

Chapter 2

Natural Gas Physical Properties Under High Pressure

It is commonly known that natural gas owns compressibility. When subjected to the reservoir pressure and temperature, the natural gas is in compression. However, various parameters of it undergo gradual changes at any stage of its flowing course which involves the underground percolation in formation and the wellbore flowing, resulting from the pressure drop and volume expansion. State equations are commonly used for gas to indicate its change in state (pressure P , volume V , and temperature T), and some high-pressure physical parameters which are quite practical in engineering are also introduced, for example, volume factor, isothermal compressibility, and viscosity ratio. This chapter will focus on these parameters that are commonly used and play a role of prerequisite in the oil and gas field development.

2.1 Apparent Molecular Weight and Density of Natural Gas

2.1.1 *Composition of Natural Gas*

1. The Definition and Classification of Natural Gas

Generally speaking, natural gas is flammable or inflammable gaseous mixtures of hydrocarbons and non-hydrocarbons, extracted from the underground, at normal temperature and pressure.

Narrowly speaking, natural gas can be classified into different types:

- (1) According to the essential features of the deposits: The natural gas can be ranged into two types: oil reservoir associated gas and gas from gas reservoir. The former one is dissolved in crude oil at the reservoir condition and released from oil as pressure drops. The other one, gas from gas reservoir, is in a

gaseous state in the underground formations and includes two types named pure gas and condense gas, respectively. The principal constituent of the gas in pure gas reservoirs is methane, with some others such as ethane, propane, and butane. The gas from gas-condensate reservoir, on analysis of the effluent at the oil wellhead, contains not only methane, ethane, propane and butane, but also some liquid C_5+ hydrocarbons between C_7 and C_{11} .

- (2) According to the composition, natural gas can be described in two ways: dry gas and wet gas, or poor gas and rich gas.

Dry gas: The content of liquid C_5+ heavy hydrocarbons in wellhead effluent is less than $13.5 \text{ cm}^3/\text{m}^3$ at standard temperature and pressure.

Wet gas: On analysis of the wellhead effluents which are subjected to standard temperature and pressure, the content of liquid C_5+ heavy hydrocarbons is more than $13.5 \text{ cm}^3/\text{m}^3$.

Poor gas: On analysis of the wellhead effluents which are subjected to standard temperature and pressure, the content of liquid C_3+ heavy hydrocarbons is less than $94 \text{ cm}^3/\text{m}^3$.

Rich gas: On analysis of the wellhead effluents which are subjected to standard temperature and pressure, the content of liquid C_3+ heavy hydrocarbons is more than $94 \text{ cm}^3/\text{m}^3$.

- (3) According to the content of the acidic gases such as H_2S and CO_2 :

Sour natural gas contains significant amount of acidic gases such as H_2S and CO_2 . This kind of natural gases is required to be processed and clarified to reach the standards for pipeline transportation.

Clean natural gas is also named as sweet gas. This kind of natural gas contains very minor amount of acidic gases, and the cleaning (purification) treatment is not required for it.

2. The Composition of Natural Gas

Natural gases are mixtures of hydrocarbons which, as stated earlier, may be characterized by composition. Some analytical instruments such as gas chromatograph can help us to know the components contained in the gaseous mixture to some extent. The composition of natural gas can be reported in terms of mole fraction (mole percentage), mass fraction (weight percentage), or volume fraction (volume percentage).

- (1) Mole fraction (mole percentage)

The mole per cent of the i th component, expressed with the symbol y_i , is the percentage ratio of the mole number of this component to the total mole number of the entire gas:

$$y_i = \frac{n_i}{\sum_{i=1}^N n_i} \quad (2.1)$$

In the equation:

n_i the mole number of the i th component;
 $\sum_{i=1}^N n_i$ the total mole number of the gas;
 N the number of different components.

(2) Volume fraction (volume percentage)

The volume percentage φ_i is:

$$\varphi_i = \frac{V_i}{\sum_{i=1}^N V_i} \quad (2.2)$$

In the equation:

V_i the volume of the i th component;
 $\sum_{i=1}^N V_i$ the total volume of the gas.

Provided that the mole number of the i th component is n_i , it is easy to obtain its volume, $22.4 n_i$, and thence, the total volume of the gas present is $22.4 \sum_{i=1}^N n_i$. According to Eqs. (2.1) and (2.2), we can get that $\varphi_i = y_i$.

Within gases, the mole percentage of a component equals the volume percentage of it, because when subjected to the same conditions of pressure and temperature, every 1 mol of any gas occupies the same volume. In particular, upon the standard conditions, the volume of 1 mol gas is 22.4 L.

(3) Mass fraction (Weight percentage)

The weight percentage G_i is:

$$G_i = \frac{w_i}{\sum_{i=1}^N w_i} \quad (2.3)$$

In the equation:

w_i the mass of the i th component;
 $\sum_{i=1}^N w_i$ the total mass of the gas.

It is easy to convert the mass fraction to mole fraction using the following equation:

$$y_i = \frac{G_i/M_i}{\sum_{i=1}^N G_i/M_i} \quad (2.4)$$

where

M_i the molecular weight of the i th component.

Table 2.1 The composition of natural gas and the mass fraction

Component	Mass fraction	Molecule weight, M_i	Mass fraction/molecule weight	Mole fraction, y_i
Methane	0.71	16.0	0.044	0.85
Ethane	0.14	30.1	0.005	0.09
Propane	0.09	44.1	0.002	0.04
Butane	0.06	58.1	0.001	0.02
Summation	1.00		0.052	1.00

Solution: the conversion and results can be seen in Table 2.1

Actually, the composition of the liquid crude oil can also be expressed by the three methods talked above.

[Example 2.1] The first two columns of Table 2.1 shows the natural gas composition and the weight percentage of each component. Please convert their weight percentage to mole percentage.

2.1.2 The Molecular Weight of Natural Gas

Since natural gas is a mixture composed of molecules of various sizes, not the same as the pure substance, it cannot be expressed by a definite chemical formula upon which the molecular weight can be calculated and gained easily. To solve this problem, the concept of “apparent molecular weight” is introduced.

The apparent molecular weight is defined as the mass of every 22.4 L natural gas when it is subjected to a condition of 0 °C and 760 mmHg. In other words, the numerical value of the apparent molecular weight is equal to the mass per mole of the natural gas. Obviously, this parameter is a hypothetical one that does not exist really, and this is why it is named “apparent molecular weight.” In practical application, it is directly called “molecular weight” for short.

If the mole fraction and molecular weight of each component are given, the following equation can be used to calculate the apparent molecular weight of natural gas:

$$M = \sum_{i=1}^N (y_i M_i) \quad (2.5)$$

where

M the molecular weight of the natural gas present;

y_i the mole per cent of the i th component;

M_i the molecular weight of the i th component.

Table 2.2 Calculation of the molecular weight of the natural gas

Component	Mole fraction, y_i	Molecular weight, M_i	$y_i M_i$
Methane	0.85	16.0	13.60
Ethane	0.09	30.1	2.71
Propane	0.04	44.1	1.76
Butane	0.02	58.1	1.16
Summation	1.000		$M = 19.23$

Result: the molecular weight of the natural gas is 19.23

Obviously, the different compositions of natural gas will lead to their different numerical values in apparent molecular weight. Generally speaking, the apparent molecular weight of dry gas is about 16.82–17.98 usually.

[Example 2.2] The mole fraction is shown in Table 2.1 to calculate the molecular weight of the natural gas.

Solution: The conversion and results are shown in Table 2.2.

2.1.3 The Density and Specific Gravity of Natural Gas

1. Density

The density of natural gas is defined as the mass of per unit volume of the natural gas.

$$\rho_g = m/V \quad (2.6)$$

where

ρ_g the density of natural gas, g/cm³ or kg/m³;

m the mass of natural gas, g or kg;

V the volume of natural gas, cm³ or m³.

The density of natural gas at given temperature and pressure can be gained through the state equation of gas (for details, see the lesson 2 of this chapter):

$$\rho_g = \frac{PM}{ZRT} \quad (2.7)$$

where

ρ_g the density of natural gas, kg/m³;

P the pressure to which the natural gas is subjected, MPa;

M the molecular weight of natural gas, kg/kmol;

T the absolute temperature of natural gas, K;
 Z the compressibility factor of natural gas;
 R universal gas constant, $R = 0.008134 \text{ MPa m}^3/(\text{kmol K})$.

2. Specific gravity

The specific gravity of natural gas is defined as the ratio of the density of the natural gas to the density of dry air, both subjected to standard conditions adopted in oil industry (293 K, 0.101 MPa). The specific gravity is dimensionless.

$$\gamma_g = \rho_g / \rho_a \quad (2.8)$$

where

ρ_g the density of natural gas;
 ρ_a the density of air.

To integrate Eqs. (2.7) and (2.8), with consideration that the molecular weight of dry air is $28.96 \approx 29$, we can get:

$$\gamma_g = M/29 \quad (2.9)$$

When the specific gravity of a natural gas is known, its apparent molecular weight can be gained through the equation written above.

Generally speaking, the specific gravity of natural gas ranges from 0.55–0.8 (lighter than air). But when the content of heavy hydrocarbons or non-hydrocarbon components is comparatively high, the value of specific gravity may be larger than 1.

2.2 Equation of State for Natural Gas and Principle of Corresponding State

2.2.1 Equation of State (EOS) for Ideal Gas

Three limiting assumptions have to be made to define the ideal gas:

- (1) The volume occupied by the molecules is insignificant with respect to the total volume occupied by the gas.
- (2) There are no attractive or repulsive forces between the molecules.
- (3) All collisions of molecules are perfectly elastic; that is, there is no loss of internal energy upon collision.

The molecules of an ideal gas must have the above-mentioned properties.

Table 2.3 Values of R for various unit systems

n	T	P	V	R
Kmol	K	MPa	m^3	$0.008314 \text{ MPa m}^3/(\text{kmol K})$
Kmol	K	Pa	m^3	$8314 \text{ J}/(\text{kmol K})$
Mol	K	Atmospheric pressure	L	$0.08205 \text{ atm L}/(\text{mol K})$
Mol	K	Pa	m^3	$8.3145 \text{ Pa m}^3/(\text{mol K})$
Mol	R	Psi	Cu ft	$10.732 \text{ Psi Cu ft}/(\text{mol R})$

The equation of state for ideal gas is:

$$PV = nRT \quad (2.10)$$

where

P the absolute pressure of the gas, MPa;

V the volume occupied by the gas, m^3 ;

T absolute temperature, K;

n the number of moles of the gas present, kmol;

R universal gas constant, $R = 0.008134 \text{ MPa m}^3/(\text{kmol K})$.

The universal gas constant is considered to be independent of the type of gas, but its numerical value depends on the system of units used. Table 2.3 shows the values of R for various unit systems.

Realizing that it is not correct to neglect the volume occupied by the natural gas molecules as well as the mutual force among them, the natural gas is not an ideal gas but a real one. At very low pressure, the molecules are relatively far apart, and the conditions of ideal gas behavior are more likely to be met. However, the situation is quite different for the real gases buried in underground reservoirs with high temperature and pressure; that is to say, the behavior of natural gas deviates drastically from the behavior predicted by the state equation for ideal gas. Therefore, based on the state equation for ideal gas, correction methods are adopted to describe the real gas state equation.

2.2.2 Equation of State (EOS) for Real Gas

The best way of writing an equation of state for real gas is to insert a correction factor to the ideal gas equation. This results in the equation of state for real gas:

$$PV = ZnRT \quad (2.11)$$

It is also known as the compressibility equation of state.

In this equation, the correction factor Z is known as the compressibility factor or deviation factor. As for its physical meaning, it is the ratio of the volume actually occupied by a gas at given pressure and temperature to the volume of the gas occupied at the same pressure and temperature if it behaved like an ideal gas.

$$Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$

Compared with the ideal gas, the molecules of real gas, on the one hand, are big enough to occupy significant volume and make it harder to be compressed; on the other hand, the molecules are close enough with each other to exert some attraction between them, which makes the real gas easier to be compressed. The compressibility factor Z just reflects the integral effect of these two opposite interactions: When Z equals 1, it indicates that the real gas behaves like ideal gas; when Z is larger than 1, it indicates that the real gas occupies greater volume and is harder to be compressed than ideal gas; when Z is smaller than 1, it indicates that the real gas occupied less volume and is easier to be compressed than ideal gas.

The Z -factor is not a constant and varies with changes in gas composition, temperature, and pressure. It must be determined experimentally. The results of our predecessors' experimental achievements, including the relationship between the Z -factor and T or P , have been made into the form of charts for reference. The Z -factor charts for methane and ethane have been, respectively, shown in Figs. 2.1 and 2.2. But in order to get the compressibility of natural gas, principle of corresponding state has to be introduced in advance.

