Fundamental Gas Laws

By DR. A. G. OBERG
Department of Chemical Engineering
Texas Technological College
Lubbock, Texas

Many of the calculations made use of in the various branches of the petroleum industry involve the pressure, temperature, and volume relationships of gases. The mathematical equations which express these relationships have been known for some time, and these are commonly and collectively known as the gas laws.

The law of Boyle, for example, states that for a given weight of gas or mixture of gases being kept at constant temperature the following relation holds:

(1) $P V =$ a constant number

or $P_1V_1 = P_2V_2$

or $P_1/P_2 = V_2/V_1$

The law of Charles states that the volume and temperature of a given weight of gas held at constant pressure follows the relation:

(2) $V/T =$ a constant number

or $V_1/T_1 = V_2/T_2$

Or, alternately, the law of Charles states that the pressure and temperature of a given weight of gas held at constant volume follows the relation:

(2a) $P/T =$ a constant number

or $P_1/T_1 = P_2/T_2$

By combining Eqs. (1) and (2) there is obtained:

(3) $P V/T =$ a constant number

or $P_1V_1/T_1 = P_2V_2/T_2$

or as is usually preferred:

(4) $PV = [w/ (\text{sp. gr.}) \times 29.0] \times RT$

W = wt. in lbs.

sp. gr. = specific gravity relative to air.

The letter R denotes a number called the gas constant and has the value of 10.73 (when P = psia, T = °R, and V = cf.)

Many gases, such as air and hydrogen, etc., follow the relationships of Eq. (4) quite closely over a wide range of pressure and temperature. The hydrocarbon gases, however, deviate above pressures of about 50 psia unless they are also at high temperatures. Usually for a given volume of gas at a fixed temperature, the pressure which the gas actually exerts is lower than indicated by using Eq. (4).

When a gas or gas mixture does follow in behavior Eq. (4) or the preceding equation, it can be designated as an "ideal" or "perfect" gas, and otherwise it is designated as a "non-ideal" gas.

When making calculations involving non-ideal gases, the best results are obtained only when carefully acquired experimental data and equations are used as a basis for the prediction of results. Frequently these are not available and yet the calculations must be made. Then the most convenient alternative involves using the modified form of Eq. (4) or

(4a) $P V = W (\text{sp. gr.}) \times 29.0 \times Z R T$, in which the letter Z corrects for deviation from ideal gas law behavior.

This so-called compressibility factor is a number (no units), does not depend on the volume or weight of the gas, and its numerical value can be determined by using the critical properties of the gas and the temperature and pressure under which the gas exists or is being considered.

It might be expected that Z factors must be obtained for each gas for which calculations must be made. However and fortunately the deviation of an actual gas from the ideal gas law is the same (with small variations) for different gases when they are all at the same corresponding state. By corresponding state is meant at the same reduced pressure and reduced temperature (pressure and temperature relative to the critical pressure and temperature respectively). Or, for example, for methane at 56° F. (516° R) and 861 psig (876 psia) the reduced pressure,

$$P_r = P/P_c = 876/673 = 1.3$$

and the reduced temperature,

$$T_r = T/T_c = 516/344 = 1.5$$

(See Table 1 for the physical constant of hydrocarbons) and from Figure 1, Z = 0.888.

The compressibility factor for ethane at 911 psig and 364° F. would likewise have the value of 0.888.

Eq. (4a) can also be used for gas mixtures. When used for a mixture the mixture is considered as a single gas in the use of the equation by calculating the reduced pressure and reduced temperature from the pseudo (or equivalent) critical pressure and critical temperature values for the mixture. The compressibility factor as obtained then from Figure 1 applies to the mixture.

Many times the percentage composition of the gas mixture is not known nor is readily obtained. If the specific gravity is known (relative to air), the following equations derived by Ducker are useful in approximating the pseudo values:

