# 8. RESERVOIR FLUID CALCULATIONS - GASES

Almost all petroleum-engineering problems use the PVT behavior of gases in one form or another. Gas reserves, gas pressure gradients in well bores, and the calculation of gas flow rates at the surface are three example problems requiring a knowledge of gas behavior.

The basic equation expressing the PVT behavior of gases is the ideal gas law:

$$P\bar{V} = \frac{RT}{M} \qquad (8.1)$$

With engineering units:

    P: pressure, absolute (psia)
    $\bar{V}$ = specific volume of the gas (ft$^3$/lb)
    T = temperature, absolute, °R = (460 + °F)
    R: arbitrary constant, = 10.73 for all gases
    M = molecular weight of the gas

Thus, as expressed by Eq. 8.1 the volume of a unit weight of an ideal gas at any equilibrium temperature and pressure can be evaluated solely from a knowledge of the molecular weight of the gas.

If Eq. 8.1 is changed to represent the PVT state of m pounds (lbs) of gas by multiplying both sides by m, we have:

$$PV = \frac{mRT}{M} \qquad (8.2)$$

    where V = total volume occupied by m (lbs) of gas (ft$^3$)

The number of unit pound molecular weights, n, comprising the system is represented by the term m/M in Eq. 8.2. In practice, n, referred to as the pound moles or moles of gas comprising the system, can be evaluated from the relation $n = \frac{m}{M}$ or it can be evaluated in terms of a volume of ideal gas measured at a reference pressure and temperature.

An example of the foregoing is that 28.97 pounds of air represents one pound mole of air, just as 16.04 pounds of methane represents one pound mole of methane. If either 28.97 pounds of air or 16.04 pounds of methane is confined at 14.7 psia and 60°F (called standard pressure and temperature conditions with engineering units), it is found that it occupies very close to 379 ft$^3$ of space. In fact, if they were "ideal" gases, they would occupy 379.4 ft$^3$ per lb mole at 14.7 psia and 60°F.

In practice, it has been found that no gas obeys this simple law over all pressures and temperatures. Hydrocarbons, in particular, deviate widely from the ideal gas law at the elevated pressures and temperatures of petroleum reservoirs.

In order to express a more exact relationship between the variables, P, V, and T, a correction factor must be introduced into Eq. 8.2. Either of two methods is normally used; the first method introduces a multiplying factor into the right side of Eq. 8.2, and the second method makes use of an adding factor. The multiplying factor goes by several names; three of the most common are compressibility factor, deviation factor, and super-expansibility factor. The compressibility factor and deviation factor are synonymous, and the super-expansibility factor is the reciprocal of these two factors. The adding factor is termed the residual volume. Both methods are accurate to the same degree, but the first is easier to use and for this reason is the most popular.

## 8.1 The Compressibility Factor

Placing the compressibility factor, Z, in the right side of Eq. (8.2) and at the same time substituting n for m/M gives:

$$PV = ZnRT \qquad\qquad (8.3)$$

Eq. 8.3 is the basic equation for gas behavior calculations. An illustration of its use is given in Example 8.1. The compressibility factor of an ideal gas is unity at all pressures and temperatures. The compressibility factor of a dry natural gas at atmospheric pressure and temperature is about 0.998 and is ordinarily assumed to be unity. At 2000 psia and 60°F, however, the compressibility factor of a dry gas may be as low as 0.63 and increase to as high at 1.58 at 10 000 psia and 60°F.

The compressibility factors of different gaseous compounds vary over wide ranges at elevated pressures. For example, at 140°F, the compressibility factors of methane, ethane, and propane vary with pressure as shown in Fig. 8.1. A considerable difference exists in the compressibility factor behavior of these first three members of the paraffin hydrocarbon series. Wide differences would also be expected for the higher members of the series.
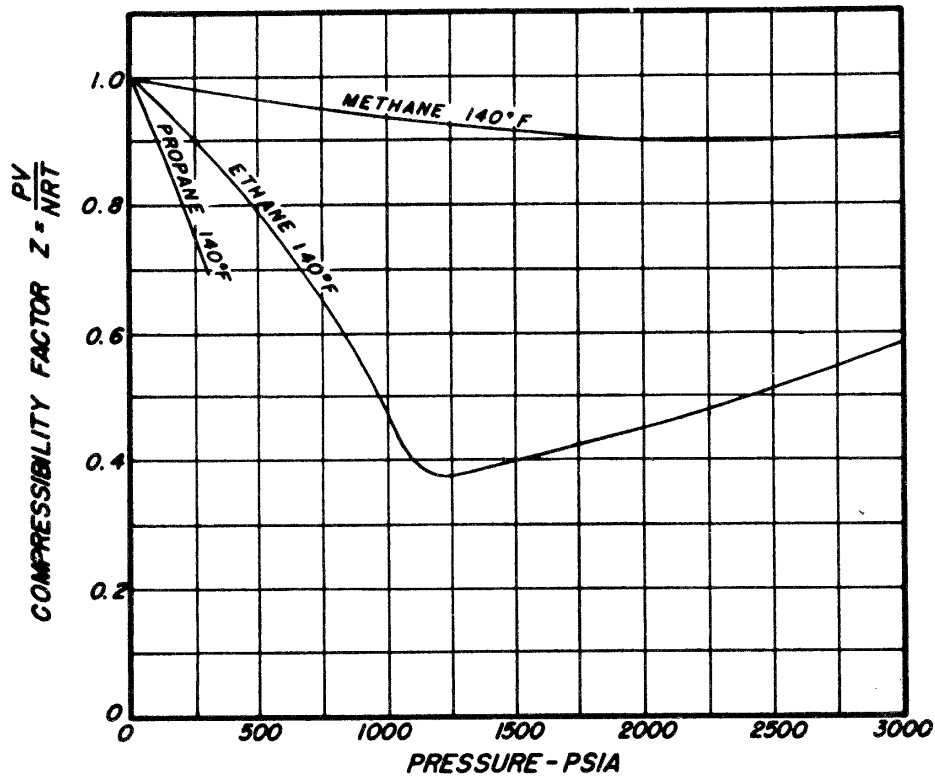


Fig. 8.1. Compressibility Factors of Methane, Ethane, and Propane at 140°F as a function of Pressure

**Example 8.1.** Calculation of Mass and Volumetric Flow of Methane in a Pipeline

To calculate the mass flow rate and the standard cubic feet per day of methane gas flowing in a 6-inch I.D. pipeline operating at 1000 psia and 140°F, assuming the average linear flow velocity in the pipe to be two feet per second

**Solution:**

$$\text{Area of pipe} = \frac{\pi}{4}\left(\frac{6}{12}\right)^2 = 0.1965\ ft^2$$

$$\text{Volumetric rate} = 0.1965 ft^2 \cdot 2\ ft/s = 0.39300\ ft^3/s$$

From Eq. 8.3:

$$PV = ZnRT = Z\frac{m}{M}RT$$

At 1000 psia and 140°F, (Fig. 8.1).

$$Z = 0.94$$

Molecular weight methane; M = 16.04

$$m = \frac{MPV}{ZRT} = \frac{16.04 \cdot 1000 \cdot 0.3930}{0.94 \cdot 10.73 \cdot (460 + 140)} = 1.043\ \text{lb/s}$$

$$\text{Mass rate} = 1.043 \cdot 3600 \cdot 24 = 9.01 \cdot 10^4\ \text{lb / day}$$

$$16.04\ \text{lb methane} = 1\ \text{lb mole} = 379\ ft^3\ \text{at 14.7 psia and 60°F}$$

$$\text{Standard cubic feet per day} = \frac{9.01 \cdot 10^4 \cdot 379}{16.04} = 2.13 \cdot 10^6\ ft^3/s$$

## 8.1.1. Corresponding states theorem

During the 1860's, many papers appeared in the scientific literature concerning the PVT behavior of individual gases. J. D. van der Waals in 1873 developed the theorem of corresponding states on which the modern correlation of compressibility factors is based. The theorem proposes that all gases will exhibit the same behavior when viewed in terms of reduced pressure, reduced volume, and reduced temperature. The term "reduced" means that each variable is expressed as a ratio of the critical value.
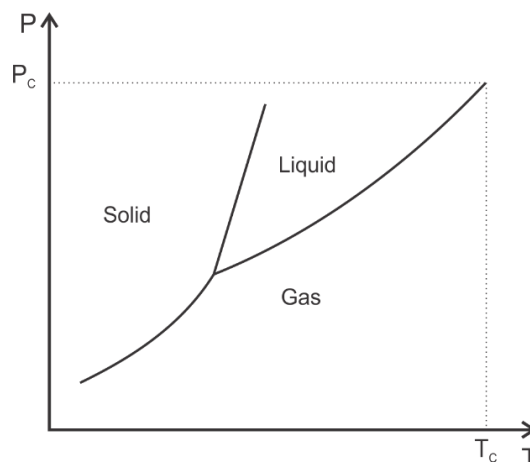


Fig. 8.2. Critical values for a pure gas in a PT diagram

Thus, all variables are reduced to a common datum, the value of the critical. The reduced conditions of volume, temperature, and pressure are expressed as

$$\bar{V}_r = \frac{\bar{V}}{\bar{V}_c}, \qquad\qquad T_r = \frac{T}{T_c}, \qquad\qquad P_r = \frac{P}{P_c} \qquad\qquad (8.4)$$

Where:

subscript r indicates the reduced state

subscript c indicates the critical state.

Critical pressure and temperature for all common gas components are listed in Tbl. 8.1

Tbl. 8.1. PHYSICAL PROPERTIES OF PARAFFIN HYDROCARBONS & MISCELLANEOUS COMPOUNDS

| Comp. | M | $T_{bp\,SC}$ °F | Critical const. | | Liquid $\rho_{L\,SC}$ | | Gas $\rho_{g\,SC}$ | | $ft^3gas/gal$ (Actual) |
|---|---|---|---|---|---|---|---|---|---|
| | | | P, psia | T, °R | g/cm³ | lb/ft³ | lb/MCF | ft³ Gas/ Gal.Liq | |
| C1 | 16.04 | -258.7 | 673 | 3 44 | — | - | 42.27 | — | - |
| C2 | 30 .07 | -127.5 | 709 | 550 | -- | --- | 79.23 | --- | --- |
| C3 | 44.09 | -43.7 | 618 | 666 | 0.5072 | 31.66 | 116.19 | 36.35 | 35.78 |
| i-C4 | 59. 12 | 10.9 | 530 | 733 | 0.5625 | 35.12 | 153.15 | 30.59 | 29.70 |
| n-C4 | 58. 12 | 31.1 | 551 | 766 | 0.5836 | 36.43 | 153.15 | 31.75 | 30.77 |
| i-C5 | 72.15 | 82.1 | 482 | 830 | 0.6241 | 38.96 | 190.11 | 27.35 | 26. 17 |
| n-C5 | 72.15 | 96.9 | 485 | 847 | 0.6305 | 39.36 | 190.11 | 27.63 | 26. 36 |
| n-C6 | 86.17 | 155.7 | 434 | 915 | 0.6637 | 41.43 | 227.07 | 24.34 | 22.83 |
| n-C7 | 100.2 | 209.2 | 397 | 973 | 0.6875 | 42.92 | 264.03 | 21.69 | 19.95 |
| n-C8 | 114.2 | 258.2 | 370 | 1025 | 0.7062 | 44.09 | 300.99 | 19.55 | 17.77 |
| n-C9 | 128.3 | 303.4 | 335 | 1073 | 0.7211 | 45.02 | 337.95 | 17.78 | 15.88 |
| n-C10 | 142.3 | 345.2 | 312 | 1115 | 0.7333 | 44.78 | 374.91 | 16.30 | 14.30 |
| AIR | 28.97 | -317.7 | 547 | 239 | | | | | |
| N₂ | 28.02 | -320.4 | 492 | 227 | | | | | |
| O₂ | 32.00 | -297.4 | 732 | 278 | | | | | |
| CO₂ | 44.01 | -109.3 | 1072 | 548 | | | | | |
| H₂S | 34.08 | -76.5 | 1306 | 673 | | | | | |
| H₂O | | 18.02 | 212.0 | 3206 | 1165 | 0.9991 | 62.37 | | |

SC – Standard conditions, 14.7 psia and 60 °F

The theorem of corresponding states is not perfect. However, when applied to gases having similar chemical structure (as paraffin hydrocarbons), it offers a correlation method with satisfactory accuracy for engineering work. This is shown by the reduced PVT data on methane, ethane, and propane plotted in Fig. 8.3. The curve in Fig. 8.3 is an average curve sketched in to show the degree of correlation.