2.2.3 Principle of Corresponding State

1. The principle of corresponding state and the method to get the Z value of natural gas

Although real gases exhibit different properties (including compressibility factor) and various critical parameters upon different conditions of temperature and pressure, they possess similar characteristics when they are at their own critical points. Taking the critical state of gas as the datum mark, all the pure-hydrocarbon gases which are subjected to the same conditions of reduced pressure P_r and reduced temperature T_r have the same compressibility factors; in other words, they obey principle of corresponding state.

Reduced temperature and reduced pressure are defined as follows:

$$P_r = \frac{P}{P_c} \quad T_r = \frac{T}{T_c} \quad (2.12)$$

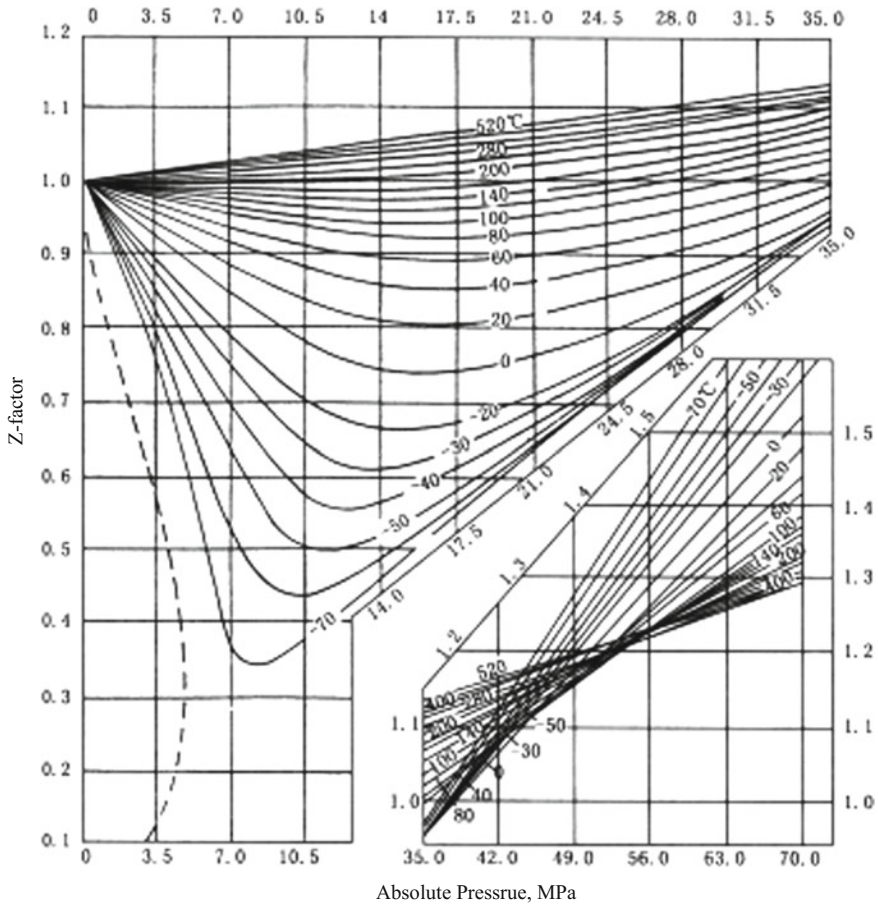


Fig. 2.1 The Z-factor charts for methane (Brown 1948)

where

P_r, T_r the reduced pressure and reduced temperature, dimensionless;

P, P_c the absolute pressure and critical pressure to which the gas is subjected (MPa);

T, T_c the absolute temperature and critical temperature of the gas (K).

Principle of corresponding state: When two gases are in the same corresponding state, many of their intensive properties (i.e., properties that are independent of volume) are approximately uniform. This law is highly accurate if the gases have similar molecular characteristics and pretty nearly the same values of critical temperature. The critical parameters of some hydrocarbon or non-hydrocarbon gases have been presented, respectively, in Table 2.4 and Table 2.5.

Table 2.4 Physical-property-related constants of some hydrocarbon gases

Component	Molecular formula	Molecular weight	Boiling point °C (at 0.1 MPa)	Critical pressure P_c (MPa)	Critical temperature T_c (K)	Density of liquid (at standard conditions) (g/cm ³)	Eccentric factor ω
Methane	CH ₄	16.043	-161.50	4.6408	190.67	0.3	0.0115
Ethane	C ₂ H ₆	30.070	-88.61	4.8835	303.50	0.3564	0.0908
Propane	C ₃ H ₈	44.097	-42.06	4.2568	370.00	0.5077	0.1454
Isobutane	<i>i</i> -C ₄ H ₁₀	58.124	-11.72	3.6480	408.11	0.5631	0.1756
Normal butane	<i>n</i> -C ₄ H ₁₀	58.124	-0.50	3.7928	425.39	0.5844	0.1928
Isopentane	<i>i</i> -C ₅ H ₁₂	72.151	27.83	3.3336	460.89	0.6247	0.2273
Normal pentane	<i>n</i> -C ₅ H ₁₂	72.151	36.06	3.3770	470.11	0.6310	0.2510
Isohexane	<i>n</i> -C ₆ H ₁₄	86.178	68.72	3.0344	507.89	0.6640	0.2957
Normal heptane	<i>n</i> -C ₇ H ₁₆	100.205	98.44	2.7296	540.22	0.6882	0.3506
Normal Octane	<i>n</i> -C ₈ H ₁₈	114.232	125.67	2.4973	569.39	0.7068	0.3978
Normal nonane	<i>n</i> -C ₉ H ₂₀	128.259	150.78	2.3028	596.11	0.7217	0.4437
Normal decane	<i>n</i> -C ₁₀ H ₂₂	142.286	174.11	2.1511	619.44	0.7342	0.4502

The meaning and application of the eccentric factor can be seen in the lesson 4 of this chapter

Table 2.5 Common physical-property-related constants of some non-hydrocarbon gases

Component	Molecular formula	Molecular weight	Boiling point °C (at 0.1 MPa)	Critical pressure P_c (MPa)	Critical temperature T_c (K)	Density of liquid (at standard conditions) (g/cm ³)	Eccentric factor ω
Air	N ₂ , O ₂	28.964	-194.28	3.7714	132.78	0.856	
Carbon dioxide	CO ₂	44.010	-78.51	7.3787	304.17	0.827	0.2250
Helium	He	4.003	-268.93	0.2289	5.278	–	
Hydrogen	H ₂	2.016	-252.87	1.3031	33.22	0.07	-0.2234
Sulfureted hydrogen	H ₂ S	34.076	-60.31	9.0080	373.56	0.79	0.0949
Nitrogen	N ₂	28.013	-195.80	3.3936	126.11	0.808	0.0355
Oxygen	O ₂	31.999	-182.96	5.0807	154.78	1.14	0.0196
Water	H ₂ O	18.015	100	22.1286	647.33	1.0	0.3210

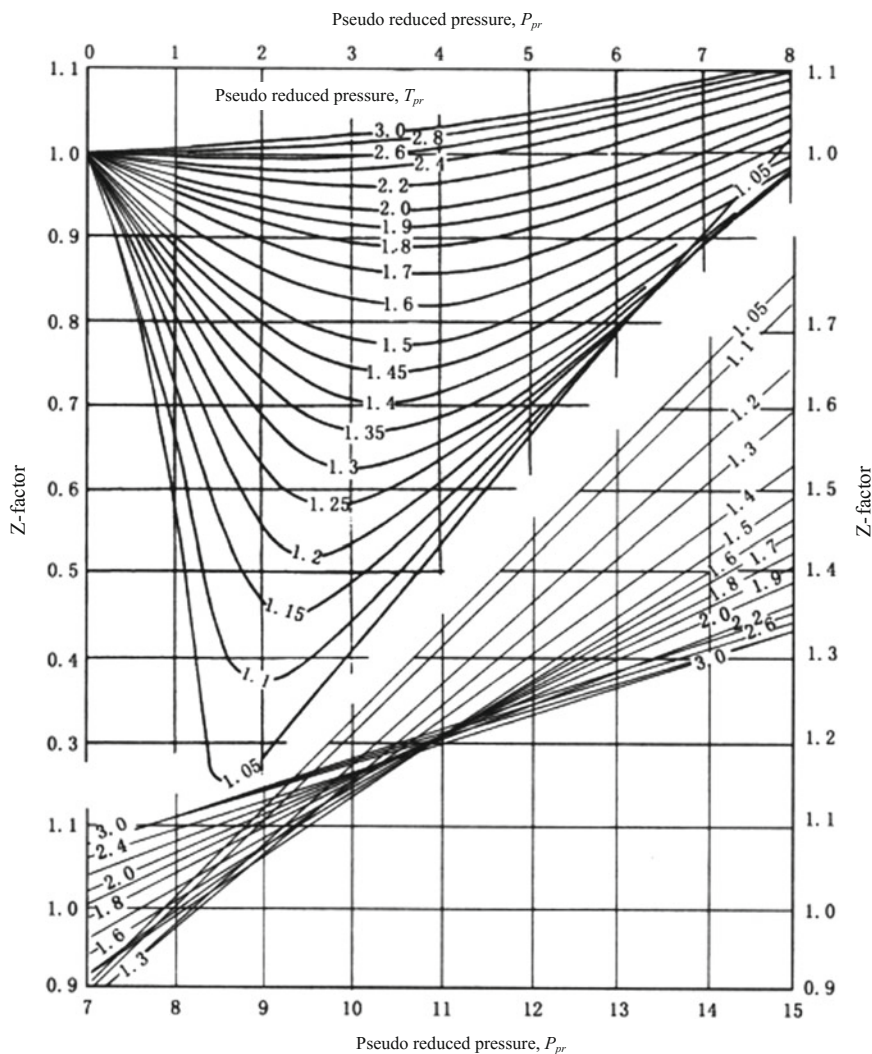


Fig. 2.3 The Z-factor charts for natural gas (Standing and Katz 1942)

In light of the impurity of natural gases, Kay introduced the concept of “pseudo-critical” and “pseudo-critical reduced” properties for treating mixtures of gases.

The pseudo-critical pressure and pseudo-critical temperature are defined mathematically:

$$\begin{aligned} P_{pc} &= \sum y_i P_{ci} \\ T_{pc} &= \sum y_i T_{ci} \end{aligned} \quad (2.13)$$

where

P_{pc} pseudo-critical pressure, MPa;
 y_i the mole fraction of the i th component;
 P_{ci} the critical pressure, MPa;
 T_{pc} pseudo-critical temperature, K;
 T_{ci} and critical temperature of the i th component, K.

With the pseudo-critical parameters obtained, the pseudo-critical reduced parameters can be easily got, too:

$$\begin{aligned} P_{pr} &= \frac{P}{P_{pc}} = \frac{P}{\sum y_i P_{ci}} \\ T_{pr} &= \frac{T}{T_{pc}} = \frac{T}{\sum y_i T_{ci}} \end{aligned} \quad (2.14)$$

Then, the compressibility factor Z of the studied natural gas can be gained according to the Z -charts (Fig. 2.3).

In engineering practice, the pseudo-critical parameters can also be obtained through Fig. 2.4, based on the values of specific gravity which are usually already known.

After that pseudo-critical parameters, P_{pc} and T_{pc} , are known, the pseudo correspondence parameters can be calculated through the equations in (2.14) and then refer to Fig. 2.3 to determine the value of the compressibility Z .

