independent path, entirely uncontrolled by forces from the other molecules, although its path may be abruptly altered in both speed and direction whenever it collides with another molecules or strikes the boundary of the containing vessel. In its simplest state, a gas may be considered as composed of particles that has no volume and between which there are no forces.

3.1.1 Equation of State

All fluids follow physical laws that define their state under given physical conditions. These laws are mathematically represented as equations, which are consequently known as equations of state (EOS). These equations essentially correlate, P, V, and T for any fluid and can be expressed, on a mole basis, as:

$$\varnothing(P,V,T) = 0 \tag{3.1}$$

Many different EOS's have been developed over the years, and only the most basic and widely used EOS's will be mentioned here.

Ideal Gas Law

The concept of an ideal gas is a hypothetical idea, but it serves as a useful tool to explain the more complex real gas behavior. An ideal gas is a gas in which;

- ✓ the molecules occupy negligible volume,
- ✓ there is no interaction between the molecules,
- ✓ collisions between the molecules are purely elastic, implying no energy loss on collision.

At low pressures (< 400 psi) most gases exhibit an almost ideal behavior. The ideal gas law that applies to such gases can be studied as follows:

$$PV = nRT \tag{3.2}$$

where P and T are the absolute pressure and temperature of the gas, n is the number of moles, and V is the volume occupied by the gas. R, the constant of proportionality, is called the universal gas constant.

Behavior of Real Gases

In general, gases do not exhibit ideal behavior. The reasons for the deviation from ideal behavior can be

summarized as follows:

- ✓ Molecules for even a sparse system, such as gas, occupy a finite volume.
- ✓ Intermolecular forces are exerted between molecules.
- ✓ Molecular collisions are never perfectly elastic.

The deviation from ideal behavior is greater for heavier gases because of the larger size of their molecules. Most gases compress more than ideal gas at low pressures, whereas the opposite is true at high pressures.

Compressibility Factor Approach

To correct for non-ideality, the simplest equation of state uses a correction factor known as the gas compressibility factor, Z:

$$PV = nZRT \tag{3.3}$$

The Z-factor can therefore be considered as being the ratio of the volume occupied by a real gas to the volume occupied by it under the same temperature and pressure conditions if it were ideal. This is the most widely used real gas equation of state. The major limitation is that the gas deviation factor, Z, is not a constant but varies with changes in gas composition, temperature and pressure. It must be determined experimentally. The results of experimental determinations of compressibility factors are presented graphically and usually take the form shown in Figure 3.1.

The shapes of isobars of compressibility factors of natural gas constituents are very similar. This realization that this is true for nearly all real gases led to the development of the law of corresponding states and the definition of the terms "reduced temperature" and "reduced pressure".

$$T_r = \frac{T}{T_c} \tag{3.4}$$

$$P_r = \frac{P}{P_c} \tag{3.5}$$

The law of corresponding states expresses that all pure gases have the same compressibility factor at the same values of reduced pressure and reduced temperature.

The law of corresponding states has been extended to cover mixtures of gases, which are closely related chemically. It is somewhat difficult to obtain the critical point for multi-component mixtures, therefore, the quantities of pseudocritical temperature and pseudocritical pressure have been conceived. These quantities are defined as:

$$T_c = \Sigma \, y_i T_{ci} \tag{3.6}$$

$$P_c = \Sigma \, y_i \, P_{ci} \qquad (3.7)$$

These pseudocritical quantities are used for mixtures of gases in exactly same manner as the actual critical temperatures and critical pressures are used for pure gases.

The compressibility factors for natural gases have been correlated using pseudocritical properties and are presented in Figure 3.2.

3.2 VISCOSITY

Knowledge of the viscosity of hydrocarbon fluids is essential for a study of the dynamic or flow behavior of these fluids through pipes, porous media, or, more generally, wherever transport of momentum occurs in fluid motion. The unit of viscosity is g/cm.s, or the poise.