In 1936, W. B. Kay" presented experimental data and outlined a correlation method that can be used for mixtures of gaseous compounds. Kay's work forms the basis for the modern methods concerned with natural gases. It can be summarized as follows;

(1) The theorem of corresponding states, with modifications, can be applied to a mixture of gases, as well as to individual gases.

(2) In order to correlate the PVT behavior of a gas mixture with the reduced states of individual gases, it is necessary to use fictitious values for the critical temperature and pressure of the mixture. The fictitious values are called pseudo critical values to differentiate them from the true critical values of the mixtures.

(3) The pseudo-critical pressure $\left( _pP_c \right)$ and temperature $\left( _pT_c \right)$ of a mixture of low molecular weight gases are obtained by summing the product of the mole fraction of each component times the component's true critical value. For example, the pseudo-critical temperature of a mixture composed of 80 mole% methane and 20 mole% propane is $0.80 \cdot 344 + 0.20 \cdot 666 = 408.4°R$.

(4) High molecular weight compounds or mixtures of compounds require pseudo-critical rather than true critical values when used in the theorem of corresponding states. The correct pseudo-critical constants are evaluated by determining the values which give the best agreement between experimentally determined volumetric data and calculated volumetric data. For example, Kay found that for a binary mixture of 26.62 mole% ethane and 73.38 mole% n-heptane, it would be necessary to use pseudocritical constants of 990°R and 355 psia for n-heptane in order for the theorem of corresponding states to apply to that mixture. The true critical values of n-heptanes are 973°R and 397 psia.
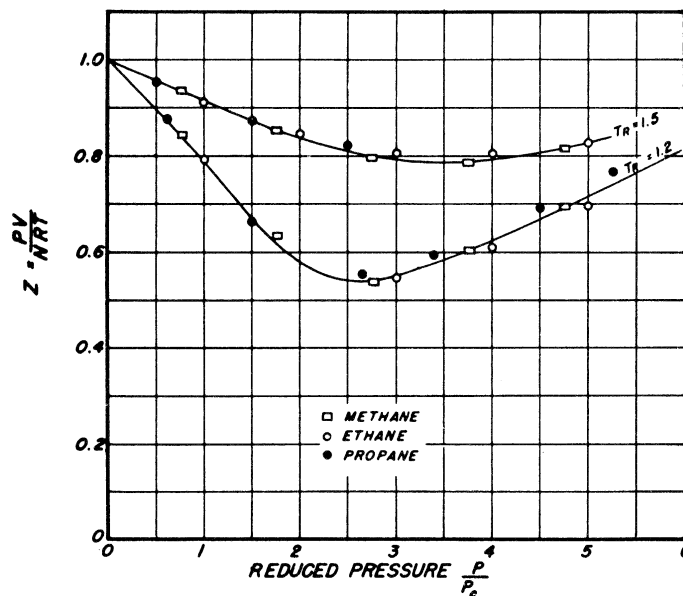


Fig. 8.3. Compressibility Factors of Methane, Ethane, and Propane as a function of Reduced Pressure $P_r$, and Reduced Temperature $T_r$ .

The pseudo-critical pressure $\left( _pP_c \right)$ and temperature $\left( _pT_c \right)$ are expressed by the equations:

$$pT_c = \sum y_i \cdot T_{c_i} \tag{8.5}$$

$$pP_c = \sum y_i \cdot P_{c_i} \tag{8.6}$$

Where $T_{c_i}$ and $P_{c_i}$ are tabled values for the individual components i (Tbl.8.1) in the gas mixture

Most natural gases handled in surface equipment contain only small fractions of hexane and heavier compounds. Because of the small quantities of heavy components, the calculated pseudo-critical constants of the mixture are only slightly in error when the true critical constants of the heavy components are used in place of proper pseudo-critical values. Furthermore, gas analyses seldom determine properties from which the pseudo-critical values can be determined for the "plus" component. Consequently, the usual practice is to use the true critical constants for all compounds except the plus component and to use the true critical value of the next highest compound to represent the plus component. This is illustrated in Example 8.2 wherein the critical constants of n-octane are assigned to the heptanes plus (C7+) fraction.
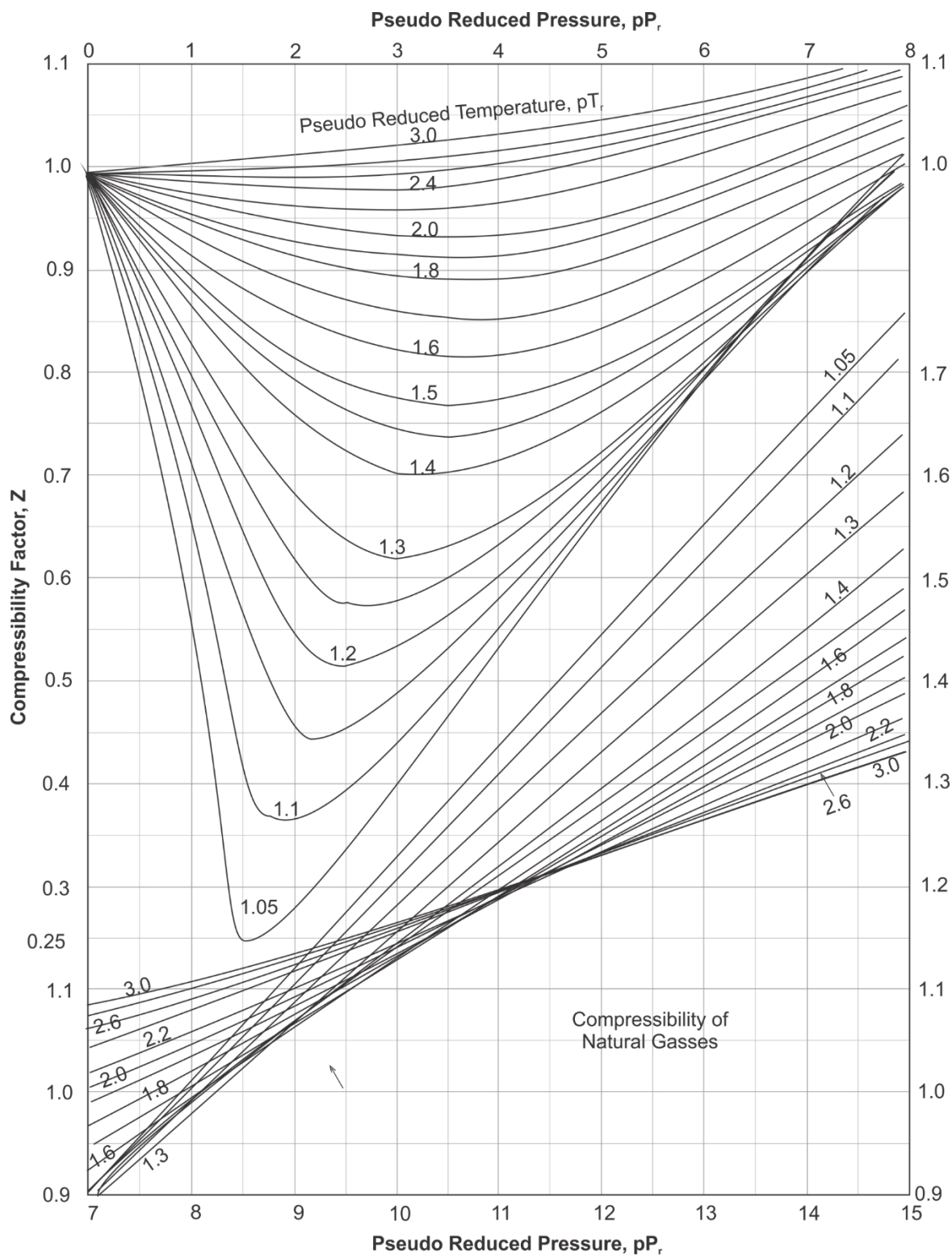
Fig. 8.4.  Compressibility Factor (Z) for Natural Gases
(After Standing and Katz, Trans. AIME, 1942)

A curve-fit program published by M. B. Standing:

$$Z = A + (1-A)/e^B + C\, P_r^D$$

where:

$A = 1.39(T_r - 0.92)^{0.5} - 0.36T_r - 0.101$

$B = (0.62 - 0.23T_r)P_r + [0.066/(T_r - 0.86) - 0.037]\, P_r^2 + 0.32\, P_r^6/10^{9(T_r-1)}$

$C = 0.132 - 0.32 \log T_r$

$D = \text{antilog}(0.3106 - 0.49T_r + 0.1824T_r^2) = 10^{(0.3106 - 0.49T_r + 0.1824T_r 2)}$

8-6

Example 8.2 illustrates also the method of evaluating a compressibility factor of a gas at an elevated pressure and temperature when the composition of the gas is known. Multiplying the mole fractions of the individual compounds by their true critical values gives the pseudo-critical constants of the mixture. By using the reduced relationship shown in Eq. 8.4, it is possible to evaluate the compressibility factor of the gas at any desired pressure and temperature from suitable compressibility factor charts.

The compressibility factor chart shown in Fig. 8.4 is applicable to most gases encountered in petroleum reservoirs. The calculated volumetric behavior of gases containing only minor amounts of nonhydrocarbons can be expected to be accurate within 3 % when using calculated pseudocritical constants and the reduced relations shown in Fig. 8.4.