$$P_c \text{ (pseudo)} = 690 - 31 \times (\text{sp. gr.})$$

$$T_c \text{ (pseudo)} = 158 + 100 \times (\text{sp.gr})/3$$

TABLE 1

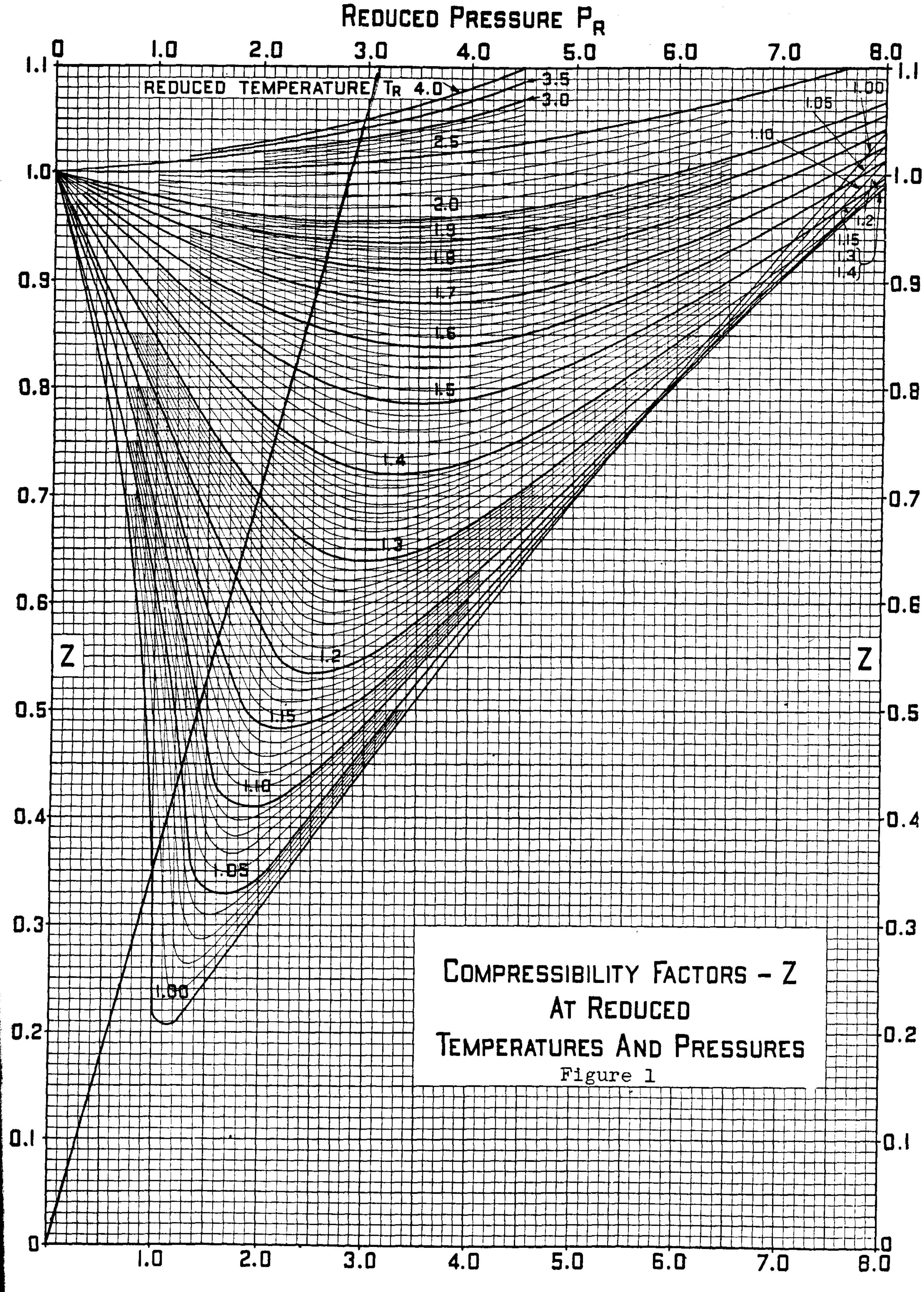
PSEUDO-CRITICAL PROPERTIES FROM SPECIFIC GRAVITY

$$P_{pc} = 690 - 31 G$$

$$T_{pc} = 158 + 1000 G/3$$

Where G is the specific gravity of the gas relative to air.

Where G is between .55 and 1.00 the above follows C.N.G.A. data with error less than 1.0.