The kinematic viscosity is the ratio of the absolute viscosity to the density:

$$\frac{\textbf{\textit{m}}}{\textbf{\textit{r}}} = \frac{centipoise}{\dfrac{g}{cm^3}} = centistokes \qquad (3.8)$$

Figure 3.3 provides a rapid and reliable method for obtaining the viscosities of mixtures of hydrocarbon gases at 1.0 atmosphere of pressure, given knowledge of the gravity and temperature of the gas. Insert plots show corrections to the value of hydrocarbon viscosity, which may be applied to take into account the effect of the pressure of low concentrations of hydrogen sulfide, nitrogen or carbon dioxide. The effect of each of the non-hydrocarbon gases is to increase the viscosity of the gas mixture.

In most instances the petroleum engineer is concerned with the viscosity of gases at pressures higher than one atmosphere so that we must now turn to a method for calculating the viscosity at pressures other than one atmosphere.

The theorem of corresponding states has been used to develop such a correlation; it is given as Figure 3.4. The pseudocritical temperature and pressure are required to obtain reduced temperature and pressure for entry into the graph.

3.3 THERMODYNAMIC PROPERTIES

The principles of thermodynamics find very wide application in correlating and predicting the properties of hydrocarbons. For example, the effect of pressure on the enthalpy of gas can be computed from PVT data. Latent heats can be computed from the slopes of vapor pressure curves. The properties of greatest interest are specific heats of gases and liquids, heats of vaporization, and the effects of pressure on the enthalpies of compressible fluids. Enthalpy-entropy charts for natural gases permit prediction of temperature change when gases are expanding or when reversible work is done by compression.

3.3.1 Specific Heat

One of the basic thermodynamic quantities is specific heat, defined as the amount of heat required raising the temperature of a unit mass of a substance through unity. It is an intensive property of a

substance. It can be measured at constant pressure (C_p), or at constant volume (C_v), resulting in two distinct specific heat values. In terms of basic thermodynamics quantities,

$$C_p = (\frac{\partial h}{\partial T})_p \qquad (3.9)$$

$$C_v = (\frac{\partial U}{\partial T})_v \qquad (3.10)$$

where h is the molal enthalpy (BTU/lbmole), U is the molal internal energy (Btu/lbmole), C_p is the molal specific heat at constant pressure (BTU/lbmole-R), and C_v is the molal specific heat at constant volume (Btu/lbmole-R).

For an ideal gas,

$$C_p - C_v = R \qquad (3.11)$$

where R is the universal gas constant.

For a real gas, C_p and C_v are functions of both   pressure as well as temperature.

The specific heats of gases and liquids are determined experimentally in a calorimeter, usually at 1 atm. For natural gases, the specific heat at 1 atm pressure is a function of temperature and of gas gravity or molecular weight.

For a given heat release in combustion, the temperature is governed by the specific heat of the combustion products of the flue gases. The specific heats of constituents of flue gases are given in Table 3.1 The values given are mean values between 15 °C and the temperature indicated.

3.3.2 Heating Value

The heating or calorific value of combustion is a prime characteristic of a natural gas, often a factor in the price received in the sale. Combustion is used to provide heat in the field or plant as well as the power for gas engines, and engineers need to understand it.

The heating value of natural gas is the heat (chemical energy) liberated when a unit of fuel is burned with oxygen under specified conditions. Methane has a heating value of 37.694 MJ/m^3 of gas at 15 °C and 1 atm, when burned with air. This heating value is obtained by cooling the products of combustion to 15 °C. When water remains as vapor, the energy recovered is the **net heating value**. When the moisture is condensed, the recovered energy is known as the **total or gross heating value**. The gross heating values of some gases are given in Table 3.2.

Table 3.1 Mean modal heat capacities of gases between 15 °C and temperature (Btu/(
[(Btu/(lbmol°F))×4.1868=(kJ/(kmol°C))]

T, °F	T, °C	H_2	N_2	O_2	Air	H_2O	CO	CO_2	CH_4
60	15	6.86	6.96	7.00	6.94	7.99	6.96	8.70	8.3
100	38	6.87	6.96	7.01	6.94	8.00	6.96	8.83	8.4
200	93	6.92	6.97	7.06	6.96	8.04	6.97	9.21	8.7
400	204	6.95	7.00	7.16	7.01	8.13	7.00	9.73	9.48
600	316	6.97	7.05	7.30	7.07	8.25	7.07	10.19	10.30
800	427	6.98	7.11	7.43	7.16	8.39	7.14	10.57	11.06
1000	538	7.00	7.17	7.55	7.24	8.54	7.23	10.93	11.76
1500	816	7.08	7.37	7.80	7.44	8.93	7.44	11.59	13.30
2000	1093	7.16	7.57	8.00	7.63	9.33	7.65	12.10	14.69
2500	1371	7.28	7.72	8.16	7.77	9.70	7.80	12.45	
3000	1649	7.39	7.85	8.26	7.91	10.04	7.93	12.75	
3500	1926	7.51	7.96	8.40	8.01	10.35	8.03	12.98	
4000	2204	7.63	8.06	8.49	8.09	10.63	8.13	13.17	

Table 3.2 Gross heating values of gases.