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**Example 8.2.** Calculation of Gas Pressure Gradient in the Annulus of a Well

To compute the pressure gradient in a gas column at 200°F and 3000 psia, given the composition of the gas.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| Comp. $i$ | Mole frac. $y_i$ | Mole Weight, $M_i$ | $y_i \cdot M_i$ | Critical Temp., $T_{c_i}$ | $y_i \cdot T_{c_i}$ | Critical Pres., $P_{c_i}$ | $y_i \cdot P_{c_i}$ |
| C1 | 0.840 | 16.0 | 13.44 | 344 | 289.0 | 673 | 565.3 |
| C2 | 0.083 | 30.1 | 2.50 | 550 | 45.7 | 709 | 58.8 |
| C3 | 0.042 | 44.1 | 1.85 | 666 | 28.0 | 618 | 25.9 |
| i-C4 | 0.007 | 58.1 | 0.41 | 733 | 5.1 | 530 | 3.7 |
| n-C4 | 0.014 | 58.1 | 0.81 | 766 | 10.7 | 551 | 7.7 |
| i-C5 | 0.005 | 72.1 | 0.36 | 830 | 4.1 | 482 | 2.4 |
| n-C5 | 0.004 | 72.1 | 0.29 | 847 | 3.4 | 485 | 1.9 |
| C6 | 0.002 | 86.2 | 0.17 | 915 | 1.8 | 434 | 0.9 |
| C7+ | 0.003 | 114* | 0.34 | 1025* | 3.1 | 370* | 1.1 |
| $\Sigma$ | 1 | | 20.17 | | 390.9 | | 667.7 |

*C7+ fraction has been assigned properties of octane, Tbl. 8.1

$$_pT_r = \frac{T}{_pT_c} = \frac{660}{290.9} = 1.69$$

$$_pP_r = \frac{P}{_pP_c} = \frac{3000}{667.7} = 4.5$$

Compressibility factor (Fig. 8.4):

$$Z = 0.862$$

Average molecular weight of gas =20.17

$$\text{Density} = \frac{1}{V} = \frac{PM}{ZRT} = \frac{3000 \cdot (20.17)}{0.862 \cdot 10.73 \cdot 660} = 9.91 \text{ lb/ft}^3$$

$$\text{Gas gradient} = \frac{9.91}{144} = 0.069 \text{ psi/ft}$$

## 8.1.2. Pseudo-critical Constants – Gas Gravity relations

Unfortunately, the composition of a gas from which to compute the pseudo-reduced state is not always available. As gas gravity measured by a Schilling Bottle or Edwards Balance is a common field measurement, it is advantageous to have a method of predicting the compressibility factor solely from gas gravity.

In Tbl. 8.1, we observe that critical pressure ($P_c$) decreases and critical temperatures ($T_c$) increases as the molecular weights of the hydrocarbons increases.

With the exception of the $P_c$ of methane and minor discrepancies caused by isomeric compounds, there is good correlation between the critical constants and molecular weight of the paraffin series of hydrocarbons found in petroleum reservoirs. As the pseudo-critical pressure ($pP_c$), the pseudo-critical temperature ($pT_c$), and the average molecular weight of a gas are always obtained by multiplying the appropriate constants of the components by their mole fractions and adding the resultant products, it would be expected that a correlation of the pseudo-critical constants with the average molecular weight of the gas would exist for gases of similar makeup.

A test of this reasoning is shown in Fig. 8.5.

The pseudo-critical constants of 71 California natural gases, calculated by the method illustrated in Example 8.2, have been plotted against their calculated gravity ($\gamma_g = \dfrac{M_g}{M_{air}} = \dfrac{M_g}{28.98}$). These 71 gases consist of high-pressure trap gases (200-500 psi), low-pressure trap gases (30-100 psi), and tank vapors, although a few condensate well effluents and laboratory mixtures have been included. As can be seen, a good correlation exists between the variables for these particular gases.

Pseudo-critical constants-gas gravity correlations similar to those shown in Fig. 8.5 have been presented by other authors. Mathews, Roland, and Katz have presented data on 25 Oklahoma City (Wilcox) gases that included high-pressure equilibrium vapors, trap gases, plant intakes, and plant residues. The relations obtained for these gases are shown in Fig. 8.6.

In addition, these authors found a relation for 150 miscellaneous gases that falls almost exactly on the California gas relation shown in Fig. 8.5. Standing and Katz obtained a slightly different relation; however, their gases differed from the California gases in that the high gravities were caused by quantities of hexane and heptanes plus material in the gas, rather than quantities of ethane and propane. Consequently, their gravity-pseudo-critical relations would not be expected to be the same as those of the California gases.

Before discussing in detail the use of Fig. 8.6, the reason for the favorable correlations should be emphasized. All the gasses in the correlations had nitrogen content less than 2%. . The carbon dioxide content of the gases was, with few exceptions, less than 1%. Finally, their hydrocarbon compositions followed a definite trend, i.e., the mole fraction of methane in the high pressure trap gases and well effluents was of the order of 85 %, the ethane about one-tenth of the methane, and the propane about one-half of the ethane. The composition of the gas used in the Example 8.2 is characteristic of the average high-pressure trap gas used in these correlations. The condensate fluids, in addition to having a relative methane-ethane-propane ratio similar to that mentioned, contained up to 5-mole % of heptanes plus material.
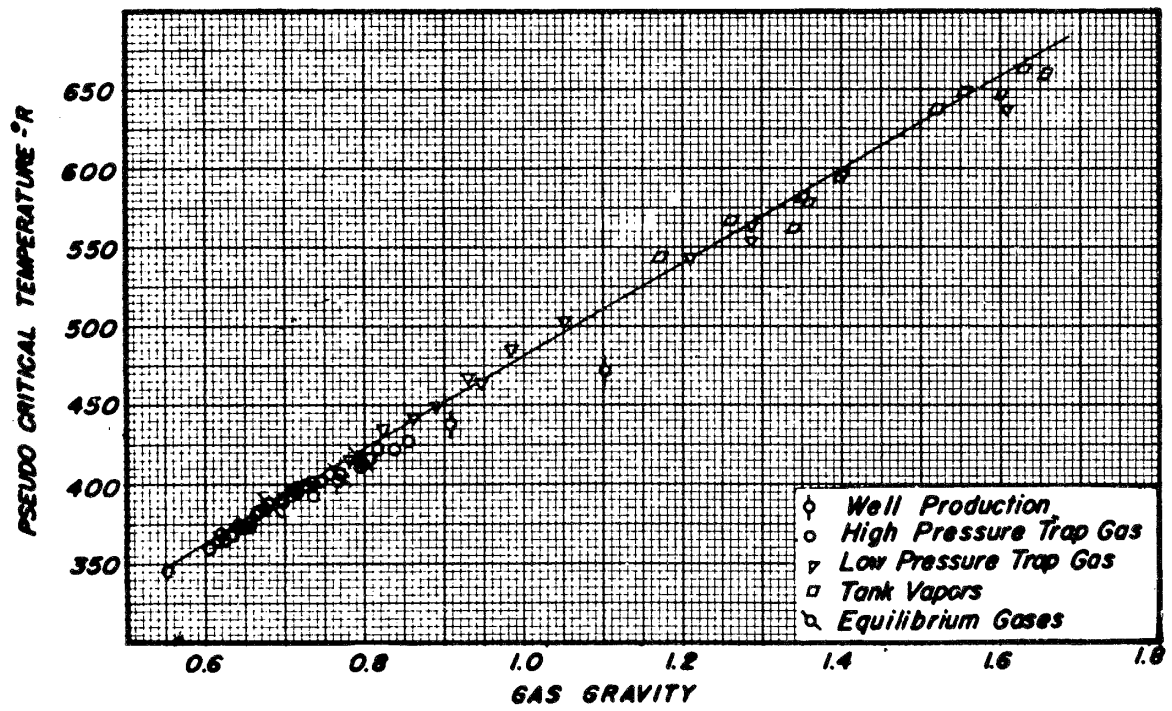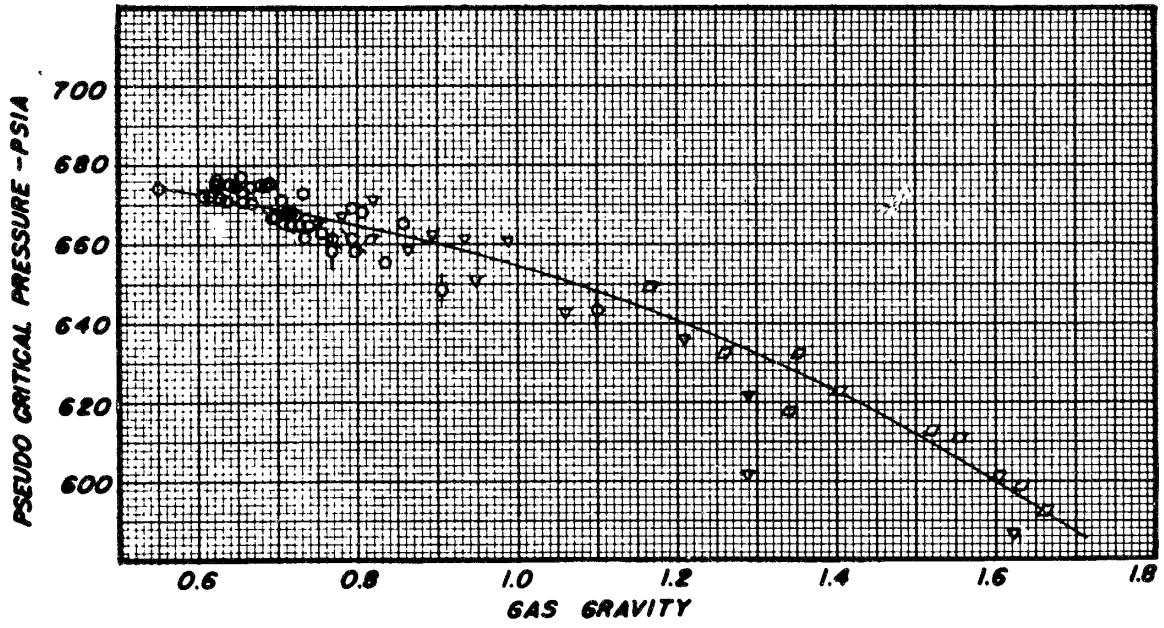
Fig. 8.5. Pseudo-critical Pressure $pP_c$, and Pseudo-critical Temperature $pT_c$, vs. Gas Gravity. California Natural Gases
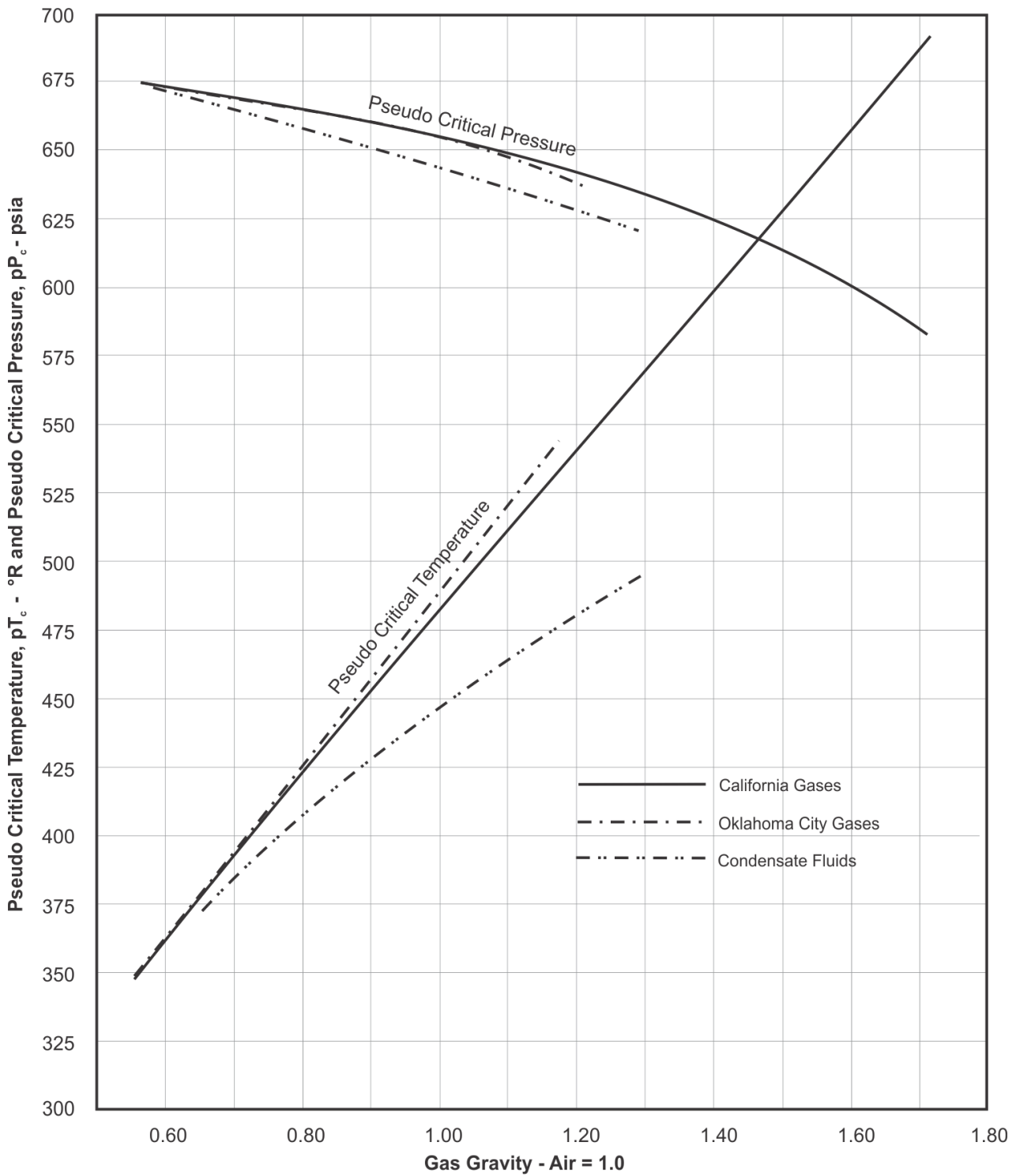
Fig. 8.6. Psuedo-critical Constants $pP_c$ and $pT_c$ of Gases and Condensate Well Fluids.