If the non-hydrocarbon content of the studied natural gas is comparatively not too high, for example, the N_2 content is less than 2 %, the empirical correlations written below, which is also based on the known specific gravity (γ_g), can be employed to obtain the approximate values of the pseudo-critical pressure P_{pc} and the pseudo-critical temperature T_{pc} .

$$T_{pc} = 171(\gamma_g - 0.5) + 182 \quad (2.15)$$

$$P_{pc} = [46.7 - 32.1(\gamma_g - 0.5)] \times 0.09869 \quad (2.16)$$

$$\begin{aligned} P_{pc} &= \sum y_i P_{ci} \\ T_{pc} &= \sum y_i T_{ci} \end{aligned} \quad (2.13)$$

where

P_{pc} , T_{pc} The pseudo-critical pressure (MPa) and pseudo-critical temperature (K);
 y_i The mole per cent of the i th component;

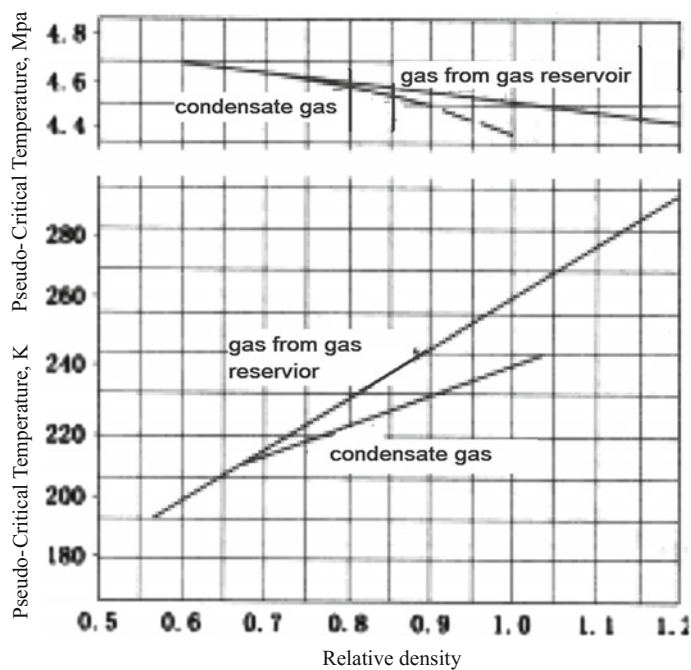


Fig. 2.4 Diagram about the natural gas special gravity and pseudo-critical parameters (Brown 1948)

Then, calculate the P_{pr} and T_{pr} according to the p and T conditions to which the studied gas is subjected to, and then, determine the value of Z through the Z -charts (Fig. 2.3).

[Example 2.3] Table 2.6 shows the composition of a certain natural gas. Please determine its Z value at 65 °C and 12 MPa, and give the volume of 1 mol of this gas.

- Solution:
- (1) List related data and figure out the pseudo-critical parameters, P_{pc} and T_{pc} , as shown in able 2.6.

Table 2.6 Calculation of the parameters of natural gas

Component	Mole fraction y_i	Critical temperature, T_{ci} (K)	$y_i T_{ci}$	Critical pressure, P_{ci} (Mpa)	$y_i P_{ci}$
CH ₄	0.85	190.5	162.0	4.6408	3.9447
C ₂ H ₆	0.09	306.0	27.5	4.8835	0.4395
C ₃ H ₈	0.04	369.6	14.8	4.2568	0.1703
<i>n</i> -C ₄ H ₁₀	0.02	425.0	8.5	3.7928	0.0759

- (2) Determine the pseudo-reduced parameters, P_{pr} and T_{pr} .

$$\text{Pseudo-reduced } T_{pr}: T_{pr} = \frac{T}{T_{pc}} = \frac{273+65}{212.8} = 1.59$$

$$\text{Pseudo-reduced } P_{pr}: P_{pr} = \frac{P}{P_{pc}} = \frac{12}{4.6303} = 2.59$$

- (3) With the gained P_{pr} and T_{pr} , refer to Fig. 2.3 and get the value of the Z-factor:

$$Z = 0.849$$

- (4) According to the compressibility equation of state, determine the volume occupied by 1 mol natural gas which is subjected to the condition of 65 °C and 12 MPa:

$$V = \frac{ZnRT}{P} = \frac{0.849 \times 1.0 \times 0.008314 \times (273 + 65)}{12} = 0.1988 \text{ (m}^3\text{)}$$

[Example 2.4] Determine the value of Z-factor at 65 °C and 12 MPa for the given natural gas (from a gas reservoir). It is already known that its specific gravity (γ_g) is 0.80.

Solution:

- (1) With the known $\gamma_g = 0.80$, refer to Fig. 2.4 to get the pseudo-critical temperature $T_{pc} = 220$ K and the pseudo-critical pressure $P_{pc} = 4.58$ MPa.
 (2) Determine the pseudo-reduced parameters:

$$T_{pr} = T/T_{pc} = (273 + 65)/228 = 1.48$$

$$P_{pr} = P/P_{pc} = 12/4.58 = 2.68$$

- (3) With the obtained T_{pr} and P_{pr} , refer to Fig. 2.3 and get the value of the Z-factor:

$$Z = 0.783$$

Sometimes, natural gases contain a small quantity of components heavier than heptane (C_7+). Since the lump of the heptane plus components should be seen as a mixture, too, the Z-factor values for this mixture can be obtained only by empirical

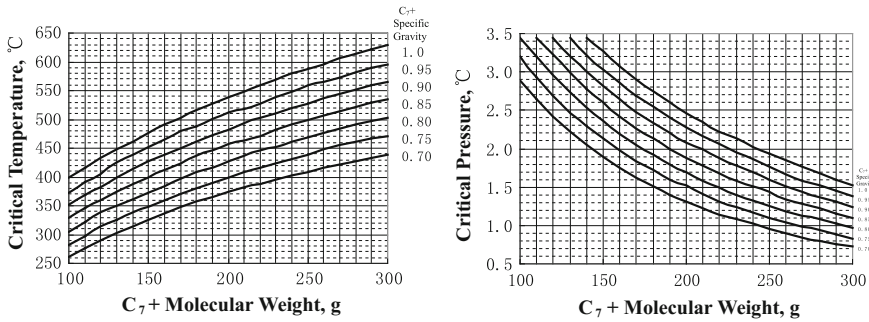


Fig. 2.5 Critical parameters of C_7+ components

methods. Figure 2.5 shows an empirical chart for the C_7+ components to determine their critical parameters, and what's more, once these parameters are got, the Z -factor can be gained by the way mentioned above.

2. Effect of Non-hydrocarbon Components

Natural gases commonly contain hydrocarbon sulfide, carbon dioxide, and nitrogen. The presence of them does affect the Z -factor obtained by the previously described methods. Hence, limits have to be put up for the usage of those methods: The content of the non-hydrocarbons in the studied natural gas must be less than 5 % by volume (the volume content of N_2 is less than 2 % and the volume content of CO_2 is less than 1 %), and what's more, the volume content of methane should not be less than 50 %. Exceeding these limits means great error (more than 3 %). For this reason, when the non-hydrocarbon or C_5+ components of a natural gas (e.g., condensate gas) make a comparatively high contribution, the methods should undergo a correction by referring to some other charts and equations. To remedy this problem, methods have been developed to eliminate the error caused by non-hydrocarbons, and three of them will be introduced below.

(1) Method of Chart Correction (Wichert Method)

In order to get a corrected Z -factor, this method adjusts the pseudo-critical parameters and the pseudo-reduced parameters, through an adjustment of the curve on the reference chart, to account for the unusual behavior of these gases containing impurities: Firstly, bring in an adjustment factor ϵ , a function of the concentrations of H_2S and CO_2 , to the pseudo-critical temperature T_{pr} ; Secondly, correct the pseudo-critical pressure P_{pc} ; thirdly, with the corrected T_{pr} and P_{pc} , calculate the T'_{pc} and P'_{pc} ; and finally get the value of Z -factor on basis of T_{pr} and P_{pr} , referring to their original Z -chart. Then, we can get the compressibility factor for the acid natural gases that contain H_2S and CO_2 .

The equations for correction are:

$$T'_{pc} = T_{pc} - \varepsilon \quad (2.17)$$

$$P'_{pc} = \frac{P_{pc} T'_{pc}}{[T_{pc} + n(1 - n)\varepsilon]}$$

where

- T_{pc} , P_{pc} respectively the pseudo-critical temperature (K) and the pseudo-critical pressure (MPa) of the mixture of hydrocarbons;
 T'_{pc} , P'_{pc} the pseudo-critical temperature (K) and the pseudo-critical pressure (MPa) after correction;
 n the mole fraction of the H_2S in natural gas;
 ε the adjustment factor for the pseudo-critical temperature (K) as a function of the concentrations of H_2S and CO_2 .

The value of ε can be obtained from Fig. 2.6.

(2) Method of Empirical Formula (Wichert and Aziz Method)

The steps of this method are the same as the method introduced above, but there lies difference in their empirical formulas upon which the ε is determined. This method is more convenient because the reference to the charts can be omitted.

$$\varepsilon = \frac{120(A^{0.9} - A^{1.6}) + 15(B^{0.5} - B^4)}{1.8} \quad (2.18)$$

where

- ε the adjustment factor for pseudo-critical temperature, K;
 A the sum of the mole fractions of H_2S and CO_2 in natural gas;
 B the mole fraction of H_2S in natural gas.

(3) Method of Weighting Treatment (Eilerts, 1948)

Firstly, extract the Z -factors for both the hydrocarbon and non-hydrocarbon components from their corresponding charts and secondly, add them up, through a weighting treatment, to get the final value of the Z -factor for the natural gas mixture. Details can be seen in Example 2.6.

[Example 2.5] The composition of a natural gas which contains H_2S and CO_2 is tabulated below (Table 2.7). Determine its Z value at 65 °C and 11 MPa.

Solution:

- (1) Calculate the pseudo-critical parameters in accordance with the mole composition of the given gas. The steps and results of calculation are listed in Table 2.7.

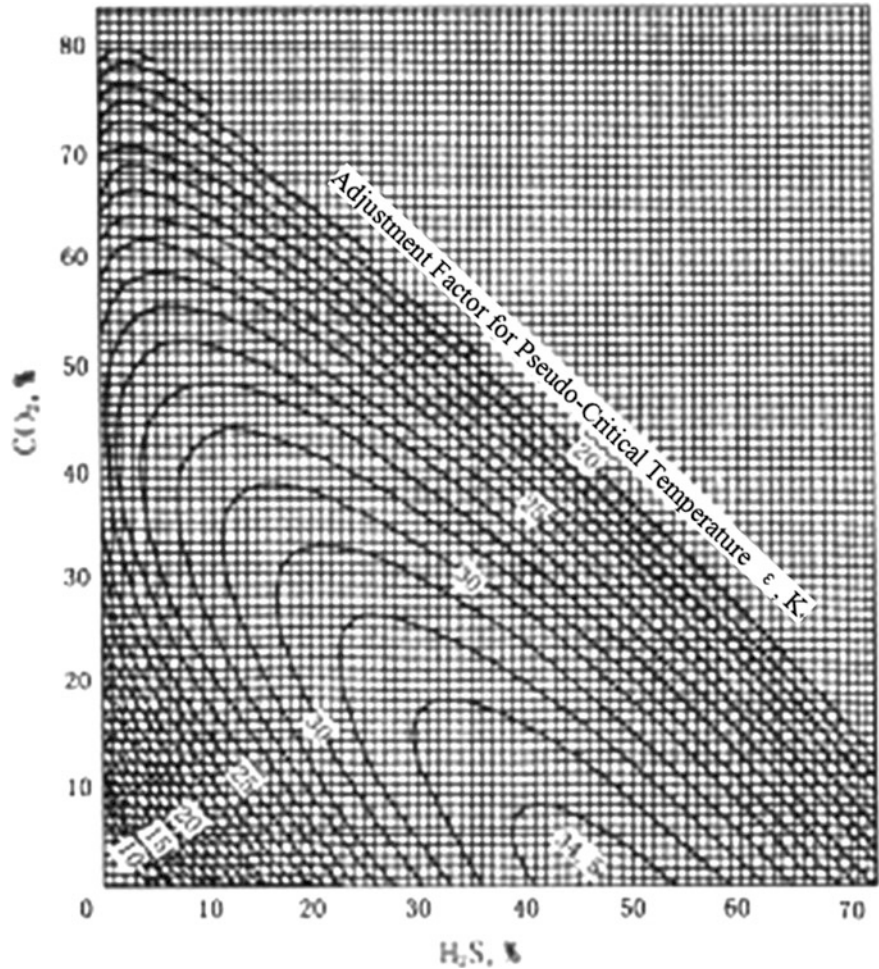


Fig. 2.6 The relationship between the adjustment factor for pseudo-critical temperature and the non-hydrocarbon concentration (White and Brown 1942)

Table 2.7 Calculation of the parameters of natural gas

Component	y_i	P_{ci} (MPa)	$y_i P_{ci}$	T_{ci} (K)	$y_i T_{ci}$
CO ₂	0.10	7.3787	0.73787	304.17	30.42
H ₂ S	0.20	9.008	1.8016	373.56	74.71
CH ₄	0.60	4.6408	2.838	190.3	114.18
C ₂ H ₆	0.10	4.8835	0.48835	306.0	30.6
$P_{pc} = \sum y_i P_{ci} = 5.8123$				$T_{pc} = \sum y_i T_{ci} = 249.91$	

- (2) With the known concentrations of H_2S and CO_2 , refer to Fig. 2.6 to get $\varepsilon = 28 \text{ K}$, so

$$T'_{\text{pc}} = T_{\text{pc}} - \varepsilon = 249.91 - 28 = 221.91 \text{ K}$$

$$P'_{\text{pc}} = \frac{P_{\text{pc}} T'_{\text{pc}}}{[T_{\text{pc}} + n(1-n)\varepsilon]} = \frac{5.8123 \times 221.91}{249.91 + 0.2 \times (1-0.2) \times 28} = 5.070 \text{ MPa}$$

- (3) Calculate the pseudo-reduced parameters:

$$T'_{\text{pr}} = T/T'_{\text{pc}} = 338/221.91 = 1.523$$

$$P'_{\text{pr}} = P/P'_{\text{pc}} = 11/5.070 = 2.169$$

- (4) Refer to Fig. 2.3 and get the value of the Z-factor: $Z = 0.833$.

