Review on Computation Models of High-Pressure Hydrogen Compressibility Factor

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Abstract

Several computation models for calculating the compressibility factor of high-pressure hydrogen are discussed, including linear equation, Virial Equation, Van der Waals Equation and Redlich and Kwong Equation. Converting NIST hydrogen density data to compressibility factor data, the compressibility factor data calculated by the models are compared with NIST data. The computation accuracy of Redlich and Kwong's Equation is less than 1% in a wide range of temperature and pressure. The hydrogen compressibility factor data from NIST can be fitted into a linear equation with linear error < 0.55% when $p/T \geq 1$ MPa/K.

1. Introduction

Hydrogen has high heat of combustion and helps protect the environment. Hydrogen energy is one of the most popular new energy sources in the world. With the development and utilization of hydrogen energy, the requirement for accurate measurement of high-pressure hydrogen gas is increasingly high.

The measuring meters of hydrogen can be Coriolis flowmeter, gas turbine flowmeter, gas roots flowmeter, V-cone Flowmeter, etc. High- pressure hydrogen gas at low or normal temperature can not be given by the equation of state of ideal gas. The discharge coefficient of sonic nozzle with high-pressure hydrogen gas is systematically studied by CFD [1]. The results show that the discharge coefficient is mainly influenced by the compressibility factor and the specific heat ratio, which appear more remarkable as the inlet stagnation pressure of nozzle increases[1]. PVTt is a kind of primary reference for gas flow measurement. The measurement accuracy of the PVTt device is directly affected by the compressibility factor of high-pressure hydrogen. The volume conversion formula of hydrogen with compressibility factor is given in reference [2].However, establishing the equation of state of real gas is a complex task, which has not been completely solved at present.

In the present paper, the computation models of high- pressure hydrogen compressibility factor are discussed, and Virial Equation, Van der Waals Equation and Redlich and Kwong Equation are given respectively. Regression analysis was carried out on the hydrogen density data given by the National Institute of Standards and Technology [3], and the data of NIST was compared with computational results of each model.

2. Gas compressibility factor

2.1 Thermal equation of state

The main parameters to determine the thermal state of gas are specific volume v, pressure p and temperature T. There is a definite relation between them, which is called the equation of state of gas, that is $f(v,p,T)=0$. For ideal gas, the equation of state of gas follows Clapeyron Equation

$$pv = \mathrm{R}T \qquad (1)$$

where, p, v, T, R are gas pressure (Pa), specific volume (m^3 / kg), temperature (K) and gas constant (J / kgK) respectively.

In molecular motion theory, the so-called ideal gas means that the geometric size of gas molecules is infinitely small, and there is no attraction or repulsion between molecules. When the pressure is low enough and the density is small enough, all kinds of gases have approximately the same properties as the ideal gas. The Clapeyron Equation of state of ideal gas shown in Eq. (1) has higher accuracy [7].

2.2 Equation of state of real gases

When the gas pressure is high and the density is high (the temperature is low), the law of molecular motion in the gas is complex. The real conditions of high-pressure hydrogen discussed in the present paper are that the pressure is (2 ~ 100) MPa and the temperature is (50 ~ 298) K. At this time, the equation of state of ideal gas cannot be used to describe the p-v-T relation under the real conditions

of hydrogen which calls for a more complex equation of state of real gas. Generally speaking, the equation of state of real gas is obtained by modifying the equation of state of ideal gas on the basis of the equation of state of ideal gas through theoretical and experimental approaches. It is a common expression method to modify the equation of state of ideal gas by introducing a compression factor.

2.3 Compressibility factor
The gas compressibility factor indicates the degree to which the real gas deviates from the ideal gas characteristics. The compressibility factor is an important physical parameter in the measurement of real gases such as hydrogen and natural gases. The compressibility factor Z is defined as

$$Z = \frac{p}{\rho RT} \qquad (2)$$

From Eq. (2), the essence of compressibility factor is a correction coefficient of equation of state of ideal gas.

American Gas Association (AGA) proposed AGA8 - 92 DC equations [4]. The computation equations of compressibility factor of natural gases in working state were given by using gas molar-composition analysis [4] [8]. However, AGA8 - 92 DC does not apply to the computation of compressibility factor of hydrogen gas.

In the present paper, several computation models of compressibility factor of high-pressure hydrogen are summarized and discussed.

3. Computation models

3.1 Isovolumic linear equation
Isovolumetric linear equation means that under isovolumetric conditions, p and T of hydrogen meet the linear relation, that is

$$p = A + KT \qquad (3)$$

where, some values of A and K are listed in Table 1.