Curve fit formulas Surface gas (dry gas):

$$_pP_r\ (psia) = 677 + 15.0\,\gamma - 37.5\,\gamma^2$$
$$_pT_r(°R) = 168 + 325\,\gamma - 12.5\,\gamma^2$$

Curve fit formulas reservoir gas (wet /condensate):

$$_pP_r\ (psia) = 706 - 51.7\gamma - 11.1\,\gamma^2$$
$$_pT_r(°R) = 187 + 330\gamma - 71.5\gamma^2$$

The relations shown in Figs. 8.3 and 8.5 greatly facilitate calculations of gas behavior. For example, the pressure-temperature-density relations of gases whose pseudo-critical-gas gravity relations follow the California gases are shown in Figs. 8.6, 8.7, and 8.8. These charts, with linear interpolations between charts, give density data which are usually in error by less than 3 %. The error to be expected when applying Fig. 8.7 to Fig. 8.9 to an unknown gas can, of course, be greater than 3 %, because of the possibility that the unknown gas contains nonhydrocarbon components or a distribution of hydrocarbons different from those used in the correlation. However, as the relations used to obtain Figs. 8.6 to 8.8 gave good agreement with Mathews, Roland, andKatz's 150 miscellaneous gases, their 25 Oklahoma City gases, and the 71 California gases, some confidence can be placed in the general use of the charts. An illustration of such general use is given in Example 8.3.

| **Example 8.3.** Calculation of the Reservoir Volume Occupied by one MCF Surface Gas. |
|---|
| To compute the volume of reservoir space at 2750 psia and 220°F occupied by one MCF of 0.75 gravity surface gas. |
| **Solution:** Interpolation at 2750 psia and 220°F between the 0.70 gravity and 0.80 gravity charts (Fig. 8.8 and 8.9) gives:<br><br>$\quad$ Density $= 8.77 + 0.5 \cdot (10.54 - 8.77) = 9.65 \text{ lb/ft}^3$<br><br>$\quad$ One MCF surface gas $= \dfrac{1000}{379} \cdot 0.75 \cdot 28.97 \mathrel{\cdotp}= 57.3 \text{ lb}$<br><br>$\quad$ Volume $= \dfrac{57.3}{9.65} = 5.94 \text{ ft}^3$<br><br>**Alternate Solution:**<br><br>From Fig. 8.6, $pT_c = 407°R$, $pP_c = 667$ psia<br><br>At 2750 psia and 220°F<br><br>$\quad pT_r = \dfrac{220 + 460}{407} = 1.67$<br><br>$\quad pP_r = \dfrac{2750}{667} = 4.12$<br><br>From Fig. 8.5, Z = 0.848<br><br>Number of lb moles, n, in 1000 standard ft$^3$ of gas<br><br>$\quad n = \dfrac{1000}{379}$<br><br>From gas law equation:<br><br>$\quad V = \dfrac{nRT}{P} = \dfrac{1000 \cdot 0.848 \cdot 10.73 \cdot (220 + 460)}{379 \cdot 2750} = 5.93 \text{ ft}^3$ |

Fig. 8.7. Pressure-Volume-Temperature Relations of 0.60 Gravity Natural Gas

Fig. 8.8—Pressure-Volume-Temperature Relations of 0.70 Gravity Natural Gas
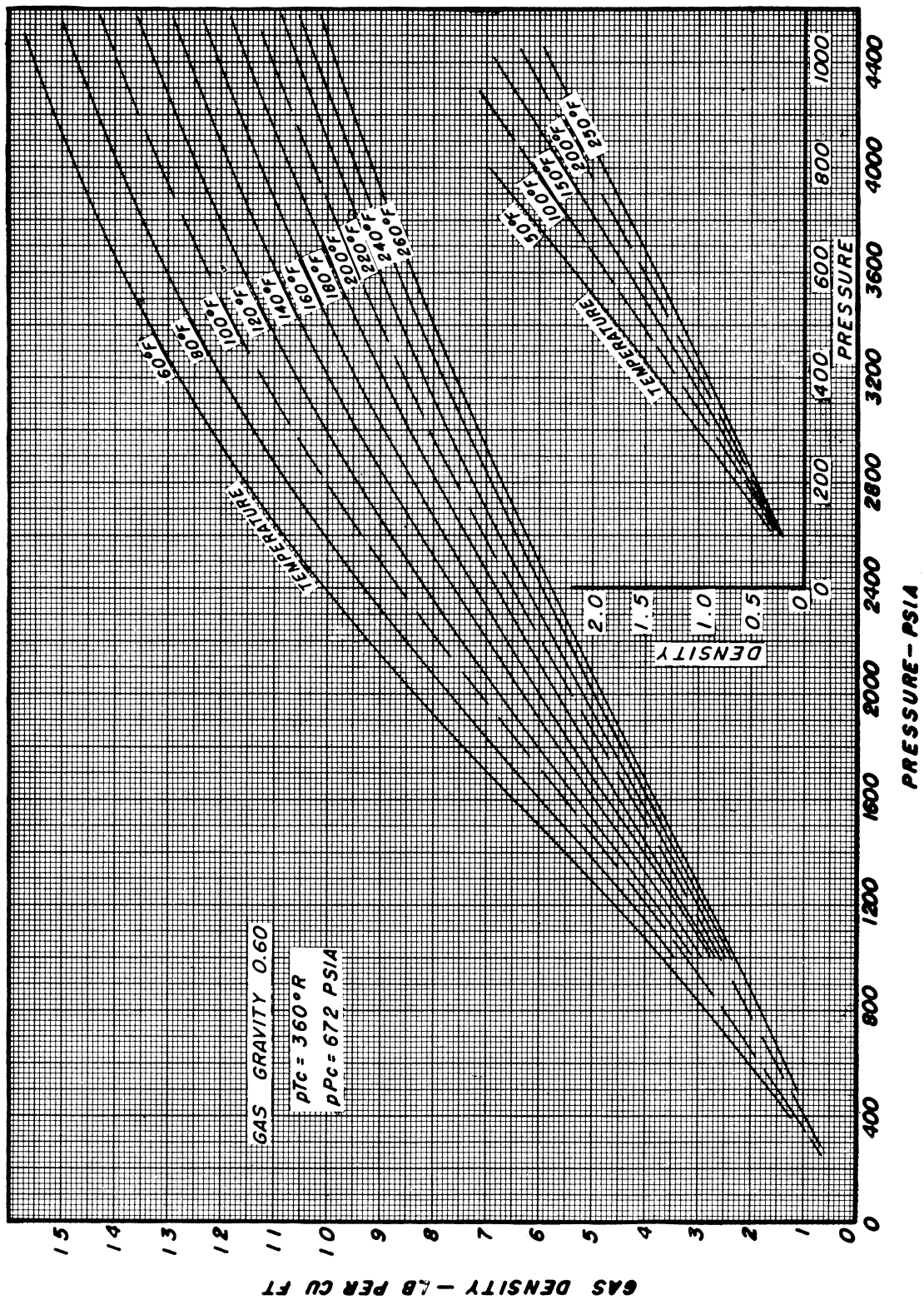
Fig. 8.9. Pressure-Volume-Temperature Relations of 0 80 Gravity Natural Gas

### 8.1.3. Use of Pseudo-critical Constant-Gas Gravity - Relations in metering Gases

The calculation of gas meter factors at high pressures is a further application of data of Fig. 8.5 and Fig. 8.6. The meter formula may be expressed as

$$q = c \cdot \sqrt{\frac{1}{\gamma}} \cdot \sqrt{\frac{520}{T}} \cdot \sqrt{\frac{1}{Z}} \cdot \sqrt{P \cdot h} \qquad (8.7)$$

where
  q = standard ft$^3$ of gas flowing per unit time
  c = meter constant, dependent on orifice diameter, pipe diameter, etc.
  γ = gas gravity (air = 1)
  T = flowing temperature of gas, (°R)
  Z = compressibility factor at flowing pressure and temperature
  P = flowing pressure (psia)
  h = orifice differential (inches of water)