[Example 2.6] Determine the compressibility factor Z for the N_2 -contained natural gas described in Table 2.8. The designated condition is 35°C and 12 MPa .

Solution:

- (1) Figure out y'_i , see Table 2.8.
- (2) Calculate and schedule the pseudo-parameters:
 Pseudo-critical temperature: $T_{\text{pc}} = \sum y'_i T_{ci} = 222.68 \text{ K}$
 Pseudo-critical pressure: $P_{\text{pc}} = \sum y'_i P_{ci} = 4.62 \text{ MPa}$;
 Pseudo-reduced temperature: $T_{\text{pr}} = T/T_{\text{pc}} = (273 + 35)/222.68 = 1.38$;
 Pseudo-reduced pressure: $P_{\text{pr}} = P/P_{\text{pc}} = 12/4.62 = 2.60$.
- (3) Since $T_{\text{pr}} = 1.38$ and $P_{\text{pr}} = 2.60$, the compressibility factor of the mixture of hydrocarbons, Z_{CH} , can easily be extracted from Fig. 2.3: $Z_{\text{CH}} = 0.712$. Furthermore, the compressibility of nitrogen at 35°C and 12 MPa can be obtained through related handbooks: $Z_{\text{N}} = 1.03$.

Table 2.8 Calculation of the parameters of nitrogen-contained natural gas

Component	Mole fraction y_i	Mole fraction of hydrocarbon $y'_i = \frac{y_i}{1-y_{\text{N}_2}}$	T_{ci} , (K)	$y'_i T_{ci}$	P_{ci} (MPa) _{i}	$y'_i P_{ci}$
N_2	0.435	—	—	—	—	—
CH_4	0.445	0.790	190.67	150.63	4.641	3.67
C_2H_6	0.062	0.110	303.56	33.39	4.884	0.54
C_3H_8	0.039	0.070	370.00	25.90	4.257	0.30
C_4H_{10}	0.019	0.030	425.39	12.76	3.793	0.11
Sum	1.000	1.000	—	222.68	—	4.62

- (4) Setting the symbol y_N as the mole fraction of non-hydrocarbon components, the compressibility factor for the nitrogen-contained natural gas can be obtained through the equation written below:

$$\begin{aligned} Z &= y_N Z_N + (1 - y_N) Z_{CH} \\ &= 0.435 \times 1.03 + (1 - 0.435) \times 0.712 \\ &= 0.8503 \end{aligned}$$

Based on this example, let us compare the Z -factor values of the nitrogen-contained and nitrogen-free natural gases.

Nitrogen-contained compressibility factor: $Z = 0.8503$

Nitrogen-free compressibility factor: $Z_{CH} = 0.712$

This result indicates that great error would occur if no correction is taken. As for the source of the error, it can be explained by the applicability of principle of corresponding state: The curves on the Z -chart (Fig. 2.3) are made on the basis of principle of corresponding state; however, this law can only apply nicely to the gases with similar molecular characteristics. It is also suggested that as a correction aimed to get more accurate results, the gained Z -factor could be multiplied by an adjustment factor C , numerically 1–1.04.

Finally, another two points should be mentioned:

- (1) The higher the pressure in gas reservoirs, the greater the compressibility factor they have. For ultradeep gas reservoirs, they have high Z -factor value. An accurate determination of the Z -factor is essential in the calculation of reserves. If the obtained Z -factor is smaller than its actual value, the original reserve figured out is greater than it really is.
- (2) It is found that when the heavy hydrocarbons make a comparatively big contribution in natural gases (e.g., the condensate gas), the value of Z -factor obtained through the charts suffers significant error, so the compressibility equation of state as stated above could not be used to describe their p – V – T relations. Therefore, in recent years, other state equations are developed for the phase equilibrium calculations of condensate gases.

2.2.4 Other Equations of State for Natural Gas

The equation of state for real gas (2.11) is established on the basis of experimental research, and the Z -factor is actually an adjustment coefficient born from experimental tests.

Another way to establish the equations is through theoretical analyses: Proceeding from the microscopic structure of the substance, research on the movement of the gas molecules and their interaction between each other and then conclude their influence on the macroscopic properties of natural gases. In this way,

corresponding corrections are added into the equation of state for ideal gas; thus, the citation of the ideal equation by real gases can be ensured.

1. VDW State Equation

One of the earliest attempts to represent the behavior of real gases by an equation was that of van der Waals (1873). Based on the kinetic theory of gases, he took the microscopic structure of gases in consideration and proposed two correction terms which were concerned essentially with the two fundamental assumptions in the definition of the ideal gas model.

- (1) The correction in consideration of the volume occupied by the molecules: When confined in a limited space, since the gas molecules take up a certain amount of volume themselves, the room for their free action or movement is reduced. Therefore, the real gas molecules strike the walls of the container more frequently, leading to an increase in the pressure exerted on the container walls, from $P = \frac{RT}{V_m}$ to $P = \frac{RT}{V_m - b}$. In the formula, the parameter b is associated with the molecules themselves, and its value is four times of the molecular volume.
- (2) The correction in consideration of the interaction between the gas molecules: Within the gases, each molecule has to expose itself to the attraction forces from the other molecules around it, and an equilibrium state will be reached because of the counteraction of their interactions. However, the molecules nearby the container walls, also called outer-layer molecules, are only acted upon by the forces from the inner part of the container, resulting in fewer strikes and lower pressure on the walls. This decrease is in direct proportion with the number of the molecules that strike on the container walls in every unit interval of time and also in direction proportion with the number of the other molecules that attract the outer-layer ones. Thus, the decrease of pressure is in direct proportion with the square of the gas density. The term $\frac{a}{V_m^2}$ is used to represent it.

From the knowledge mentioned above, we can get the corrected equation of state for real gases, the VDW equation:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (2.19)$$

where

- a constant, MPa m³/(kmol K);
- b constant, m³/kmol;
- P the pressure, MPa;
- T the temperature, K;
- V_m the specific volume (the volume of every 1000 mol gas), m³/kmol;
- R universal gas constant, $R = 0.008134$ MPa m³/(kmol K).

According to the index of the specific volume, the equation above can be written in another form with descending indexes:

$$PV_m^3 - (bP + RT)V_m^2 + aV_m - ab = 0 \quad (2.20)$$

This is the VDW equation in cubic form, and when the temperature is fixed, V_m has three roots in the coordinate system of V_m - P .

2. RK (Redlich–Kwong) State Equation

Soon after the appearance of the van der Waals equation, other researchers began attempts to improve it. The RK equation is one of the improved:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)T^{0.5}} \quad (2.21)$$

Among the parameters: $a = \frac{C_a R^2 T_c^{2.5}}{P_c}$ $b = \frac{C_b R T_c}{P_c}$

$$C_a = 0.42747; \quad C_b = 0.08664;$$

where

T_c the critical temperature, K;

T temperature, K;

P_c the critical pressure, MPa;

P pressure, MPa;

V mole volume, m^3/kmol ;

R universal gas constant, $R = 0.008134 \text{ MPa m}^3/(\text{kmol K})$.

In Eq. (2.21), which is comparatively simple, only two empirical constants are involved in. But it is able to offer reasonable accuracy for ordinary gases.

3. PR(Peng–Robinson) State Equation

In 1975, Peng and Robison proposed another state equation in corrected form.

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V - b)} \quad (2.22)$$

Upon critical conditions:

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c;$$

$$b(T_c) = 0.07780 R T_c / P_c;$$

At other temperatures:

$$\begin{aligned} a(T) &= a(T_c)\beta(T_r, \omega); \\ b(T) &= b(T_c); \\ \beta(T_r, \omega) &= [1 + m(1 - T_c^{0.5})]^2; \\ m &= 0.37464 + 1.54226\omega - 0.26992\omega^2; \end{aligned}$$

where

ω eccentric factor, refer to Table 2.1 and Table 2.2;

P_c critical pressure, Pa;

T_c critical temperature, K;

Equation (2.22) can be written in a cubic form expressed by the compressibility factor:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2.23)$$

$$A = \frac{aP}{R^2T^2} \quad B = \frac{bP}{RT}$$

4. SRK State Equation

To make use of the state equations in the numerical simulation of gas-condensate reservoirs, Soave made a correction upon the PK state equation and suggested that $1/T^{0.5}$ be replaced with a temperature-dependent term α , regarding the term of attraction force as a function of the eccentric factor and temperature.

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)} \quad (2.24)$$

To set that:

$$A = aP/(R^2T^2)$$

$$B = bP/(RT)$$

$$V_m = ZRT/P$$

Then, the Eq. (2.24) can be transformed into a cubic equation expressed by the compressibility factor:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (2.25)$$

where

For pure components:

$$A = \frac{C_a \alpha_i P T_{ci}^2}{P_{ci} T^2} \quad (2.26)$$

$$B = \frac{C_b P T_{ci}}{P_{ci} T} \quad (2.27)$$

For mixed gases:

$$A_m = C_a \frac{P}{T^2} \left(\sum y_i \frac{T_{ci} \alpha^{0.5}}{P_{ci}^{0.5}} \right)^2 \quad (2.28)$$

$$B_m = C_b \frac{P}{T} \sum y_i \frac{T_{ci}}{P_{ci}} \quad (2.29)$$

$$\alpha_i = [1 + m_i (1 - T_{ri}^{0.5})]^2 \quad (2.30)$$

$$m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \quad (2.31)$$

$$b = \sum_i^c x_i b_i \quad (2.32)$$

$$b_i = 0.08664 \frac{R T_{ci}}{P_{ci}} \quad (2.33)$$

$$a = \sum_i^c \sum_j^c x_i x_j (a_i a_j)^{0.5} (1 - \bar{K}_{ij}) \quad (2.34)$$

$$a_i = a_{ci} \alpha_i \quad (2.35)$$

$$a_{ci} = 0.42748 \frac{(R T_{ci})^2}{P_{ci}} \quad (2.36)$$

where

- ω_i the eccentric factor of the i th component, refer to Table 2.1 and Table 2.2;
- T_{ri} the reduced temperature of the i th component;
- \bar{K}_{ij} a coefficient for the binary interactive effect;
- i, j, c represent the i th and j th component and the number of components, respectively .

The equations of state have various forms, and each one has their own rules. Owing to the limitation of space, not all these equations can be introduced here, so it is better for the interested readers to get some reference books for more details.

[Example 2.7] Calculate the pressure exerted by the CO (3.7 kg, 215 K) which is confined in a vessel of 0.03 m³, respectively, using (1) the equation of state for real gas and (2) the van der Waals equation. It is already known that the pressure in actual measurement is 6.998 MPa.

Solution: Refer to related charts and get molecular weight of CO which is $\mu = 28.01$ kg/kmol, and thence, the mole number of it is $n = \frac{3.7}{28.01} = 0.13209$ (kmol).

The volume every 1000 mol of CO is $v_m = 0.030/0.13209 = 0.227$ (m³/kmol).

(1) Using the equation of state for real gas:

$$P = \frac{RT}{V_m} = \frac{0.008311 \times 215}{0.227} = 7.874 \text{ (MPa)}$$

The error is: $\frac{7.874-6.998}{6.998} \times 100\% = 12.52\%$

(2) Using the van der Waals equation:

Refer to related charts and get the van der Waals constants:

$$a = 0.14739 \text{ Pa m}^6/\text{mol}^2 = 0.14739 \text{ MPa m}^6/\text{kmol}^2$$

$$b = 0.03949 \times 10^{-3} \text{ m}^3/\text{mol} = 0.03949 \text{ m}^3/\text{kmol}$$

Substitute a and b into the Eq. (2.19):

$$P = \frac{R_m T}{V_m - b} - \frac{a}{V_m^2} = \frac{0.008314 \times 215}{0.227 - 0.03949} - \frac{0.14739}{0.227^2} = 6.672 \text{ (MPa)}$$

The error is: $\frac{6.672-6.998}{6.998} \times 100\% = -4.65\%$

Comparing the two results, in this example, the result obtained through the van der Waals equation is more close to the real situation.