Component	Gross heating value (MJ/m^3)
Nitrogen	0.0
Methane	37.694
Ethane	66.032
Propane	93.972
i-butane	121.426
n-butane	121.779
Pentane+	163.521

Equation 3.12 is used to compute the heating value of a gas from gas analysis.

Gross heating value of mixture $= \sum$ (mole fraction $\times$ gross heating value) of pure components (3.12)

3.3.3 Limits of Flammability - Safety

Unwanted combustion of or explosion of fugitive gas mixed with air is a prime safety manner; an engineer should know the limits of combustion at which various gases explode when mixed with air and ignited. Composition limits of flammability represent a safety problem that should be familiar to engineers.

Air and natural gas in the proper proportions will ignite, liberating heat, which is absorbed primarily by the products of combustion. The temperature rise of the gas causes an increase in pressure and, under confinement, can result in an explosion. It is important that everyone connected with natural gas industry understand flammability limits and the nature of combustion.

There are two composition limits of flammability for air and a gaseous fuel under specified conditions. **The lower limit** corresponds to the minimum concentration of combustible gas that will support combustion, **the higher limit** the maximum concentration. Table 3.3 lists lower and higher limits for pure hydrocarbons in air at atmospheric pressure and room temperature.

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The lower limits of gaseous mixtures can be predicted from the limits of the pure constituents by a simple formula:

$$\sum_i \frac{n_i}{N_i} = 1.0 \qquad (3.13)$$

where **n** is the mole fraction of each constituent in the total mixture at lower limit and **N** is the lower limit for each constituent as a pure hydrocarbon.

Table 3.3 Limits of flammability of gases with air at 1 atm (volume or mol%).

Constituent	Lower limit	Higher limit
Methane	5.0	15.0
Ethane	2.9	13.0
Propane	2.1	9.5
n-butane	1.8	8.4
i-butane	1.8	8.4
n-pentane	1.4	8.3
i-pentane	1.4	8.3
Hexane	1.2	7.7
Hydrogen sulfide	4.3	45.5

Pressure influences the flammability limits. At low pressures, say 50 mm Hg, natural gas-air mixtures are not combustible. At high pressures, the upper limit rises rapidly. The diluting of a fuel-air mixture with inert constituents, such as nitrogen and carbon dioxide also changes the limits of flammability. Natural gas or any fuel is very combustible when mixed with oxygen-enriched air or pure oxygen. Usually, odorant is added into natural gas to alert operators when the natural gas concentrations in air reaches 20 percent of the lower flammability limits.

6.2.1 Joule-Thomson Effect

The Joule-Thomson coefficient is defined as the change in temperature upon expansion which occurs without heat transfer or work and is expressed with the formula,

$$m = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p}\left[T \left(\frac{\partial V}{\partial T} \right) - V \right]$$

(3.14)

It is a useful and practical property for estimating the isenthalpic temperature drops of the gas per unit pressure drop. In terms of reduced quantities the above equation becomes,

$$m = \left(\frac{R T_r^2}{P_r} \right)\left(\frac{T_c}{P_c} \right)\left(\frac{1}{C_p} \right)\left(\frac{\partial z}{\partial T_r} \right)_p$$

(3.15)