The first three square-root terms may be combined as a single correction factor, $F_{\gamma TZ} = \sqrt{\frac{520}{\gamma TZ}}$ and the total factor plotted for any particular gas as a function of flowing temperature and pressure. An illustration of this is shown in Fig. 8.10.
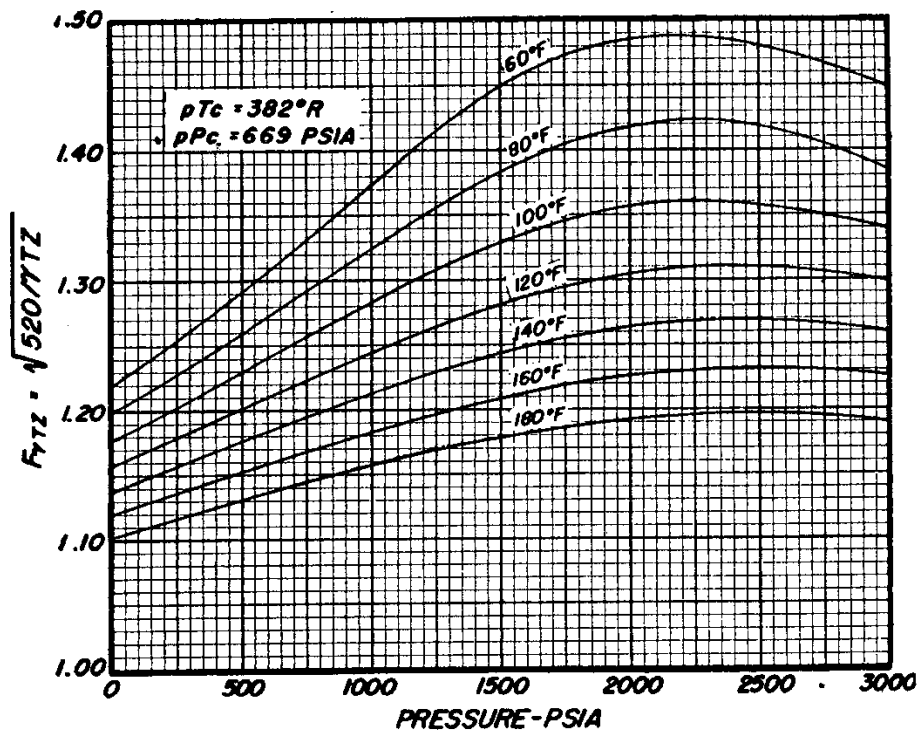


Fig. 8.10. Meter Factors. Murphy-Coyote 0.67 Gravity Gas

### 8.1.4 Effect of Nonhydrocarbon Components on Compressibility Factors

Nitrogen and carbon dioxide are often present in appreciable concentrations in natural gases. As can be seen in Tbl. 8.1, the critical constant-gravity relationship of these compounds does not fit in with that of the paraffinic hydrocarbons. It is to-be expected, therefore, that correction based on gas gravity can be in error when applied to gasses containing large quantities of the nonhydrocarbons.

Eilerts, Mullens, and Carlson studied the compressibility of nitrogen and natural gas mixtures. They proposed that the compressibility of a nitrogen bearing natural gas be determined by separately

evaluating the compressibility factors of the hydrocarbon portion and the nitrogen portion of the gas mixture and then obtaining an "additive" compressibility factor as follows:

$$Z_a = nZ_n + (1 - n)Z_h \qquad (8.8)$$

where

$Z_a$ = additive compressibility factor

$Z_n$ = compressibility factor of the nitrogen in the gas sample

$Z_h$ = compressibility factor of the mixture of hydrocarbons in the gas sample

n = mole fraction nitrogen in the sample

The computed value of the additive compressibility factor, $Z_a$, then has to be corrected to the actual compressibility factor, Z, by the equation:

$$Z = c \cdot Z_a \qquad (8.9)$$

where c is an arbitrary factor to account for the fact that volumes -of natural gas and nitrogen are not quite additive. Values of c, presented by the authors in chart form, indicate that the correction factor, c, is between 1.00 and 1.04 at temperatures above 70°F, and for nitrogen concentrations less than 20%.

The above method is, of course, complicated by the requirement for c charts as well as compressibility charts both for the hydrocarbon gases and for nitrogen. Use of critical constants of nitrogen, 492 psia and 227°R, in the theorem of corresponding states yields a much easier way of calculating a compressibility factor. At nitrogen concentrations of less than 20%, the compressibility factor of the entire gas evaluated by the theorem of corresponding states is usually in error less than 4 %.

Olds, Sage, and Lacey" investigated the behavior of carbon dioxide-methane mixtures. Reamer, Olds, Sage, and Lacey" determined compressibility factors for the ethane-carbon dioxide system.

Application of the theorem of corresponding states will yield satisfactory results for natural gases having 2 % carbon dioxide or less. Olds, Sage, and Lacey indicated a possible error of 5 % in the compressibility factor at a concentration of 4 % carbon dioxide.


### 8.1.5 Residual Volume Methods

Residual volumes present the second or "additive" method of calculating PVT behavior of gases. The residual specific volume of an individual gas is defined by the equation:

$$\bar{V}_\sim = \bar{V}_{(perfect)} - \bar{V}_{(actual)} = \frac{RT}{MP} - \bar{V} \qquad (8.10)$$

where

$\bar{V}_\sim$: residual specific volume, ft$^3$/lb

$\bar{V}$: specific volume, ft$^3$/lb

R : gas constant, per mole

M : molecular weight of the gas

T : temperature, R

P : pressure, Psia

Thus, the residual volume is the difference between the volume of a gas computed as an ideal gas and the actual gas volume. The residual becomes negative in the region of temperature and pressure where the actual gas occupies a volume larger than the corresponding volume of an ideal gas. (This is comparable to the region of Fig. 8.5 wherein Z is greater than unity.)

The use of residual volumes becomes more complicated when a multicomponent gas is considered. Just as in the case of the compressibility factor method, it is necessary to take into account the composition of the gas when calculating the deviation of the gas behavior from the ideal behavior.

In calculating a compressibility factor, the weighting is accomplished by multiplying the mole fraction of each component by the critical constants of the component and summing the products. In the residual volume method the weighting is accomplished as shown by the following equations:

$$\bar{V}_\sim = \bar{V}_{\sim 1} n_{\sim 1} + \bar{V}_{\sim 2} n_{\sim 2} + \cdots\cdots + \bar{V}_{\sim j} n_{\sim j} \tag{8.11}$$

or as can be seen from Eq. 8.11 :

$$\bar{V} = \frac{RT}{M_a P} - \left( \bar{V}_{\sim 1} n_{\sim 1} + \bar{V}_{\sim 2} n_{\sim 2} + \cdots\cdots + \bar{V}_{\sim j} n_{\sim j} \right) \tag{8.12}$$

where

$M_a$ : average molecular weight of the whole gas

$n_j$ : weight fraction of a component in the gas

$\bar{V}_\sim$ : residual partial specific volume of a component in the gas, ft$^3$/lb

The first term in Eq. 8.12 represents the specific volume of the whole gas if it follows the ideal gas law, whereas the succeeding terms are the deviation from this idealized behavior of each of the components in the gas. In Eq. 8.12, the residual partial volume of each component is a function of pressure, temperature, and the nature and amount of all the other components present in the gas.* (The method of determining residual partial specific volumes and their mathematical significance has been given by Sage and Lacey. The discussion will not be repeated here).

Sage and Lacey and their co-workers have studied systematically the behavior of binary systems composed of the lighter components found in natural gases. By 1939, residual partial specific volume data had been reported on methane, ethane, propane, and n-butane at pressures to 3000 psia and at temperatures between 70°F and 250°F. Since then, partial volume data (from which residual partial volumes can be calculated) have been extended to 10,000 psia and 460°F. Additional systems composed of methane - decane, and methane - n-butane - decane have been investigated.

Let us consider the use of residual partial specific volume data in computing the specific volume of a gas at an elevated pressure and temperature. In order to use the published residual data," it must be assumed that the residual partial volume of the material that is heavier than isobutane can be represented by that of n-butane. If we let $(\bar{V}_{\sim 1})_{1:2}$, $(\bar{V}_{\sim 1})_{1:3}$, and $(\bar{V}_{\sim 1})_{1:4}$ represent the residual partial specific volume of methane in the methane - ethane, methane - propane, and methane - n-butane systems, and give weight to the individual methane values in direct proportion to the concentration of the heavier component in the three binary systems, the weighted residual partial volume of methane may be established from the following relation:

$$\bar{V}_{\sim 1} = \frac{(\bar{V}_{\sim 1})_{1:2}(n_{\sim 2}) + (\bar{V}_{\sim 1})_{1:3}(n_{\sim 3}) + (\bar{V}_{\sim 1})_{1:4}(n_{\sim 4})}{1 - n_j} \tag{8.13}$$

In absence of similar data to calculate weighted residual partial volumes of ethane, propane, and butane, it is necessary to assume that the value determined in combination with methane is applicable to any multicomponent system.

Substituting the value of $\bar{V}_{\sim 1}$ in. Eq. 8.13 into the second term in Eq. 8.12 gives the following equation:

$$\bar{V} = \frac{10.73\, T}{M_a P} - \left[ \frac{n_1}{1 - n_1} \right] [(\bar{V}_{\sim 1})_{1:2}(n_{\sim 2}) + (\bar{V}_{\sim 1})_{1:3}(n_{\sim 3}) + (\bar{V}_{\sim 1})_{1:4}(n_{\sim 4})]$$
$$- (\bar{V}_{\sim 2} \cdot n_{\sim 2} + \bar{V}_{\sim 3} \cdot n_{\sim 3} + \bar{V}_{\sim 4} \cdot n_{\sim 4}) \tag{8.14}$$

The calculation of the specific volume of 0.675 gravity gas at 3000 psia and 250°F, shown in Example 8.4, illustrates the use of Eq. 8.14 and residual partial volume data.