2.2.5 The Calculation of Z-Factor Using State Equation Correlations

Apart from the methods based on preprepared charts as previously mentioned, another way used to calculate the Z-factor is a computational method, which can be further divided into two branch ways. The first one is called “fitting method,” using

the algebraic expressions to fit the Z -factor charts. Because the Z -curves are non-monotonic ones, piecewise fitting is required. The second method is to calculate the compressibility factor through state equations (e.g., the SRK equation and the PR equation). The improvements in computer technology have also promoted the development in the analytical computation of the Z -factor. Two of the methods that are used to make a straightforward calculation of Z -factor will be presented here.

1. The calculation formula for Z -factor at low pressure ($p < 35$ MPa)

$$Z = 1 + \left(0.31506 - \frac{1.0467}{T_{pr}} - \frac{0.5783}{T_{pr}^3} \right) \rho_{pr} + \left(0.5353 - \frac{0.6123}{T_{pr}} \right) \rho_{pr}^2 + 0.6815 \frac{\rho_{pr}^2}{T_{pr}^3} \quad (2.37)$$

$$\rho_{pr} = 0.27P_{pr}/(ZT_{pr}) \quad (2.38)$$

where

ρ_{pr} the dimensionless reduced density;
the others the same as mentioned before.

When the p and T conditions are already given, only by the trial calculation approach can the value of Z -factor be obtained. Usually, an alternation approach is used on computer to obtain the result, and the computation flow process is listed here:

- (1) With the given conditions, calculate the T_{pr} , P_{pr} , or T'_{pr} , P'_{pr} ;
- (2) With the given p and T , calculate the T_{pr} and P_{pr} ;
- (3) For initialization, set $Z^{(0)} = 1$, and resort to Eq. (2.38) to get ρ_{pr} ;
- (4) Substitute the value of ρ_{pr} into Eq. (2.37) and get $Z^{(1)}$;
- (5) Go back to the step (3) using $Z^{(1)}$. By controlling the cycle number in the program execution, output the result after 5 iterations. The accuracy is already fine enough to meet engineering need.

2. The DPR Method

In 1974, Dranchuk, Purvis, and Robinson used the BWR state equation to fit the Z -factor charts and proposed the equation below:

$$Z = 1 + \left(A_1 + A_2/T_{pr} + A_3/T_{pr}^3 \right) \rho_{pr} + \left(A_4 + A_5/T_{pr} \right) \rho_{pr}^2 + \left(A_5 A_6 \rho_{pr}^5 \right) / T_{pr} + \left(A_7 \rho_{pr}^2 / T_{pr}^3 \right) \left(1 + A_8 \rho_{pr}^2 \right) \exp \left(-A_8 \rho_{pr}^2 \right) \quad (2.39)$$

$$\rho_{pr} = 0.27P_{pr}/(ZT_{pr}) \quad (2.40)$$

In the equation, A_1 – A_8 are all coefficients:

$$\begin{aligned} A_1 &= 0.31506237; & A_2 &= -1.0467099; \\ A_3 &= -0.57832729; & A_4 &= 0.53530771; \\ A_5 &= -0.61232032; & A_6 &= -0.10488813; \\ A_7 &= 0.68157001; & A_8 &= 0.68446549; \end{aligned}$$

When the p and T conditions are already given, the simultaneous equation of the two can be used to obtain ρ_{pr} . Then, substitute the ρ_{pr} back to one of the two equations to get the value of the Z -factor.

The new function F is constructed by the two equations:

$$\begin{aligned} F(\rho_{pr}) &= \rho_{pr} - 0.27P_{pr}/T_{pr} + \left(A_1 + A_2/T_{pr} + A_3/T_{pr}^3\right)\rho_{pr}^2 \\ &\quad + \left(A_4 + A_5/T_{pr}\right)\rho_{pr}^3 + \left(A_5A_6\rho_{pr}^6\right)/T_{pr} + \left(A_7\rho_{pr}^3/T_{pr}^3\right)\left(1 + A_8\rho_{pr}^2\right)\exp\left(-A_8\rho_{pr}^2\right) \\ &= 0 \end{aligned} \quad (2.41)$$

Equation (2.41) is a nonlinear equation, and the value of ρ_{pr} can be obtained through the Newton's alternation method. The computation steps are listed hereunder:

- (1) Initialization: $\rho_{pr}^{(0)} = 0.27P_{pr}/T_{pr}$;
- (2) Calculate $F(\rho_{pr})$ using Eq. (2.41);
- (3) Calculate $F'(\rho_{pr})$: figure out the differential coefficient of Eq. (2.41);

$$\begin{aligned} F'(\rho_{pr}) &= 1 + \left(A_1 + A_2/T_{pr} + A_3/T_{pr}^3\right)(2\rho_{pr}) + \left(A_4 + A_5/T_{pr}\right)(3\rho_{pr}^2) \\ &\quad + \left(A_5A_6/T_{pr}\right)/(6\rho_{pr}^5) + \left(A_7/T_{pr}^3\right)\left[3\rho_{pr}^2 + A_8(3\rho_{pr}^4) - A_8^2(2\rho_{pr}^6)\right]e^{-A_8\rho_{pr}^2} \end{aligned} \quad (2.42)$$

- (4) Obtain the value of ρ_{pr} through the Newton's alternation method;

$$\rho_{pr}^{(k+1)} = \rho_{pr}^{(k)} - \frac{F(\rho_{pr})}{F'(\rho_{pr})} \quad (2.43)$$

- (5) Estimate the accuracy, and when $\left|\rho_{pr}^{(k+1)} - \rho_{pr}^{(k)}\right| < 0.0001$, the accuracy is fine enough; then, calculate the value of Z through Eq. (2.39);

- (6) Go back to the step (2) and continue with the alternation until $F(\rho_{pr}) \approx 0$;
- (7) Substitute the ρ_{pr} which is already accurate enough for engineering requirement back to Eqs. (2.39) or (2.40) and get the value of the Z-factor.

2.3 Physical Properties of Natural Gas Under High Pressure

2.3.1 Natural Gas Formation Volume Factor (FVF)

In reservoir engineering calculations, sometimes it is necessary to convert the gas volume upon reservoir conditions (high temperature and high pressure) to standard gas volume, which also called surface volume. Hereupon, the concept of the volume factor of natural gas can be introduced.

The natural gas formation volume factor is defined as the ratio of the volume of a certain amount of natural gas under reservoir conditions to the volume of it under surface standard conditions, that is the volume of gas under reservoir conditions required to produce one unit volume of oil or gas at the surface:

$$B_g = \frac{V}{V_{sc}} \quad (2.44)$$

where

B_g the volume factor of natural gas, m^3/m^3 ;
 V_{sc} the volume of a certain amount of natural gas under reservoir conditions, m^3 ;
 V the volume of a certain amount of natural gas under surface standard conditions, m^3 .

Under surface standard conditions, the natural gas is approximately regarded as ideal gas; that is to say, its compressibility is $Z = 1$. Then, the volume of gas can be calculated according to the state equation:

$$V_{sc} = \frac{nRT_{sc}}{P_{sc}} \quad (2.45)$$

In the equation, P_{sc} , V_{sc} , and T_{sc} , respectively, represent the pressure, volume, and temperature under standard conditions.

At reservoir conditions with a pressure of p and a temperature of T , the volume occupied by the same amount of natural gas can also be obtained through the compressibility equation of state:

Table 2.9 Definitions of standard state in different countries and organizations

Country or organization		Temperature and pressure set as standards	Volume of 1 mol ideal gas
Standard state		0 °C, 760 mmHg (0.101325 MPa)	22.4 L
China	Petroleum industry	20 °C (293 K), 0.101325 MPa	24.04 L
Russian	Petroleum industry	20 °C (293 K), 0.101325 MPa	24.04 L
USA	Petroleum industry	20.0 °C (68°F), 0.101325 MPa	24.04 L
USA	High-pressure gas association	20.0 °C (68°F), 1 atm	24.04 L
USA	Gas association	60°F (15.6 °C), 30 in Hg (760 mmHg)	23.68 L
Britain		60°F (15.6 °C), 30 in Hg (760 mmHg)	23.68 L

$$V = \frac{ZnRT}{P} \quad (2.46)$$

Substitute Eqs. (2.45) and (2.46) into Eq. (2.44):

$$B_g = \frac{V}{V_{sc}} = \frac{ZTP_{sc}}{T_{sc}P} = \frac{273 + t}{293} \frac{P_{sc}Z}{P} \quad (2.47)$$

In the equation, the unit for B_g is $\text{m}^3/(\text{standard}) \text{m}^3$; t is the reservoir temperature, °C.

In fact, the natural gas volume factor B_g describes the conversion coefficient of the gas volumetric change from the reservoir state to the land-surface state.

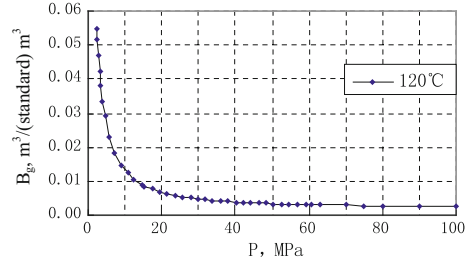
Table 2.9 shows the details about the standard state.

For real reservoirs, their pressure is much higher than that on the land surface (about dozens or hundreds of times), while the reservoir temperature is about several times of the temperature on the surface. So, when the underground gases are subjected to surface conditions, their volume is ten times greater, resulting in a B_g far less than 1. The definition of the swelling coefficient is the ratio of the surface gas volume to the underground gas volume, symbolically $E_g = 1/B_g$, and it is the swelling coefficient of the gas from underground to the surface.

Along with the development of the reservoirs, the gases are continuously depleted out and the reservoir pressure decreases in companion, while the reservoir temperature is comparatively stable and can be seen as a constant. Therefore, in such a situation, it is reasonable to regard the B_g as a function only of the reservoir pressure. That is, $B_g = CZ/P$ (C is a coefficient).

An example curve about the P - B_g relationship is shown in Fig. 2.7.

Fig. 2.7 The P – B_g relationship of a studied natural gas



2.3.2 Isothermal Compressibility of Natural Gas

In reservoir engineering calculations, especially when considering the elastic reserve of the reservoirs, it is necessary to calculate the volumetric change rate of gas along with the change of pressure. Symbolically:

$$C_g = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (2.48)$$

In companion with the increase of pressure, the volume of gas drops, and hence, the $\left(\frac{\partial V}{\partial P} \right)_T$ is negative. To ensure C_g to have a positive value, a minus should be added before the right formula of Eq. (2.48).

By equation of state for real gas, the volumetric change rate of gas in Eq. (2.48) can be obtained.

$$V = nRT \frac{Z}{P} \quad (2.49)$$

To calculate the differential of it:

$$\left(\frac{\partial V}{\partial P} \right)_T = nRT \frac{P \frac{\partial Z}{\partial P} - Z}{P^2} \quad (2.50)$$

Substitute Eqs. (2.50) and (2.49) into Eq. (2.48), and get the expression of C_g :

$$\begin{aligned} C_g &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{P}{ZnRT} \left[\frac{nRT}{P^2} \left(P \frac{\partial Z}{\partial P} - Z \right) \right] \\ &= \frac{1}{P} - \frac{1}{Z} \frac{\partial Z}{\partial P} \end{aligned} \quad (2.51)$$

The $\frac{\partial Z}{\partial P}$ in Eq. (2.51) can be determined by the Z-charts: Resort to the p – Z curve at the corresponding temperature, and find the point in accordance with the given Z ; then, extract value of the Z -factor and figure out the slope of the tangent line at this point, $\Delta Z / \Delta P$; finally, substitute them into the equation presented above and get the value of C_g .

For real gases, since $Z = 1.0$ and $\frac{\partial Z}{\partial P} = 0$, we can know that $C_g = \frac{1}{P}$; in other words, the value of C_g is proportional to the reciprocal of pressure. For real gases, since $Z \neq 1$, the $\frac{1}{Z} \frac{\partial Z}{\partial P}$ must have a certain value which sometimes can be quite considerable.

We can know from the Z -charts that the value of $\frac{\partial Z}{\partial P}$ is not uniform when the conditions of pressure are different. It can be either positive or negative. For example, at low pressure, the value of the compressibility factor decreases with the increase in pressure, and hence, the value of $\frac{\partial Z}{\partial P}$ is negative. As a result, the corresponding C_g is greater than that of the ideal gas. On the contrary, under high pressure, the value of the compressibility factor increases with the increase in pressure, and hence, the value of $\frac{\partial Z}{\partial P}$ is positive. As a result, the corresponding C_g is smaller than that of the ideal gas.