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where,

T_r, P_r = reduced temperature and pressure of the gas,

T_c, P_c = critical temperature and pressure of the gas,

μ=Joule-Thomson coefficient,

C_p = specific heat capacity of the gas

According to the definition, the gas cools down when the coefficient is positive and heats up when the coefficient is negative.
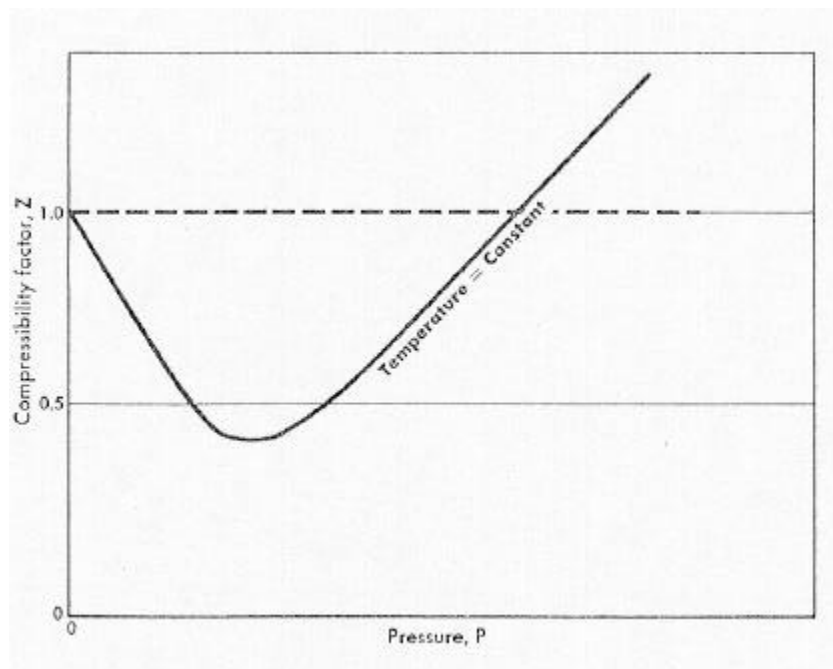

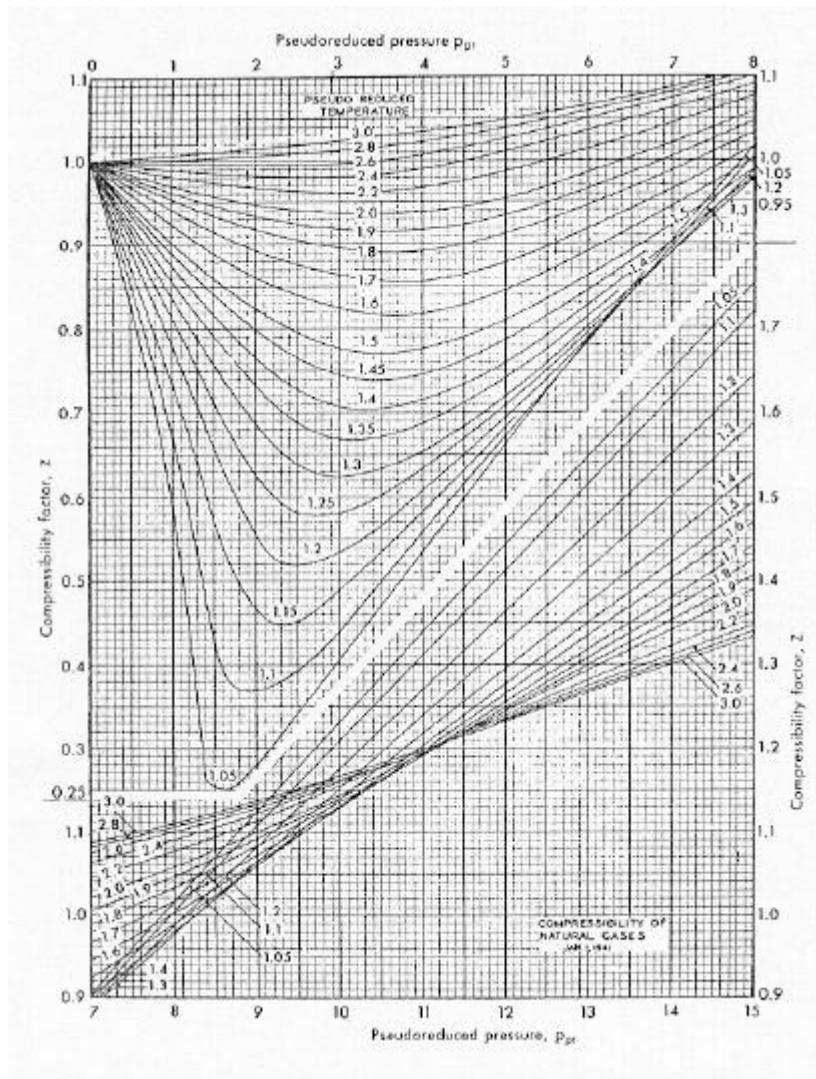Figure 3.1 Typical plot of compressibility factor.