**Example 8.4.**

Calculation of the Specific Volume of a Gas Using Residual Volume Data, Pressure 3000 PSIA, Temperature 250°F.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| Comp | mole frac. n | Molecular Weight, M | n·M | Weight frac. n | | $(\bar{V}_{\sim 1})_{1:-}$ | $\bar{V}_{\sim}$ |
| C1 | 0.8602 | 16.0 | 13.80 | 0.7128 | | - | - |
| C2 | 0.0770 | 30.1 | 2.32 | 0.1201 | | 0.00648 | 0.0352 |
| C3 | 0.0426 | 44.1 | 1.88 | 0.0973 | | 0.0066 | 0.0320 |
| i-C4 | 0.0057 | 58.1 | 0.33 | 0.0171 | | | |
| n-C4 | 0.0087 | 58.1 | 0.51 | 0.0264 | Weight frac. i-C4+ = 0.0699 | 0.037 | 0.0315 |
| i-C5 | 0.0011 | 72.2 | 0.08 | 0.0041 | | | |
| n-C5 | 0.0014 | 72.2 | 0.10 | 0.0052 | | | |
| C6+ | 0.0033 | 100 | 0.33 | 0.0177 | | | |
| | 1.0000 | | 19.32 | 1.000 | | | |

**Solution:**

Values for $\bar{V}_{\sim 1}$, $(\bar{V}_{\sim 1})_{1:2}$ , etc. at 3000 PSIA and 250°F are from data tabulated in [1]

Specific volume:

$$\bar{V} = \frac{10.73 \cdot T}{M_a P} - \left[\frac{n_1}{1-n_1}\right][(\bar{V}_{\sim 1})_{1:2}(n_{\sim 2}) + (\bar{V}_{\sim 1})_{1:3}(n_{\sim 3}) + (\bar{V}_{\sim 1})_{1:4}(n_{\sim 4})] - (\bar{V}_{\sim 2} \cdot n_{\sim 2} + \bar{V}_{\sim 3} \cdot n_{\sim 3} + \bar{V}_{\sim 4} \cdot n_{\sim 4}) =$$

$$\frac{10.73 \cdot 710}{19.32 \cdot 3000} - \left[\frac{0.7143}{1-0.7143}\right][0.0648 \cdot 0.1201 + 0.0066 \cdot 0.0973 + 0.0037 \cdot 0.0699] - (0.0352 \cdot 0.1201 + 0.0320 \cdot 0.0973 + 0.0315 \cdot 0.0683)$$
$$= 0.1168$$

Specific volume, $\bar{V}$ =0.1168 ft3/lb

The length of the calculations would appear to be about equal to the length using compressibility factors. However, residual partial volumes are not interpolated easily between tabulated pressures and temperatures, so the usual calculation is actually more laborious than indicated here. When a problem calls for a solution of pressure, with the temperature, volume, and composition of the gas given, the calculations may become excessively complicated because the pressure must be roughly known in order to evaluate the residual partial volumes. In other words, it is necessary to resort to a trial and error calculation method of determining the pressure.

The accuracy of the residual volume method is at present no better than that of the compressibility factor method. For example, specific volumes of the gas, shown in Example 8.4 calculated at 3000 psia and 250°F by the three methods outlined in this chapter, gave the following agreements with the experimentally determined specific volume:

| | Specific Volume (ft³/lb) | % Error |
|---|---|---|
| Experimental | 0.1217 | - |
| By Fig. 8.6 and Fig. 8.7 | 0.1203 | - 1.15 |
| By pseudo-critical method | 0.1197 | - 1.65 |
| By residual volume method | 0.1168 | -4.40 |

## 8.2. Gas reservoir reserve calculations

For the real gas equation, $PV = ZnRT$ , the following relations can be put forward:

Density:

$$\rho = \frac{m}{V} = \frac{PM_g}{ZRT}$$

(8.15)

Specific volume:

$$v = \frac{1}{\rho} = \frac{ZRT}{PM_g}$$

(8.16)

Specific gravity:

$$\gamma_g = \frac{\rho_g}{\rho_{air}} = \frac{M_g}{M_{air}} = \frac{M_g}{28.96}$$

(8.17)

Compressibility factor:

$$Z = f(pT_r, pP_r)$$

(8.18)

### 8.2.1 Dry gas reservoirs

Dry gases are predominantly composed of methane and non-hydrocarbons such as nitrogen and carbon dioxide. Fig. 8.11 shows the phase diagram of a dry gas. The phase envelope is relatively tight and mostly located below the ambient temperature. Note that the gas remains single phase from the reservoir to the separator conditions. Water, however, may condense at the surface conditions due to the gas cooling. PVT tests in the laboratory are limited to the gas compressibility measurement.
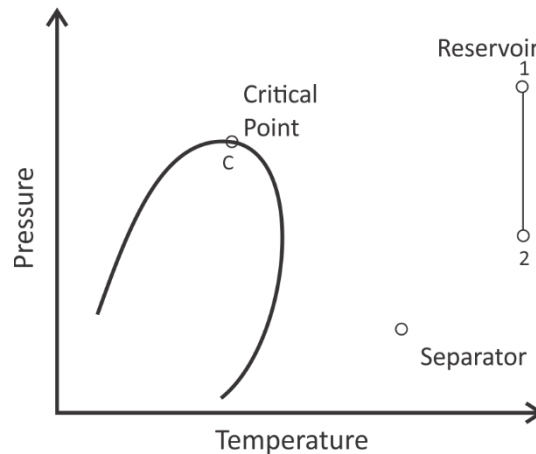


Fig. 8.11. Phase diagram of dry gas.

Gas formation volume factor:

$$B_g = \frac{(V_g)_{res}}{(V_g)_{SC}} = \frac{P_{SC} \cdot Z_{res} \cdot T_{res}}{T_{SC} \cdot P_{res}}$$

(8.19)

Gas in place (GIP):

$$GIP = \frac{HCPV}{B_g} \tag{8.20}$$

Recovery factor (closed reservoir):

$$R_g = \frac{(n_i - n)}{n_i} = 1 - \frac{Z_i P}{Z P_i} \tag{8.21}$$

Cumulative production:

$$G_p = G_i R_g \tag{8.22}$$

Symbols:
HCPV: hydro carbon pore volume
$n_i$: number of moles at $P_i$
n: number of moles at P
$P_i$: initial pressure
P: actual pressure
$G_i$: initial gas in place, IGIP, SC.


## 8.3. Content of water

Prior to the drying process (glycol treatment) the gas produced from the reservoir is supposed to be in equilibrium with liquid water. Water is not ordinary reported in the composition table. In order to estimate the amount of water produced it is sometimes convenient to add water to the laboratory analysis. By supposing an equilibrium with liquid water, this can be done by using Dalton´s law:

$$y_w = \frac{P_w}{P} \tag{8.23}$$

where;
$y_w$: molefraction of water
$P_w$: partial pressure of water at given temperature
$P$: total pressure

A normalized final composition analysis of the gas is then:

$$(y_i)_c = (1 - y_w)(y_i)_1 \tag{8.24}$$

where;
$(y_i)_c$: corrected mole fraction of component i including all components.
$(y_i)_1$: mole fraction from laboratory analysis of component i (not included $H_2O$)

This way of estimating the amount of water in the gas is based on the ideal conditions (Dalton´s law), and at high pressure, the amount of water is underestimated.


Mc. Carthy et al. (Trans. AIME, 1950, p.189) have summarized empirical data for the content of water in natural gas using charts. The weight of water pr. standard volume unite of gas can be determined from the empirical relationship:

$$W_w = 4.73 \cdot 10^4 \frac{P_w}{P - P_w} \tag{8.25}$$

where;
$W_w$: weight of water, (lb/$10^6$ SCF)
$P_w$: partial pressure of water
$P$ : total pressure

### 8.3.1. Hydrate formation

A natural gas hydrate is a solid mixture of water and natural gas with a freezing point which depends on the gas composition, available water, pressure, and temperature.

It is often stated that free water is required for hydrate formation. There are two crystalline structures for gas hydrates;

**Structure 1:**

Small molecules ($CH_4$, $C_2H_6$, $H_2S$) form a body centered cubic structure. The bonding ratio is:

| | | |
|---|---|---|
| Small gases: | $H_2O$: $CH_4$ | = 5.75 |
| Medium gases: | $H_2O$: $C_2H_6$ | = 7.66 |

**Structure 2:**

Larger molecules ($C_3H_8$, $i$-$C_4H_{10}$) form a diamond lattice structure with 17 $H_2O$ per gas molecule.
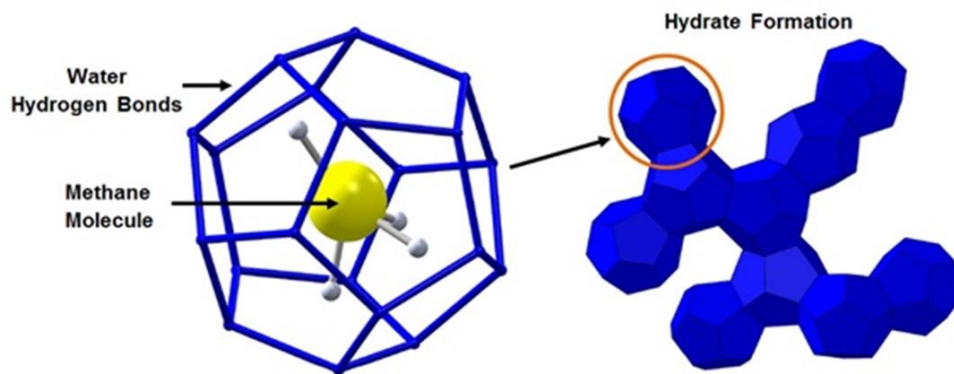


Fig. 8.12 . Hydrate structure - type 1

### 8.3.2. Prediction of Hydrate formation

Temperature drop is associated with pressure drops, i. e., the so-called Joule-Thompson Effect.