[Example 2.8] Calculate the isothermal compressibility C_g of the natural gas at 20 °C and 6.8 MPa.

Solution:

- (1) Refer to the P - Z -charts of methane (Fig. 2.1) and get $Z = 0.89$;
- (2) Calculate the slope at this point: $\frac{\partial Z}{\partial P} = -0.01551 \text{ MPa}^{-1}$;
- (3) Calculate the value of C_g through Eq. (2.51):

$$\begin{aligned} C_g &= \frac{1}{P} - \frac{1}{Z} \frac{\partial Z}{\partial P} = \frac{1}{6.8} - \left(\frac{1}{0.89} \right) (-0.0155) \\ &= 1.645 \times 10^{-4} \text{ MPa}^{-1} \end{aligned}$$

It is not convenient to calculate by Eq. (2.51) for multicomponent natural gases. With the reference of principle of corresponding states, therefore, Eq. (2.51) can be converted into another form, i.e., to change the pressure p to the pseudo-reduced pressure P_{pr} . The details of the derivation are presented here:

From the relational equation, $P_{pr} = P/P_c$, we can get that:

$$P = P_{pc} \cdot P_{pr} \quad (2.52)$$

where

P_{pc} , P_{pr} the pseudo-critical pressure and the pseudo-reduced pressure of natural gas, respectively.

Because that:

$$\frac{\partial Z}{\partial P} = \frac{\partial Z}{\partial P_{pr}} \cdot \frac{\partial P_{pr}}{\partial P} \quad (2.53)$$

From Eq. (2.52), we can get that:

$$\frac{\partial P_{pr}}{\partial P} = \frac{1}{P_{pc}} \quad (2.54)$$

Substitute Eq. (2.54) into the Eq. (2.53):

$$\frac{\partial Z}{\partial P} = \frac{1}{P_{pc}} \cdot \frac{\partial Z}{\partial P_{pr}} \quad (2.55)$$

Substitute Eqs. (2.52) and (2.55) into Eq. (2.51):

$$\begin{aligned} C_g &= \frac{1}{P} - \frac{1}{Z} \frac{\partial Z}{\partial P} = \frac{1}{P_{pc} \cdot P_{pr}} - \frac{1}{Z P_{pc}} \frac{\partial Z}{\partial P_{pr}} \\ &= \frac{1}{P_{pc}} \left(\frac{1}{P_{pr}} - \frac{1}{Z} \frac{\partial Z}{\partial P_{pr}} \right) \end{aligned} \quad (2.56)$$

Equation (2.56) is commonly used to calculate the compressibility factor C_g of natural gas. Given the composition of a certain gas, the pseudo-critical parameter (P_{pc}) and the pseudo-reduced parameter (P_{pr}) can be figured out. Then, make use of the Z-charts (Fig. 2.3) and get the value of Z, as well as the $\frac{\partial Z}{\partial P_{pr}}$. Finally, refer to Eq. (2.56) and calculate the value of C_g .

Sometimes, people prefer to cancel out the dimension of C_g and define the pseudo-reduced compressibility factor of natural gas as follows:

$$C_{pr} = C_g \times P_{pc} \quad (2.57)$$

where

C_{pr} the pseudo-reduced compressibility factor of natural gas, dimensionless;

C_g the compressibility factor of natural gas, MPa^{-1} .

Substitute Eq. (2.56) into Eq. (2.57):

$$\begin{aligned} C_{pr} &= P_{pc} \cdot \left[\frac{1}{P_{pc}} \left(\frac{1}{P_{pr}} - \frac{1}{Z} \frac{\partial Z}{\partial P_{pr}} \right) \right] \\ &= \frac{1}{P_{pr}} - \frac{1}{Z} \frac{\partial Z}{\partial P_{pr}} \end{aligned} \quad (2.58)$$

With the known values of the pseudo-reduced parameters (P_{pr} , T_{pr}), the pseudo-reduced compressibility factor of natural gas, C_{pr} , can be obtained by referring to Fig. 2.8.

[Example 2.9] Using the gas composition given in Example 2.3, calculate the isothermal compressibility C_g of the natural gas at 49 °C and 10.2 MPa (102 atm).

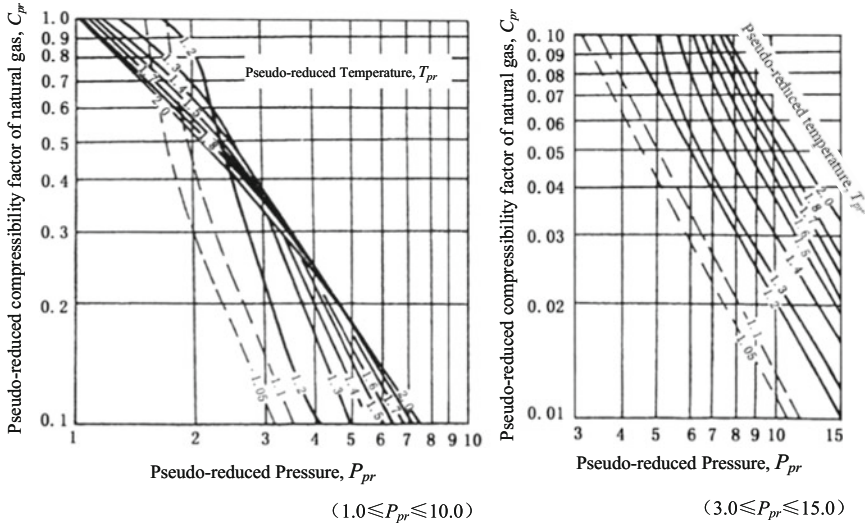


Fig. 2.8 C_{pr} - T_{pr} , P_{pr} charts (Mattar 1975) ($1.0 \leq P_{pr} \leq 10.0$) ($3.0 \leq P_{pr} \leq 15.0$)

Solution:

- (1) Calculate pseudo-critical parameters and the pseudo-reduced parameters (already known from the Example 2.3):

$$P_{pc} = 4.54 \text{ MPa}; \quad T_{pc} = 212.8 \text{ K};$$

$$P_{pr} = 2.25; \quad T_{pr} = 1.51.$$

- (2) Refer to the Z -charts (Fig. 2.3), extract $Z = 0.813$, and figure out $\frac{\partial Z}{\partial P} = -0.053$.
- (3) Calculate the value of C_g through Eq. (2.56):

$$\begin{aligned}
 C_g &= \frac{1}{P_{pc}} \left(\frac{1}{P_{pr}} - \frac{1}{Z} \frac{\partial Z}{\partial P_{pr}} \right) \\
 &= \frac{1}{4.54} \left[\frac{1}{2.25} - \frac{1}{0.813} (-0.053) \right] \\
 &= \frac{1}{4.54} \times 0.5096 = 1122 \times 10^{-4} \text{ MPa}^{-1}
 \end{aligned}$$

[Example 2.10] Using the gas composition given in Example 2.3, calculate the isothermal compressibility C_g of the natural gas at 49 °C and 10.2 MPa (102 atm) by referring to Fig. 2.8.

Solution:

(1) Calculate the values of:

$$P_{pc} = 4.54; \quad T_{pc} = 212.9K;$$

$$P_{pr} = 2.25; \quad T_{pr} = 1.51.$$

- (2) Refer to Fig. 2.8 and determine that when $P_{pr} = 2.25$ and $T_{pr} = 1.51$, $C_{pr}T_{pr} = 0.77$ and $C_{pr} = (C_{pr}T_{pr})/T_{pr} = 0.77/1.51 = 0.51$;
- (3) Calculate the value of C_g through Eq. (2.57):

$$C_g = \frac{C_{pr}}{P_{pc}} = \frac{0.51}{4.54} = 1123 \times 10^{-4} \text{ MPa}^{-1}$$

2.3.3 Viscosity of Natural Gas

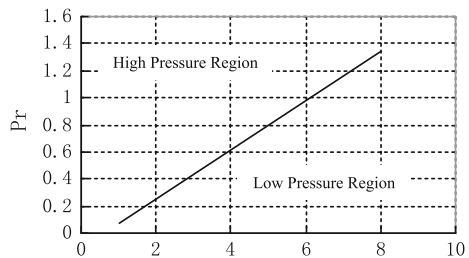
The natural gas is a viscous fluid. Its viscosity is much lower than that of water and oil; hence, the unit used for it is μP .

The viscosity of gas depends on its composition and the temperature and pressure conditions to which it is subjected. The changing regularities of it are not uniform at high- and low-pressure conditions. The partition between high and low pressure is shown in Fig. 2.9.

1. Viscosity of Natural Gas at Low Pressure

When the natural gas is put under pressure condition as low as atmospheric pressure, its viscosity almost has nothing to do with the pressure, but the viscosity increase with increase in temperature.

Fig. 2.9 The division of high- and low-pressure regions in gas viscosity calculation



According to the molecular dynamics of gas:

$$\mu = \frac{1}{3} \rho \bar{v} \bar{\lambda} \quad (2.59)$$

where

- μ the viscosity of gas, g/cm s;
- ρ the density of gas, g/cm³;
- \bar{v} the average velocity of gas molecules, cm/s;
- $\bar{\lambda}$ the average free-travel length of gas molecules, cm.

Equation (2.59) indicates that the viscosity of gas has a connection with the quantities of ρ , \bar{v} , and $\bar{\lambda}$. Among the three parameters, the velocity of gas molecules \bar{v} has nothing to do with pressure; the density ρ is proportional to pressure; and the free-travel length $\bar{\lambda}$ is inversely proportional to pressure. On the whole, we can conceive that the product of the three quantities is indispensable of pressure. What needs to be stressed is that this conclusion is feasible only for low-pressure conditions that are near the atmospheric pressure.

As the temperature is increased, the kinetic energy of molecules increases in companion with accelerated movement of the molecules and more collisions occur between each other, and thus, the internal friction of the fluid is raised, resulting in greater viscosity.

Figure 2.10 shows the viscosity of single-component natural gases at atmospheric pressure. From the chart, it is obvious that for hydrocarbon gases, an increase in temperature causes an increase in viscosity, and the viscosity decreases with the increase in molecular weight.

2. Viscosity of Natural Gas under High Pressure

The viscosity of natural gas under high pressure tends to increase with the increase in pressure, decrease with the increase in temperature, and increase with the increase in molecular weight. That is to say, the gases under high pressure possess characteristics that typically belong to liquid fluids.

3. Methods for Determining the Viscosity of Natural Gases

(1) Carr (1954) Viscosity Chart

The viscosity retentions of paraffin hydrocarbons at atmosphere pressure, correlated with temperature, molecular weight, and gas specific gravity, are presented in Fig. 2.11: (1) The viscosity of natural gas decreases with the increase in molecular weight; (2) the inset charts in the figure, at the top right corner and the bottom left corner, provide means of correcting the viscosity for the presence of non-hydrocarbon components, including N₂, CO₂, and H₂S.