Table 1: Values of constants A and K in Eq. (3) [6]

V_M (×10⁻⁶ m³/mol)	A (×10⁵ Pa)	K (×10⁵ Pa/K)
30	174.3	7.58*
32	169.2	6.64
34	157.1	5.82
36	142.9	5.10
38	126.7	4.45

*Note: The original data was 7.08.
3.2 Virial Equation

For gases with low density, Virial Equation can be used, that is

$$p V_M = R_M T \left(1 + \frac{B}{V_M} + \frac{C}{V_M^2} \right) \qquad (4)$$

where, R_M is universal gas constant, B and C are the second and third Virial coefficients, which can be given by the following equations [6]

$$B = \sum_{i=1}^{4} B_i \left(\frac{T_0}{T} \right)^{\frac{(2i-1)}{4}}$$

$$C = c_0 \left(\frac{T_0'}{T} \right)^{1/2} \times \left[1 + c_1 \left(\frac{T_0'}{T} \right)^3 \right]$$

$$\times \left[1 - \exp\left(1 - \left(\frac{T_0'}{T} \right)^{-3} \right) \right] \times 10^{-12}$$

where, B_1=42.464, B_2=-37.1172, B_3=-2.2982, B_4=-3.0484, T_0=109.781K; c_0=1.8105*×10⁻⁸m⁶/mol² (*Note: The original data was 1.3105.), c_1= 2.1486, T_0'=20.615K[6].
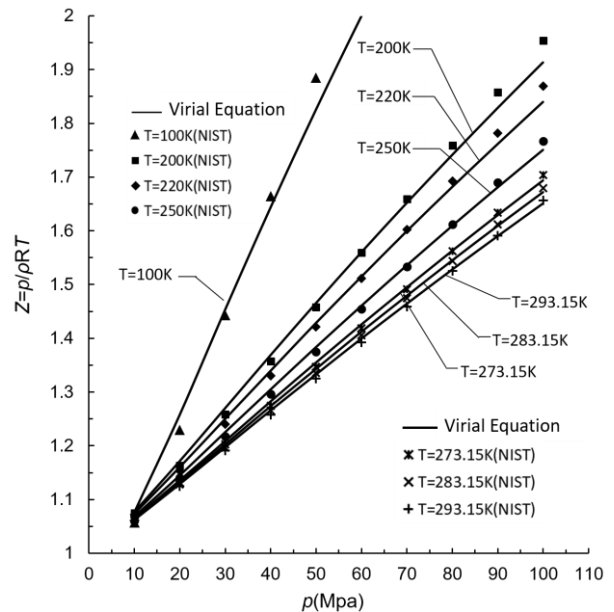

Figure 1: Virial Equation and NIST data [3].

The computation results of Eq. (4) are compared with NIST data, as shown in Fig. 1.

It is found that when T > 200K, p = (10 ~ 70) MPa, the maximum error of Virial Equation is less than 0.9%. But when the temperature T < 200K (T=100K,for example) and the pressure p = (10 ~ 70) MPa, the error of Virial Equation is large due to the high density of hydrogen, and the maximum error can reach 6.3%.

3.3 Van der Waals Equation

Considering the occupied volume of molecules and the interaction force between molecules, Van der Waals modified the equation of state of ideal gas, and put forward the Van der Waals Equation, as follows[7]

$$(p + \frac{a}{v^2})(v - b) = RT \tag{5}$$

$$a = \frac{27}{64}\frac{(RT_c)^2}{p_c}, b = \frac{RT_c}{8p_c}$$

where, the critical parameter is denoted by the subscript "c". For hydrogen, p_c=1.2966MPa, T_c=33.24K, v_c=0.0322m³/kg, Z_c=0.304[7]. Substitute Eq. (5.1) into Eq. (5), and express the equation in contrast form, as