Fig. 8.13. Hydrate formed in pipeline

By combining the correlation of Vondy et al., $P_i$ = f($\Delta P$,$\Delta T$) Fig. 8.14, and the hydrate formation diagram of Katz ( Tras. AIME 160, 1945) , $P_h$ = f($\gamma_g$,T) Fig. 8.15, it is possible to estimate the possibility of hydrate formation after pressure drops.
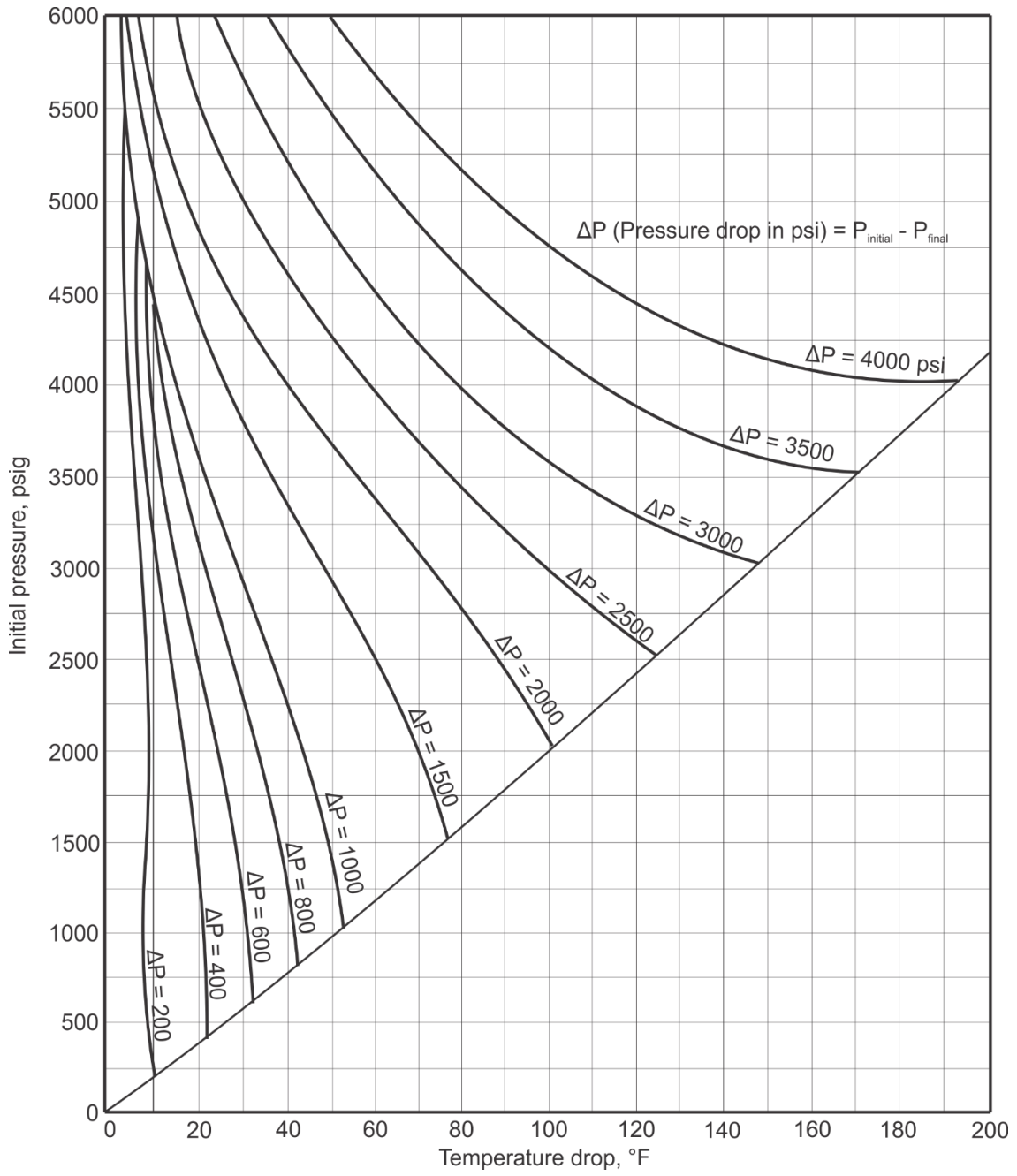
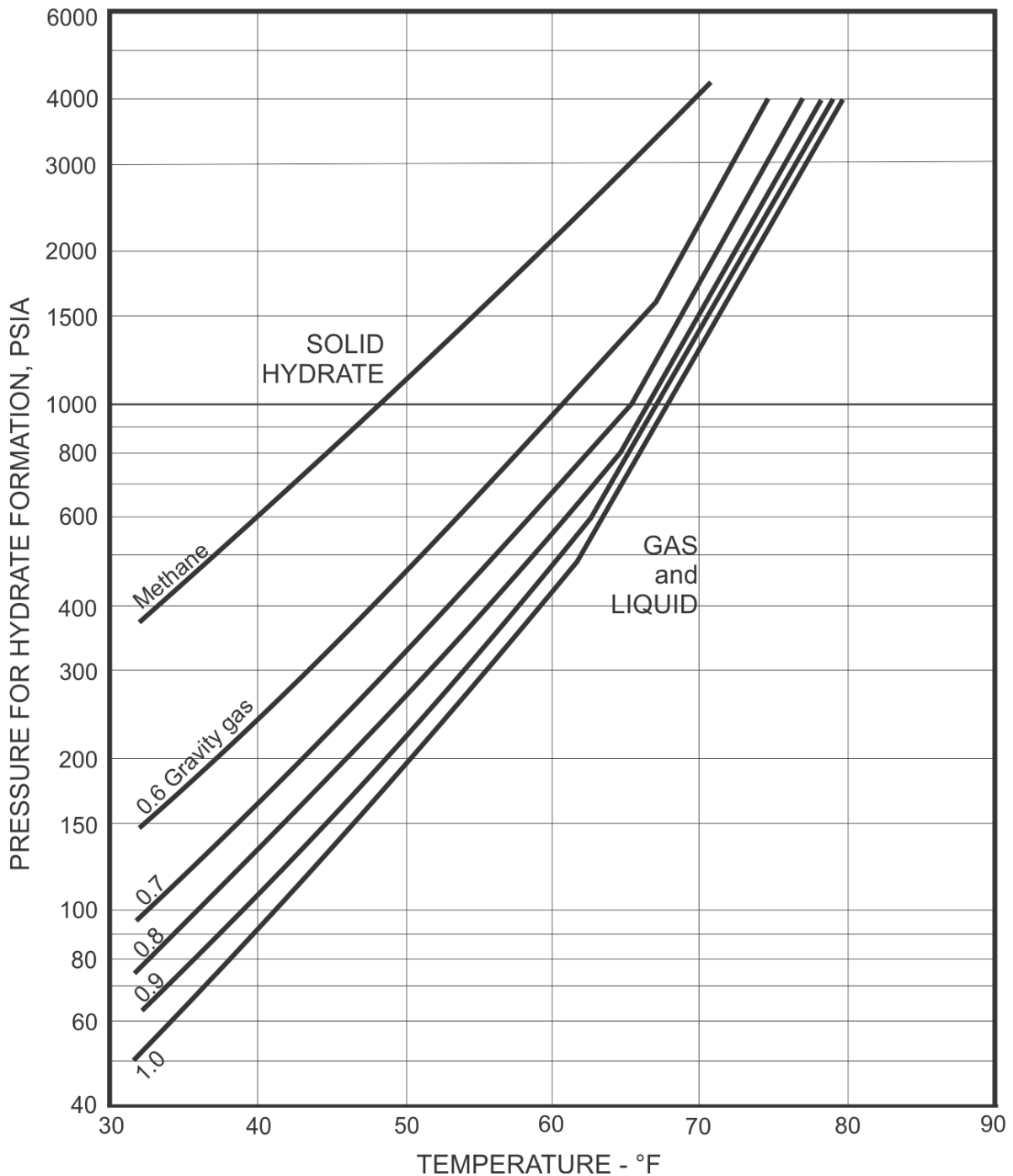Fig. 8.14 Temperature change due to pressure drop. (Vondy et al.).

Fig. 8.15. Pressure-temperature curves for predicting hydrate formation (Katz et al.)

### 8.3.3.Hydrate prevention

Hydrate formation is a serious problem in cold tempered areas. Especially in subsea production and pipe line systems hydrate problems need to be accounted for during the design of the production facilities.

Electrical heating systems are commonly used.

Different chemicals are also used as hydrate inhibitors (methanol and glycol). Rather large quantities are needed to prevent hydrate formation.

## 8.4. Gas Viscosity

Viscosity is an internal resistance of the material to flow. Suppose two layers of fluid in relative motion. $F$ is the force in the upper layer required to maintain the difference in velocity of $dv$. The viscosity $\mu$ is defined by:

$$\frac{F}{A} = \mu \frac{dv}{dy} \tag{8.26}$$

$$\mu = \frac{\frac{F}{A}}{\frac{dv}{dy}} \tag{8.27}$$

where;
$\quad$ $F$ : the difference in the force to obtain dv
$\quad$ $A$ : area of each of the layers
$\quad$ $\mu$: viscosity
$\quad$ $dv$: velocity difference between the layers
$\quad$ $dy$: distance between the layers

The viscosity unit is dyne sec/cm$^2$ = poise, which is not a SI unit.

For hydrocarbon fluids it is convenient to use centipoise ( 1 poise = 100 centipoise). The viscosity of gases is a function of temperature, pressure and composition. The composition can be related to the molecular weight or gravity of the gas:

$$\mu = f\left(T, P, M_g \text{ or } \gamma_g\right) \tag{8.28}$$

It is of interest to note that at given pressure the viscosity increases as the temperature increases. The viscosity also increases as the size of the gas molecules decreases as illustrated by Fig. 8.16. In both cases, the collision frequency (intermolecular contact) of the gas molecules increases causing the increase in viscosity. This is an opposite behavior compared to liquids.

Different methods have been suggested to determine the viscosity of natural gas mixtures:

1. Bicher and Katz (Trans AIME 155, 1944) used a methane-propane mixture to study

$$\mu = f\left(T, P, \gamma_g\right) \tag{8.29}$$

2. Carr (Trans AIME 1954, p. 201) used viscosity ratio μ/μ1 correlations with pseudo-reduced pressure, pP$_r$, and temperature, pT$_r$:

$$\frac{\mu}{\mu_1} = f\left(pT_r, pP_r\right) \tag{8.30}$$

Where:
$\quad$ $\mu$: viscosity at actual P and T.
$\quad$ $\mu_1$: viscosity at 1atm and T, determined from correlation $\mu = f\left(T, M_g\right)$, Fig. 8.17.

4. Herning and Zipper (Gass und Wasserfach 79, 1936) used a weight average value of the viscosity defined by:

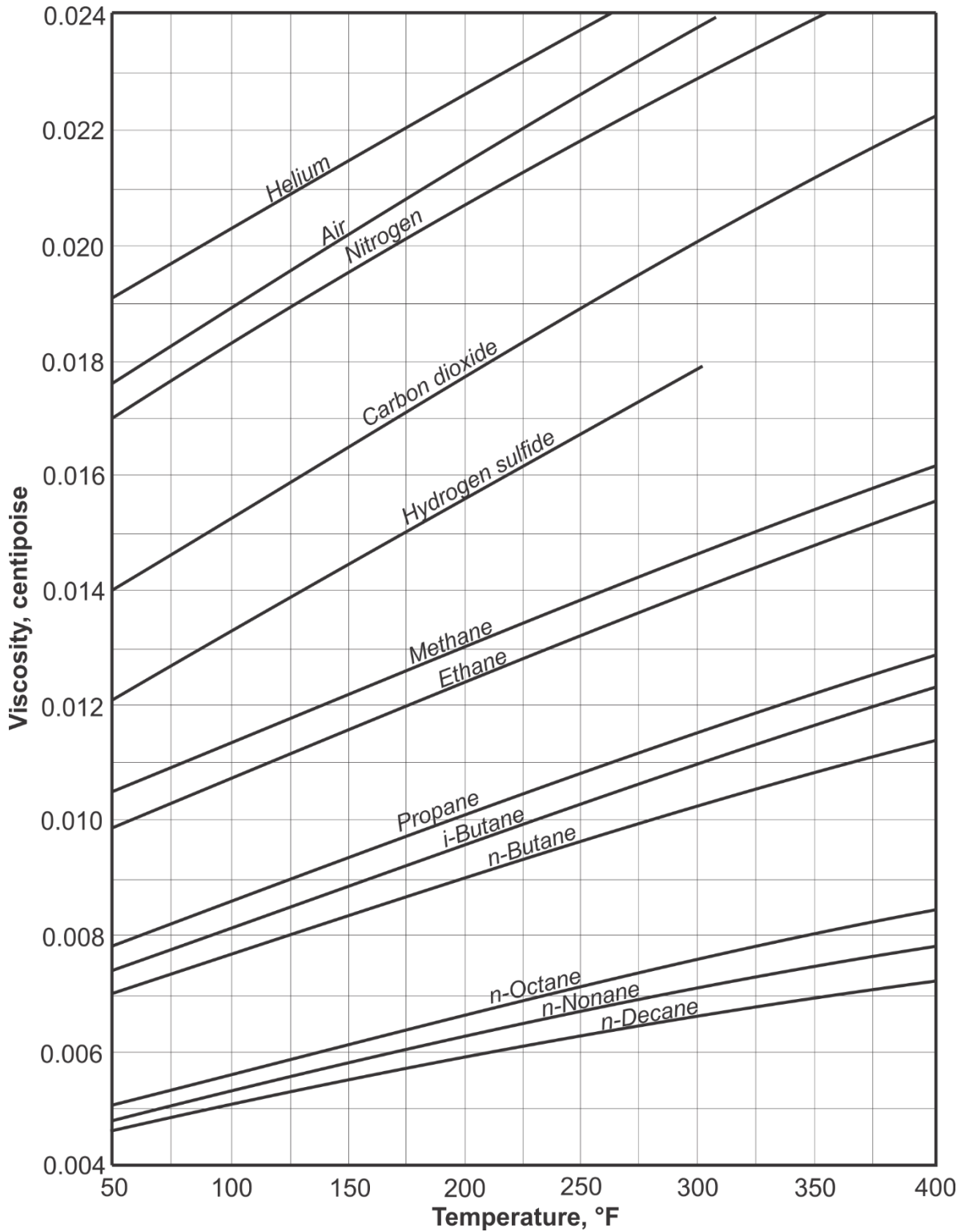$$\mu = \frac{\sum \mu_i y_i M_i}{\sum y_i M_i} \tag{8.31}$$