The correction method follows this way: Firstly, refer to the corner charts and extract the corresponding value of the adjustment factor in accordance with the mole fraction shared by the non-hydrocarbon components; secondly, add the

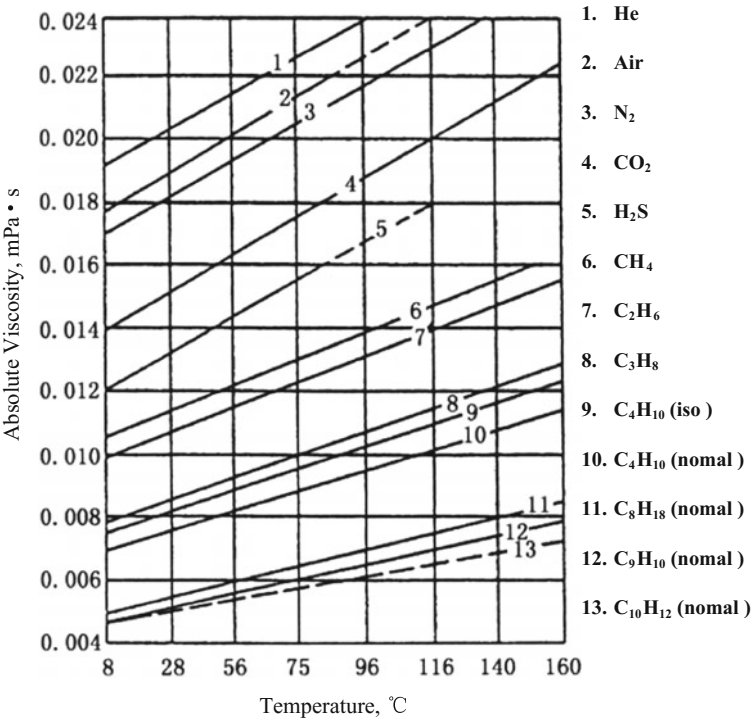


Fig. 2.10 The viscosity–temperature relation curve at atmospheric pressure (Carr 1954)

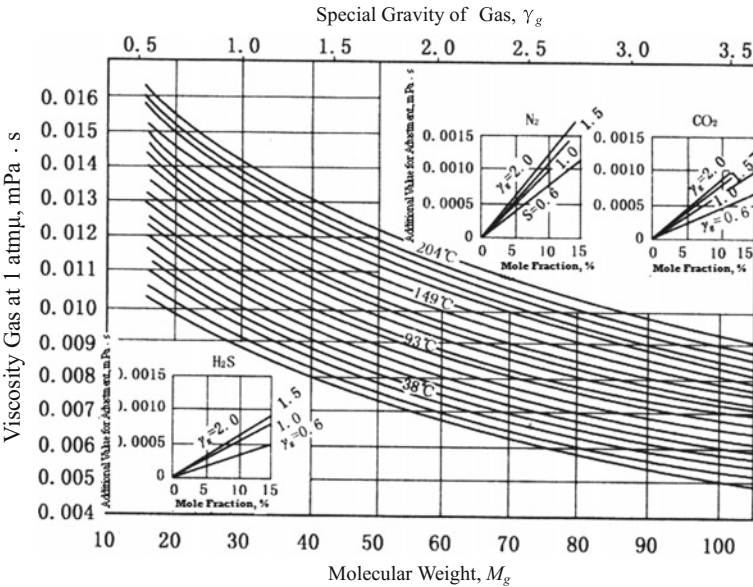


Fig. 2.11 Viscosity of paraffin hydrocarbon gases at 1 atm (Carr et al. 1954)

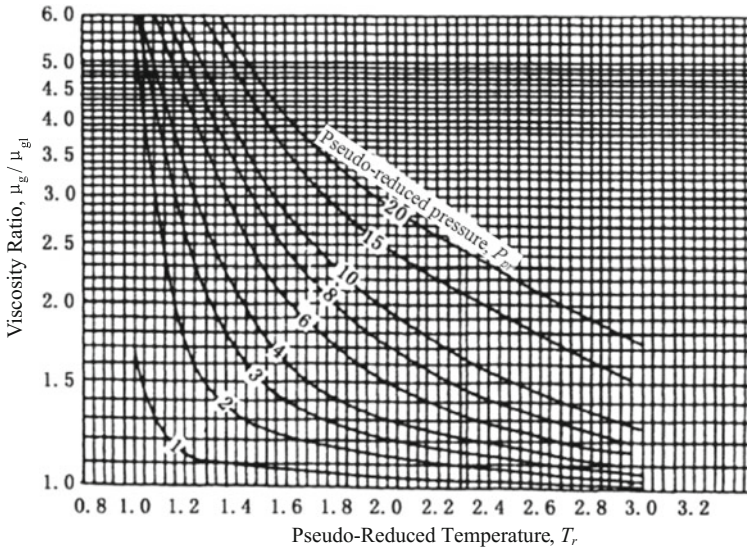


Fig. 2.12 Relationship between viscosity ratio and pseudo-reduced parameters (Carr et al. 1954)

adjustment factor to the viscosity value obtained through viscosity charts, and the sum of them is the viscosity result.

[Example 2.11] Calculation of Gas Viscosity. A natural gas having 10 % H_2S (mole fraction) and a special gas gravity of 0.6 exist at the pressure of 0.1 MPa and the temperature of 43.3 °C. What is the viscosity of the gas?

Solution:

- (1) With the known specific gravity of 0.6 and the temperature 43.3 °C, refer to Fig. 2.11 and get the viscosity $\mu = 0.0113$ mPa s.
- (2) With the known mole fraction of H_2S , 10 %, as well as the specific gravity of 0.6, refer to the inset chart at the bottom left corner of Fig. 2.11 and get the value of the adjustment factor: 0.0002 mPa s.
- (3) After correction, the viscosity of the given natural gas at 0.1 MPa is:

$$\mu_g = 0.0113 + 0.0002 = 0.0115 \text{ mPa s}$$

The viscosity of natural gas under high pressure can be obtained through the charts in Fig. 2.12, and the steps to use this chart are:

- (1) According to the known specific gravity or apparent molecular weight and the temperature, refer to Fig. 2.11 and extract the viscosity at atmospheric pressure, μ_{gl} ;
- (2) Calculate the pseudo-critical parameters (P_{pc} , T_{pc}) and the pseudo-reduced parameters (P_{pr} , T_{pr});

- (3) Refer to Fig. 2.12 and get the ratio of the viscosity values at high and low pressure, symbolically $\left(\frac{\mu_g}{\mu_{g1}}\right)$.
- (4) Finally, figure out the natural gas viscosity at the designated temperature and pressure:

$$\mu_g = \left(\frac{\mu_g}{\mu_{g1}}\right) \times \mu_{g1} \quad (2.59)$$

2) Method Based on the Composition of Natural Gas

Besides the charts, some computational methods have been developed to obtain the viscosity of natural gas. For example, when the composition of a gas is already known, its viscosity at 1 atm and varied temperatures can be obtained through the equation below:

$$\mu_{g1} = \frac{\sum y_i \mu_{gi} M_i^{0.5}}{\sum y_i M_i^{0.5}} \quad (2.60)$$

where

μ_{gi} the viscosity of the i th component (refer to Fig. 2.10 for its value);

M_i the molecular weight of the i th component;

[Example 2.12] Calculation of Gas Viscosity. Determine the viscosity of the gas described in Table 2.10. The designated condition is 93.3 °C and 0.1 MPa.

Solution:

- (1) Refer to Fig. 2.10 to get the values of viscosity at 93.3 °C for each component present in the gas, and list them in Table 2.10.
- (2) According to the Eq. (2.60), calculate the natural gas viscosity at 93.3 °C and 0.1 MPa:

Table 2.10 Calculation of the viscosity of natural gas

Composition	y_i	M_{gi}	μ_{gi}, cP	$M_i^{0.5}$	$y_i M_i^{0.5}$	$\mu_{gi} y_i M_i^{0.5}$
CH ₄	0.85	16.0	0.0130	4.0	3.40	0.0442
C ₂ H ₆	0.09	30.1	0.0112	5.48	0.493	0.0055
C ₃ H ₈	0.04	44.1	0.0098	6.64	0.266	0.0026
<i>n</i> -C ₄ H ₁₀	0.02	58.1	0.009 1	7.62	0.152	0.0014
Sum					4.311	0.0537

$$\mu_g = \frac{\sum y_i \mu_{gi} M_i^{0.5}}{\sum y_i M_i^{0.5}} = \frac{0.0537}{4.311} = 0.0125 (\text{mPa s})$$

3) Method of Empirical Formula—Residual Viscosity Method

When it is necessary to determine the gas viscosity under different pressures, many empirical formulas are applicable. The residual viscosity method is one of them:

$$(\mu - \mu_0)\eta = 1.08[\exp(1.439\rho_{\text{pr}}) - \exp(-1.111\rho_{\text{pr}}^{1.858})] \quad (2.61)$$

$$\eta = T_{\text{pc}}^{1/6} / M^{1/2} P_{\text{pc}}^{2/3}; \quad \rho_{\text{pr}} = \rho / \rho_{\text{pc}}$$

$$\rho_{\text{PC}} = P_{\text{pc}} / (ZRT_{\text{pc}}); \quad M = \sum y_i M_i$$

$$Z = \sum y_i Z_{ci}$$

where

- μ the viscosity of natural gas under high pressure, 10^2 mPa s;
- μ_0 the viscosity of natural gas at low pressure, 10^2 mPa s;
- η coefficient;
- ρ_{pr} the pseudo-reduced density of natural gas;
- ρ_{pc} the pseudo-critical density of natural gas;
- M the molecular weight of natural gas;
- Z compressibility factor.

4) Method of Empirical Formula—Lee–Gonzalez Semiempirical Method (1966)

On the analysis of the eight oil samples from four oil companies, a semiempirical equation can be derived from the laboratory measurements taken by Lee, Gonzalez, and Eakin:

$$\mu_g = 10^{-4} K \exp(X \rho_g^y) \quad (2.62)$$

Among the parameters:

$$K = \frac{2.6832 \times 10^{-2} (470 + M) T^{1.5}}{116.1111 + 10.5556M + T} \quad (2.63)$$

$$X = 0.01009 \left(350 + \frac{54777.7}{T} + M \right) \quad (2.64)$$

$$Y = 2.447 - 0.2224X \quad (2.65)$$

where

- μ_g the viscosity of natural gas under the given condition of p and T , mPa s;
 T the temperature to which the studied natural gas is subjected, K;
 M the apparent molecular weight of natural gas, g/mol;
 ρ_g the density of natural gas, g/cm³.

Actually, the influence of pressure on natural gas is implicit in the computing formula for the gas density ρ_g .

This method is exclusive of the correction for non-hydrocarbon gases, and when it is applied to pure-hydrocarbon gases for viscosity determination, the standard calculation error is $\pm 3\%$, and the maximum error allowed is 10% . This degree of accuracy is good enough for the calculations in gas reservoir engineering.

2.4 Natural Gas with Water Vapor and the Gas Hydrate

2.4.1 Water Vapor Content in Natural Gas

Reservoir pressures are well in excess of the saturation pressure of water at prevailing reservoir temperatures. Therefore, due to longtime connection with underground gases, a part of the reservoir water tends to be volatilized into the gas, in which it exists as water vapor, and at the same time, the gases can be dissolved in the reservoir water, too. The term “natural gas with water vapor” refers to the natural gases containing water vapor. The water vapor content (use “water content” for short) depends on the factors written below:

- (1) Pressure and temperature: The water content decreases with the increase in pressure and increases with the increase in temperature.
- (2) The salinity of reservoir water: The water content decreases with the increase in salinity;
- (3) The specific gravity of natural gas: The greater the specific gravity of natural gas, the less the water vapor contained in it.

Generally speaking, absolute humidity and relative humidity are used to describe water content in natural gas.

1. Absolute Humidity (Absolute Content)

The absolute humidity refers to the mass of the water vapor contained in 1 m^3 wet natural gas. The relational expression is:

$$X = \frac{W}{V} = \frac{P_{vw}}{R_w T} \quad (2.66)$$

where

- X absolute humidity, kg/m^3 ;
 W the mass of water vapor, kg ;
 V the volume of the wet natural gas, m^3 ;
 P_{sw} the partial pressure of water vapor, Pa ;
 T the absolute temperature of wet natural gas, K ;
 R_w the gas constant of water vapor, $R_w = 461.53 \text{ kg m}^3/(\text{kg K})$.

If the partial pressure of water vapor reaches as high as the saturation vapor pressure, the saturation absolute humidity can be written like this:

$$X_s = \frac{P_{sw}}{R_w T} \quad (2.67)$$

where

- X_s the saturation absolute humidity, kg/m^3 ;
 P_{sw} the saturation vapor pressure of water vapor, Pa .

The saturation absolute humidity reflects the maximum weight of water that can be hold in natural gas at a specific temperature.

2. Relative Humidity (Relative Content)

The relative humidity is defined as the ratio of the absolute humidity to the saturation absolute humidity, both subjected to the same specific temperature. Symbolically:

$$\phi = \frac{X}{X_s} = \frac{P_{vw}}{P_{sw}} \quad (2.68)$$

For absolute dry natural gases, $P_{vw} = 0$; thence, $\phi = 0$; when the natural gas studied reaches its state of saturation, $P_{vw} = P_{sw}$; thence $\phi = 1$. For ordinary natural gases: $0 < \phi < 1$.