$$(Z + \frac{27p_r}{64ZT_r^2})(1 - \frac{p_r}{8ZT_r}) = 1 \tag{6}$$

where, p_r=p/p_c, T_r=T/T_c are the contrast pressure and temperature, respectively. Eq. (6) does not contain any constants representing the specificity of the substances particularity. Therefore, according to the thermodynamic similarity, Eq.(6) is applicable to all substances in line with the Van der Waals Equation such as hydrogen. The compressibility factor curve plotted by Van der Waals Equation is shown in Fig. 2.
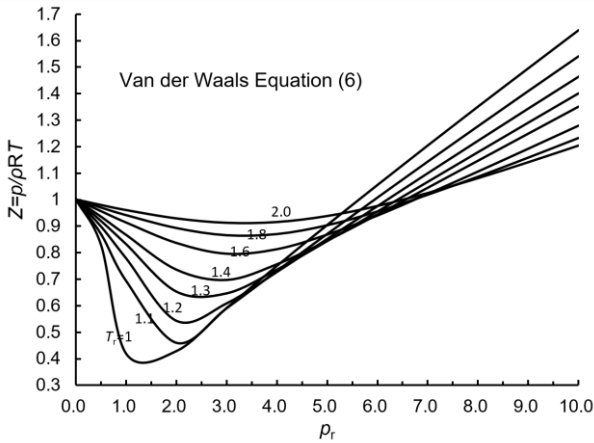

Figure 2: Van der Waals curve.

For applications with $p_r < 7$ and $Z < 1$, the Van der Waals Equation is consistent with the experimental relation among Z and p_r and T_r of some real gases, including CH_4, C_mH_n, CO_2 and N_2, etc. as shown in Fig.3. However, for high-pressure hydrogen with $p > 10$MPa, the compressibility factor calculated by Eq. (5.2) has a large deviation compared with NIST data, as shown in Fig. 4. Therefore, it is not recommended to use Van der Waals Equation to calculate the compressibility factor of high-pressure hydrogen.
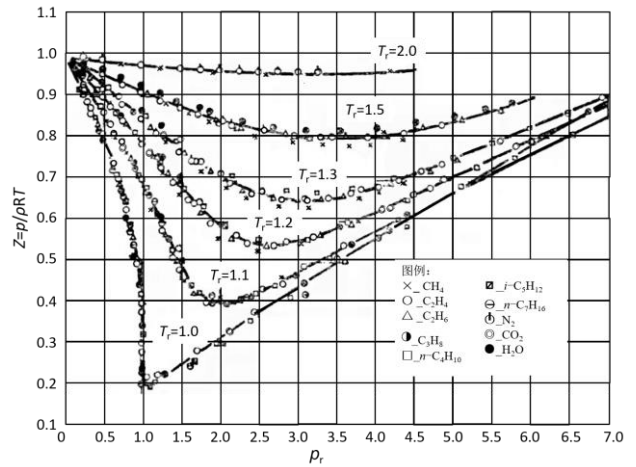

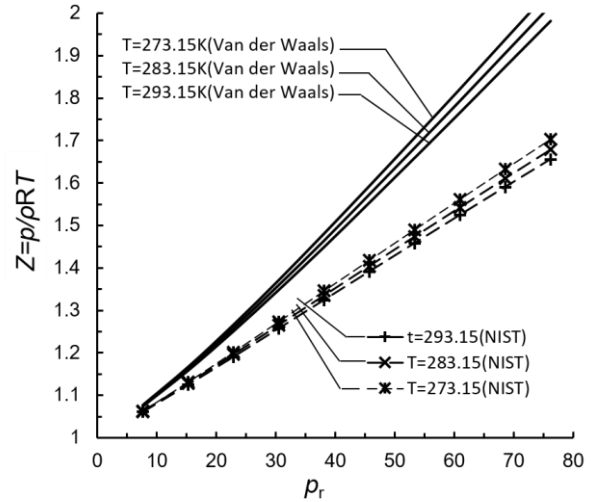**Figure 3:** Van der Waals curve and experimental data of some substances ($p_r<7$, $Z<1$) [7].

Figure 4: Van der Waals curves and the data of hydrogen in NIST ($p_r>7$, $Z>1$).

3.4 Redlich and Kwong Equation

Redlich and Kwong have improved the Van der Waals Equation to obtain more accurate compressibility factor, as follows [5]

$$p = \frac{RT}{v - b} - \frac{a_0}{v(v + b_0)}\left(\frac{T_c}{T}\right)^n \tag{7}$$

where a_0, b_0 and b are constants related to the critical parameters of the gas, as follows

$$a_0 = 0.42747\left(\frac{R^2T_c^2}{p_c}\right)$$

$$b_0 = 0.08664\left(\frac{RT_c}{p_c}\right)$$

$$b = b_0 - c_0, \quad c_0 = \frac{R T_c}{p_c + \dfrac{a_c}{v_c(v_c + b_c)}} + b_c - v_c$$