Fig. 8.16. Viscosity of natural gases at atmospheric pressure

It is believed that Carr´s correlations yield the best data for viscosity of natural gas mixtures, combining Fig. 8.17 for gas viscosity at 1 atm and T with Eq. 8.30 and Fig. 8.18 to correct viscosity to actual Pressure using pseudo reduced pressure and temperature.

As discussed previously, the corresponding state theorem is not valid if the hydrocarbon gas contains significant amounts of inorganic components like $N_2$, $CO_2$ and $H_2S$. Curve fit equations are available for reservoir gas viscosity determinations involving correction terms for inorganic material (Standing).
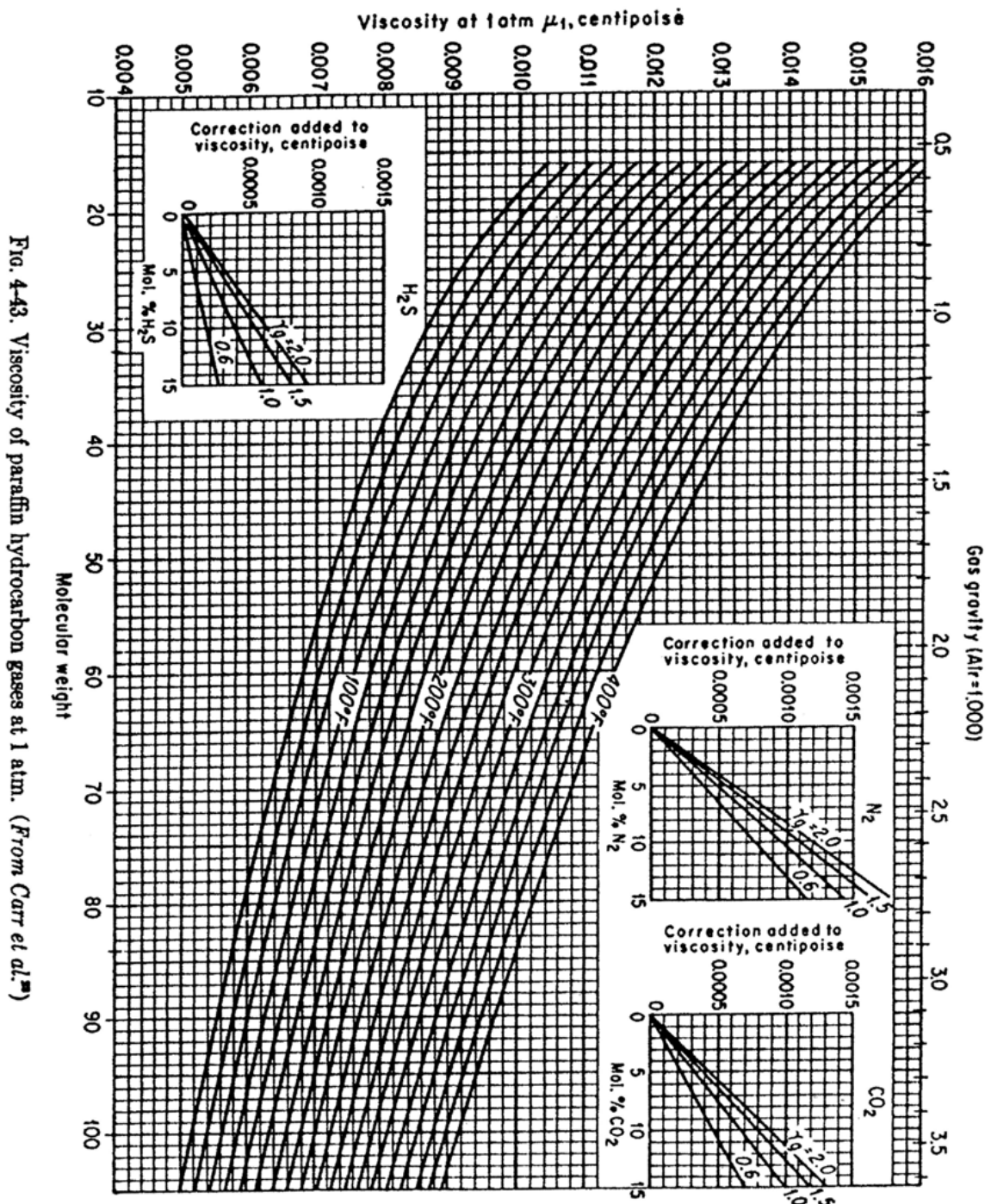


Fig. 4-43. Viscosity of paraffin hydrocarbon gases at 1 atm. (*From Carr et al.*)

Fig. 8.17. Viscosity of hydrocarbon gases at 1 atm. (From Carr et al.)
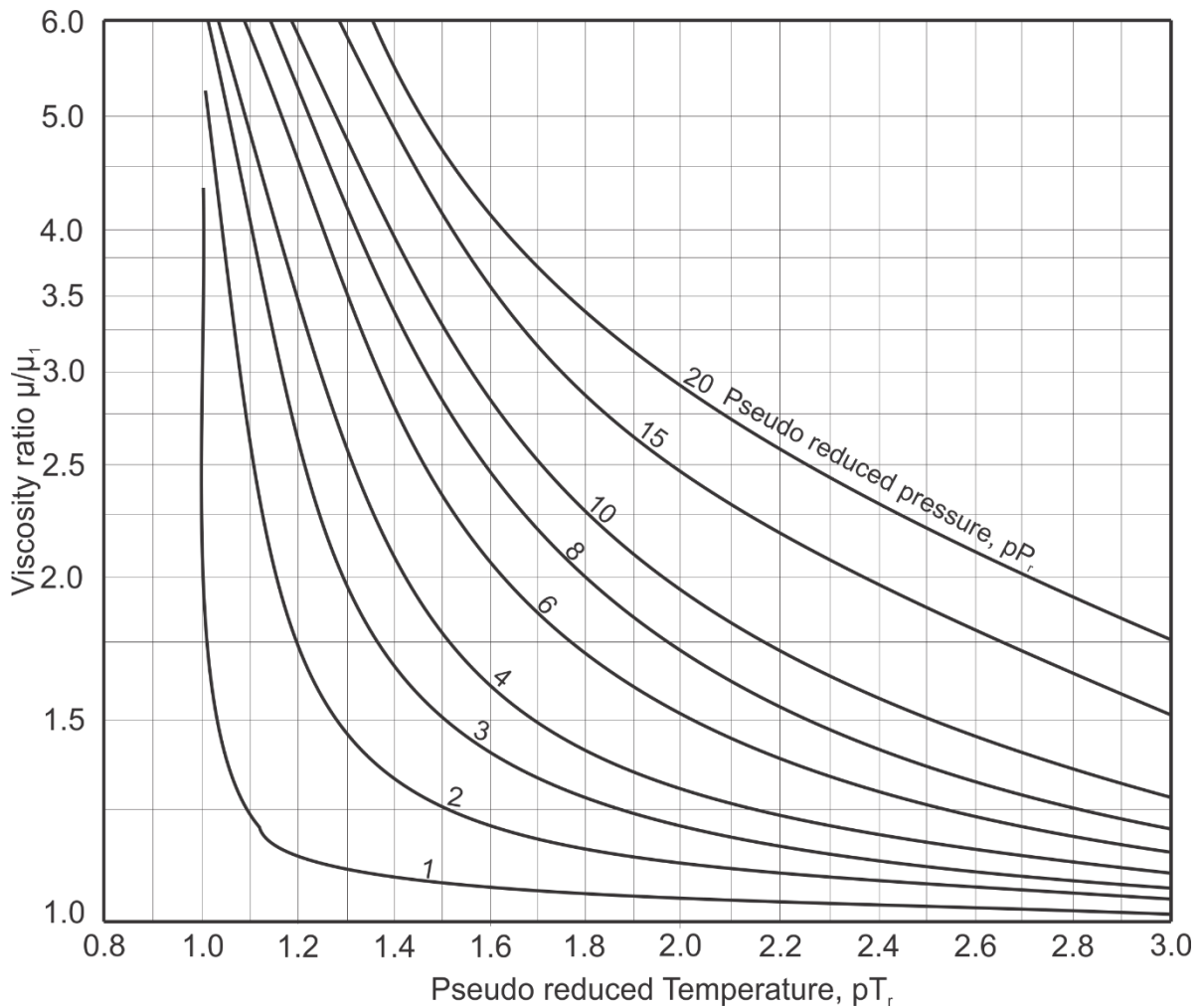
Fig. 8.18. Viscosity ratio $\mu/\mu_1$ versus pseudo reduced properties

## 8.4 Summary of Principal Points

The equation, PV= ZnRT, and the two constants, 10.73 (R) and the molar volume ($V_m$) of 379, are the most important factors in making gas calculations. Remembering these three factors will allow one to solve any gas PVT problem.

When gravity with respect to air is the only known parameter of a gas, the PVT behavior of the gas is best obtained by use of Figs. 8.7, 8.8 and 8.9. At gas gravities greater than 0.8, the pseudo-critical gas gravity relations shown in Fig. 8.7 can be used to evaluate a compressibility factor at the desired pressure and temperature. In gases containing only 1 or 2 % of heavy fractions, the true critical constants of the next higher compound should be used for the –"plus" fraction. Thus, a hexanes plus fraction uses the critical constants of n-heptane.