3. Determination of the Water Content in Natural Gas

The method commonly used to calculate the water content in natural gas relies on experimental curves. A brief introduction will be given here. In 1958, Mcketta and Wehe proposed a correlation diagram of water content on the basis of analyzing the testing data (Fig. 2.13). This diagram, also named dew-point diagram, indicates the saturation content of water vapor in natural gases upon different conditions of pressure and temperature. The dashed line in the diagram signifies that the hydrates begin to form. When the pressure condition is below the temperature point at which the hydrate formation can start, the gas reach an equilibrium with the hydrates;

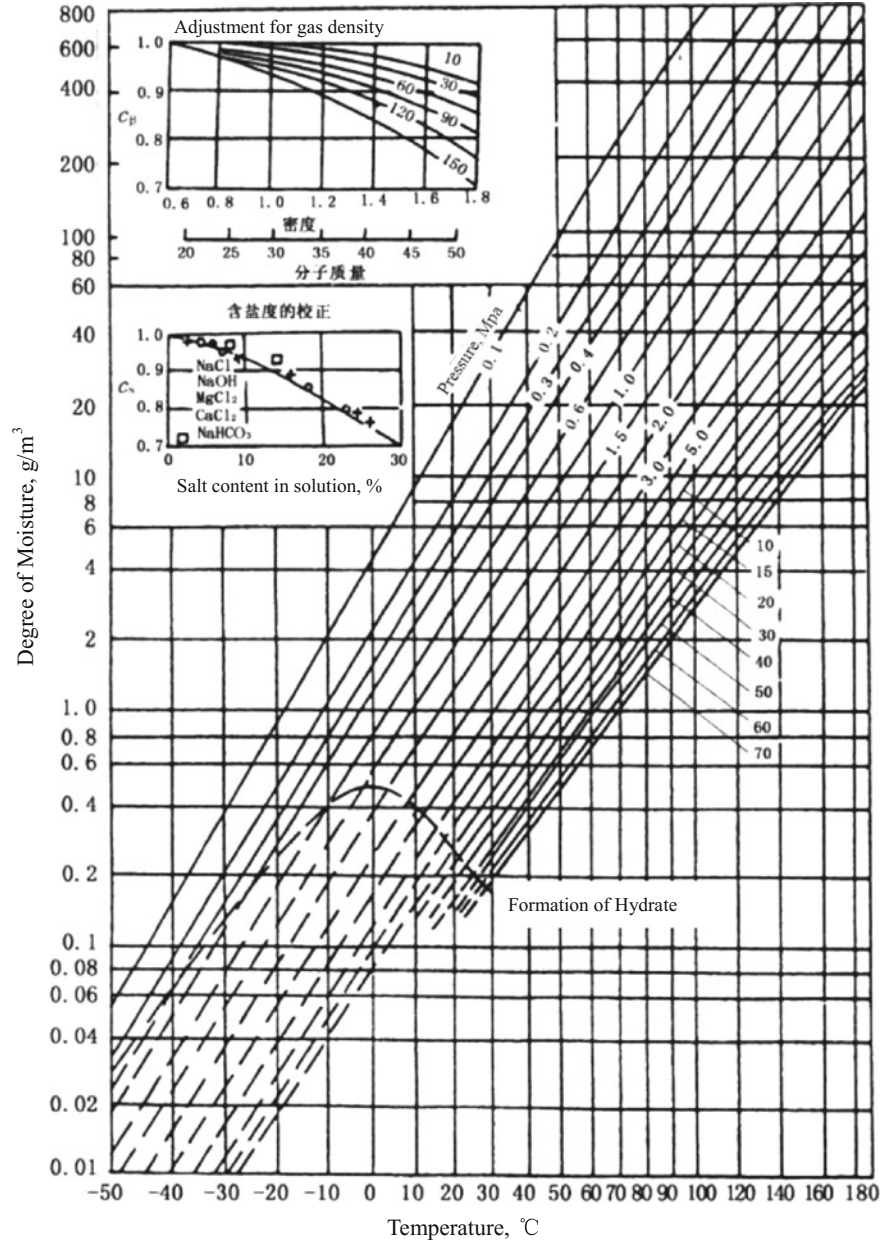


Fig. 2.13 The water content in natural gas (Mcketta-Wehe 1958)

when the temperature is above that point, the gas stays in equilibrium with the liquids.

This diagram can only be applied directly to the gases whose specific gravity is 0.6; for other gases, adjustment coefficients have to be added to their specific gravity values and salt content values:

$$X = X_o \times C_s \times C_\beta \quad (2.69)$$

where

- X the water vapor content of the natural gases with a specific gravity of r_g , g/m^3 ;
- X_o the water vapor content of the natural gases with a specific gravity of 0.6 g/m^3 ;
- C_β the adjustment coefficient for specific gravity equals X/X_o ;
- C_s the adjustment coefficient for salt content equals the ratio of the water vapor content when the gas is in contact with salty water to the water vapor content when the gas is in contact with pure water.

[Example 2.13] The given natural gas has a specific gravity of 0.6 and a temperature of 311 K. It is already known that the salinity of the water in contact with it is 30,000 mg/L (about 3 % NaCl); please calculate the water vapor content in it at a pressure of 3.44 MPa.

Solution:

- (1) Refer to Fig. 2.13, when $\gamma_g = 0.6$, $T = 311 \text{ K}$, $P = 3.44 \text{ MPa}$:
 $X_o = 1.8 \times 10^{-3} \text{ kg/(\text{standard}) m}^3$
- (2) Refer to the correction curve for specific gravity, when $\gamma_g = 0.6$, $T = 311 \text{ K}$: $C_\beta = 0.99$
- (3) Refer to the correction curve for salt content, when the salt content is 3 %:
 $C_s = 0.93$

Substituting the obtained data into Eq. (2.69), we can get:

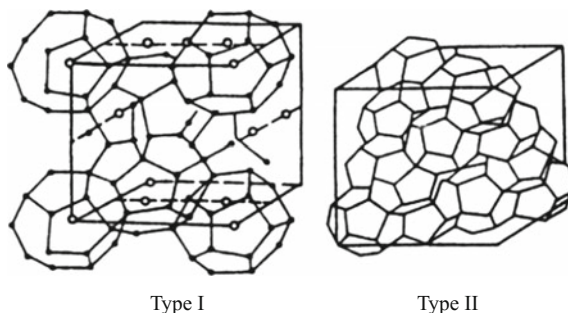
$$X = 1.8 \times 10^{-3} \times 0.99 \times 0.93 = 1.66 \times 10^{-3} \text{ kg/(\text{standard})m}^3$$

The water concentration in the underground natural gases is determined by the pressure and temperature of them. For example, when the pressure is 14.0 MPa and the temperature is 60 °C, the water content in natural gas is 1.740 $\text{g/(\text{standard})m}^3$. Besides, water vapor is usually not considered in engineering calculations when the concentration is quite low.

2.4.2 Natural Gas Hydrate

At specific conditions of pressure and temperature, hydrocarbon gas and liquid water combine to form crystal solids. The solids are called “natural gas hydrates” or “hydrates” for short. The hydrates are one of the forms of complexes known as

Fig. 2.14 Diagram of the crystalline clathrate complexes



crystalline clathrates, evolving water and low molecular weight hydrocarbon or non-hydrocarbon components. The main framework of the hydrate crystal is formed with water molecules, and the hydrocarbon molecules occupy void spaces within the water molecules (see Fig. 2.14). The structure of the water framework complies with the shape and size of the gas molecules that are in contact with it, while the level to which the void spaces are filled depends on the temperature and pressure in the studied system.

A natural gas hydrate is a solid solution of water and natural gas with a “freezing point” which depends on the gas composition, the available water, the pressure, and the temperature. In the solid solution, the solvent is the crystalline framework formed by the water molecules, and the dissolved gas molecules distribute within it. Obviously, that is the reason why the natural gas hydrate is classified into the category of clathrate complexes. Hydrocarbon formation is physical rather than chemical in nature. Apparently, no strong chemical bonds are formed between the molecules: The water molecules form the clathrate crystal lattice by H-bonds between each other, while the hydrocarbon molecules are held within the void spaces in the lattice by van der Waals forces. The gas components that take part in the formation of the hydrates (e.g., N_2 , CH_4 , C_2H_4 , C_3H_8 , $i-C_4H_{10}$, CO_2 , and H_2S) decide the size of the gas hydrate molecules. The mentioned gases, which can form hydrates when conditions allow, all have a molecular diameter less than 6.7 Å. For the gases whose molecular diameter is greater than 6.7 Å, such as the normal butane, hydrates cannot form. In addition, when the size of the molecules is too small (e.g., hydrogen), their van der Waals forces with water molecules are too weak to ensure the stability of the lattice, which make it impossible for them to form hydrates. However, it is also found that when a great amount of methane is present, the hydrogen and normal butane can also join in the formation of natural gas hydrates.

In petroleum engineering, the significance of the research on natural gas hydrates lies in three aspects: (1) The hydrates is a kind of resources, it can exist in underground formations under specific conditions; (2) during natural gas production, hydrates may occur in wellbores and at the surface chokes making great difficulties for gas production; (3) on the surface, the gaseous natural gas may change to hydrates, which improves the efficiency of storage and transportation.

1. The Formation of Hydrates and the Natural Gas Hydrates Resource

Since all reservoirs are believed to contain connate water, it is generally assumed that all mixtures which exist as a gas phase in the reservoirs are saturated with water vapor. Upon certain temperature and pressure conditions, the hydrate starts forming. The hydrates are ice-like crystalline solids with a density of $0.88\text{--}0.90\text{ g/cm}^3$. The gas amount in a hydrate is determined by the gas compositions, and, generally speaking, there are 0.9 m^3 of water and $70\text{--}240\text{ m}^3$ of gas in every 1 m^3 when subjected to standard state.

Not all the void spaces within a stable hydrate are occupied by gas molecules. The formation of hydrates obeys the non-chemical quantitative relation written below:



where

M the gas molecules to form hydrates;

n the ratio of the water molecular number to the gas molecular number, depending on the pressure and temperature in the studied system.

With the exception of methane, nitrogen, and inert gases, the other gas components contained in nature gases all possess their own critical temperature, a threshold above which no hydrates can start forming. Figure 2.15 shows the hydrate-forming conditions for several component gases, and Fig. 2.16 shows the conditions for natural gases. We can know from the figures that only when appropriate pressure and temperature are present can the gas hydrates form.

Fig. 2.15 The forming conditions for pure component gases (Katz 1945)

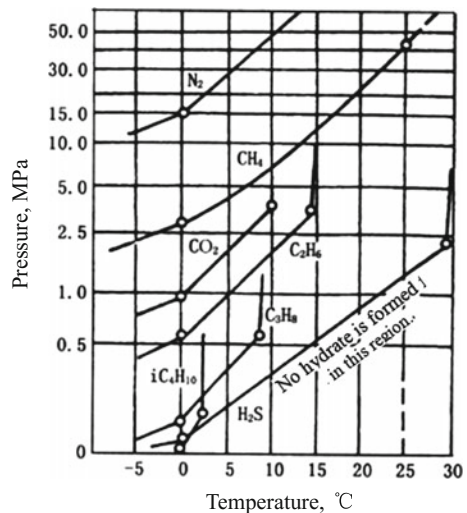
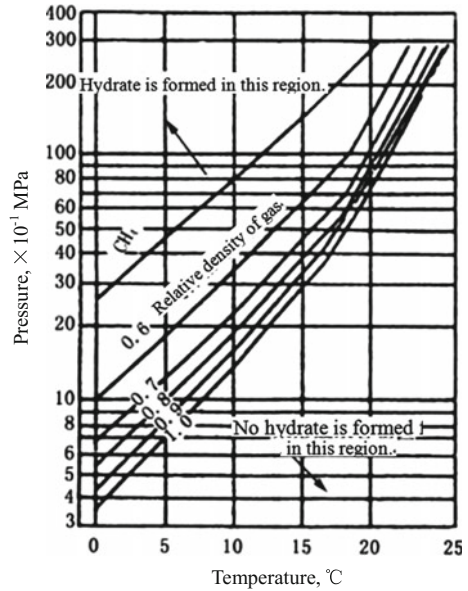


Fig. 2.16 The forming conditions for natural gases (Katz 1945)



In the continental frozen crust or the sedimentary structures beneath the ocean bed, thermodynamic conditions are ready for the hydrate forming upon reservoir conditions. In the 1920s, the first discovery of the hydrate resource is found in Siberia, Russia. It was also found in Alaska, USA. In China, researches and study on the gas hydrate are in progress, and hydrate resources have been found in the rock formations beneath the bottom of South China Sea.

2. Prevention of Gas Hydrates in Wellbores During Gas Well Production

During the production of natural gases, the temperature and pressure of the mixture are reduced as it flows from the formation to wellbore and pipe. In particular, resulting from the pressure drop caused by choking restriction, when the gases pass through chokes and needle valves, their volume will expand and their temperature will drop, which creates conditions for the water-containing gases to form hydrates. Once the gas hydrates are formed, pipelines may be plugged and the production can be suspended.

The most important consideration in hydrate formation is the presence of liquid water in the natural gases. Thus, the fundamental approach to prevent hydrate formation is to remove the water from the gases. Besides, some other methods of prevention include raising the temperature of the gases before and after they encounter the chokes and injecting inhibiting agent into the gas flow ahead of the chokes.

3. Transform the Natural Gases into Hydrates for Storage and Transportation

Normally, natural gases are transported by pipelines. But when the pipeline is not convenient, it is needed to resort to high-pressure vessel transportation, which implies low efficiency and insecurity. If the natural gases are transformed to hydrates before transportation, high efficiency and security can be warranted. This technology is still under study.

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