COMPRESSIBILITY FACTORS – Z
AT REDUCED
TEMPERATURES AND PRESSURES

Figure 1

TABLE 2

CRITICAL DATA ON THE ALKANE SERIES HYDROCARBON

	Form	Mol. Wt.	Critical Temperature degrees R	Critical Pressure psia
Methane	CH_4	16.04	344	673
Ethane	C_2H_6	30.07	549	712
Propane	C_3H_8	44.09	666	617
n-Butane	C_4H_{10}	58.12	766	551
ISO-Butane	C_4H_{10}	58.12	732	544
n-Pentane	C_5H_{12}	72.15	846	485
ISO-Pentane	C_5H_{12}	72.15	829	483
n-Hexane	C_6H_{14}	86.17	914	435
n-Heptane	C_7H_{16}	100.20	972	397
n-Octane	C_8H_{18}	114.22	1024	362

Ducker has shown that these equations are consistent with the comprehensive data on the composition of natural gases which are published by the Railroad Commission of Texas and for gases having specific gravities between 0.55 and 1.03, or for pure methane and pure ethane and for mixtures of methane and ethane.

On the following pages are three detailed illustrations of the use of Eq. (4a) together with Table I (Critical Data on the Alkane Series of Hydrocarbons) and Figure 1 (The Compressibility Factor Chart).

The use of the compressibility factor and Eq. (4a) in gas calculations may be made clear by the following examples:

Illustration 1.

Volume of a Single Gas is Known.
Specific Gravity is Known.
Calculate the volume of one pound of ethane at 144°F. and 1000 psig pressure.

From Table I:

$P_c = 712$ psia $\quad T_c = 549°R$

and $P_r = 1000 + 14.7/712 = 1014.7/712 = 1.42$

$T_r = 460 + 144/549 = 604/549 = 1.10$

the specific gravity of ethane = 1.03.

From Figure 1: $Z = 0.507$.

Using Eq. (4a):

$V = w \times Z \times R \times T/(\text{sp. gr.}) \times 29.0 \times P = 1 \times 0.507 \times 10.73 \times 604/ 1.03 \times 29.0 \times 1014.7 = 0.1082$ cubic feet

Illustration 2.

Volume of Mixed Gas Unknown.

Composition of Mixed Gas is Known.

The residue gas from a gasoline plant is known to be 80.00 percent by volume methane and 20.00 percent ethane. Calculate the volume of 10 pounds of this gas at 500 psig and 100°F.

From Table I: for methane,

$P_c = 673$ psia and $T_c = 344°R$.

For ethane,

$P_c = 712$ psia and $T_c = 549°R$.

The pseudo values for the mixture are calculated as follows:

P_c (pseudo) $= 0.80 \times 673 + 0.20 \times 712 = 780$ psia

T_c (pseudo) $= 0.80 \times 344 + 0.20 \times 549 = 385°R$

The specific gravity of the mixture is,

sp. gr. $= 0.80 \times 16 + 0.20 \times 30/29.0 = 18.8/29.0 = 0.648$

Then, P_r (pseudo) $= 500 + 14.7/780 = 514.7/780 = 0.660$

T_r (pseudo) $= 460 + 100/385 = 560/385 = 1.45$.

And from Figure 1: $Z = 0.932$.

Using Eq. (4a): $V = w \times Z \times R \times T/(\text{sp. gr.}) \times 29.0 \times P = 10 \times 0.932 \times 10.73 \times 560/0.648 \times 29.0 \times 514.7 = 5.79$ cubic feet.

Illustration 3.

Pressure of a Single Gas is Unknown.

Specific Gravity is Known.

Calculate the pressure exerted by one pound of ethane at 144°F. when occupying 0.1082 cubic feet of volume.

From Table I: $P_c = 712$ psia $T_c = 594°R$.

And $T_r = 460 + 144/549 = 604/549 = 1.10$

the specific gravity of ethane = 1.03.

Using Eq. (4a), and the facts that $P = P_r \times P_c$ and $T = T_r \times T_c$

$Z = (P_r \times P_c \times V)/(R \times T_r \times T_c \times w)/(\text{sp. gr.}) \times 29.0 = P_r \times$ (a constant).

Substituting in the values,

$Z = (712 \times 0.1082)/(10.73 \times 1.10 \times 549)/(1.03 \times 29.0)$

or $Z = P_r \times (0.355)$

This last equation can be represented by a straight line on the compressibility factor chart starting at $Z = 0$ and $P_r = 0$, and ending at $Z = 1.10$ and $P_r = 3.1$.

The P_r value sought corresponds to the intersection of this line and the $T_r = 1.10$ curved line.

Ordinarily the Z value is not of importance (but note that $Z = 0.507$), and $P_r = 1.42$ and $P = P_r \times P_c = 1.42 \times 712 = 1014.7$ psia.

(It may be of interest to note that Illustrations 1 and 3 are related in the use of data).