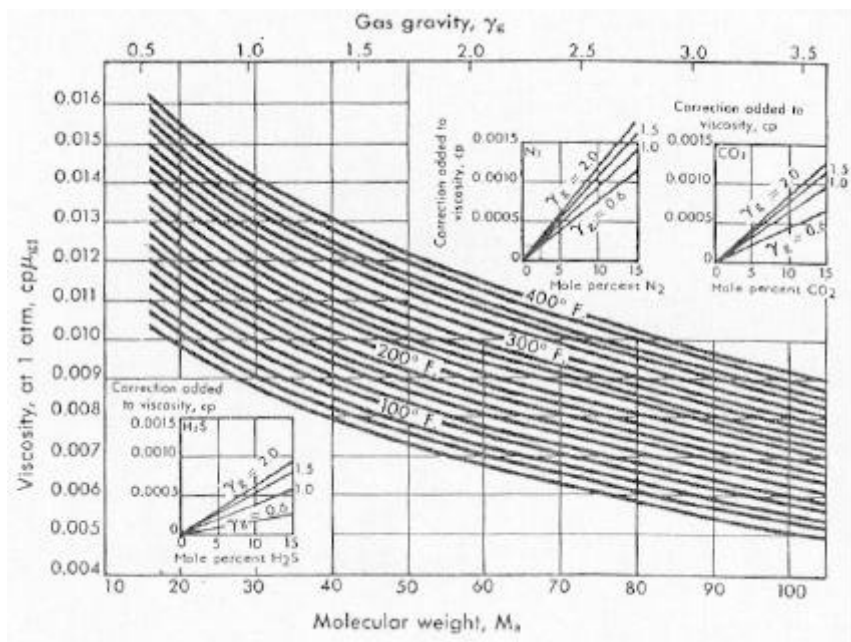Figure 3.2 Compressibility factor for natural gas.

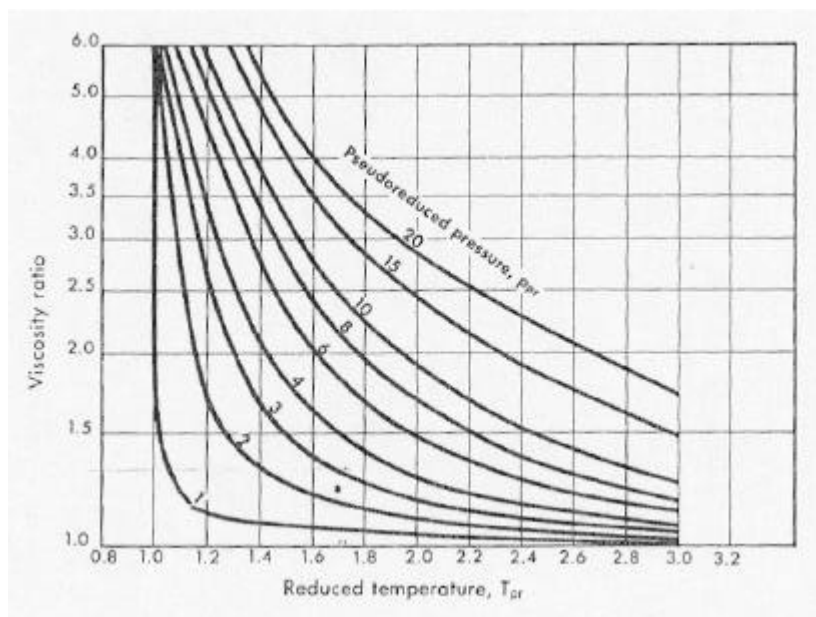Figure 3.3 Viscosity of paraffin hydrocarbon gases at 1 atm pressure.

Figure 3.4 Correlation of gas viscosity ratio with reduced temperature and pressure.