$a_0 = 6099.48$, $b_0 = 0.009$ and $c_0 = 3.5 \times 10^{-6}$ can be given by substituting the critical parameters of hydrogen into the above formula, so $c_0 \ll b_0$, thus, $b \approx b_0$. Substitute them into Eq. (7), and rewrite the equation in form of corresponding state, as

$$\frac{1}{Z\left(1 - 0.08664 \dfrac{p_r}{Z T_r}\right)} - \frac{0.42747 \, p_r}{Z^2 T_r^{(2+n)}\left(1 + 0.08664 \dfrac{p_r}{Z T_r}\right)} = 1 \tag{8}$$

where, n is a constant related to substances. For natural gases, higher computation accuracy can be obtained by taking n as 0.47 in Eq.(8) . For example, for #1, #4, #6 three groups of gas samples given in AGA8, the error between the calculated results and the measured values given in AGA8 is less than 1.2%[8][9]. In the case of high pressure hydrogen gas, the n value is taken by n=0.31 in the present paper. The computation results are shown in Fig. 5.
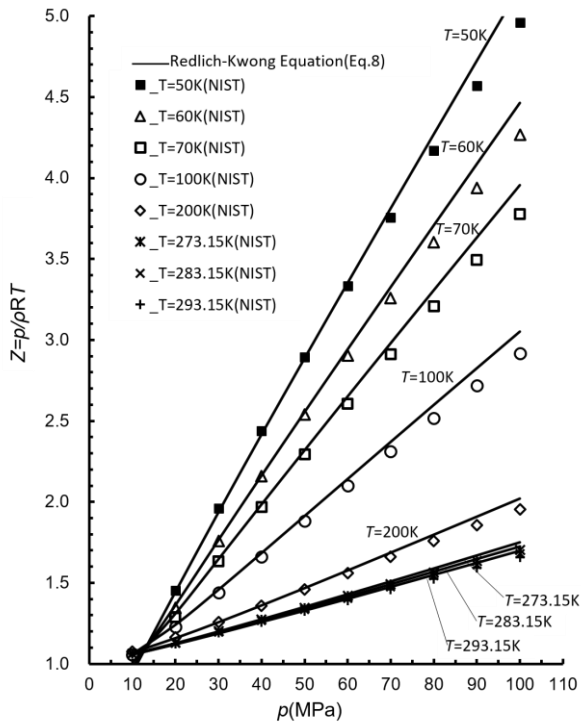

Figure 5: Redlich and Kwong curves (n=0.31) and the data of hydrogen in NIST.

The results show that the Redlich and Kwong curves of high-pressure hydrogen compressibility factor are consistent with the data in NIST, as

shown in Fig. 5. The computational results show that the maximum error between them is less than 5% in the range of temperatures within (50 ~ 293) K and pressure within (10 ~ 100) MPa, and the maximum error is less than 1% in the range of temperatures within (200 ~ 293) K and pressures within (10 ~ 600) MPa.

The hydrogen compressibility factor at normal temperature and pressure calculated by Redlich and Kwong Equation is also consistent with NIST data. For example, it is shown that the error is less than 0.4% when T = 298K and pressure p = (2 ~ 50) MPa, as shown in Fig. 6.
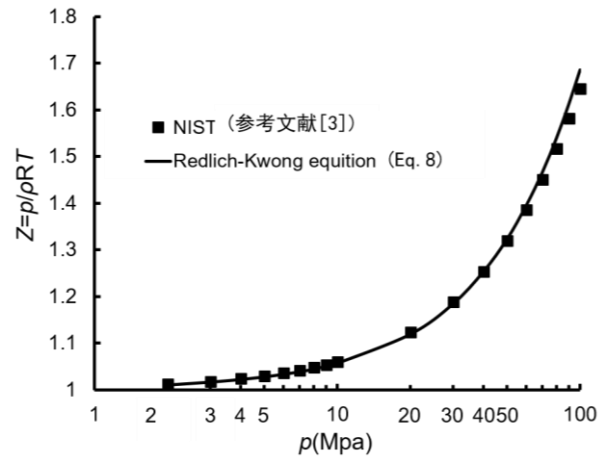

Figure 6: Hydrogen compressibility factor (T=298K) by Redlich and Kwong Equation.

4. NIST Data

NIST (the National Institute of Standards and Technology) has published the NIST Chemistry WebBook online [3]. The data of various chemical substances can be searched on the WebBook.

Convert the density of high-pressure hydrogen ρ searched on the WebBook into compressibility factor Z by Eq. (2).

If p/T is taken as the horizontal coordinate, Z-(p/T) can be fitted into a linear equation when $(p/T) \geqslant$ 1MPa/K, as shown in Fig.7. The fitted linear equation is

$$Z = 0.8576 + 2.0522\left(\frac{p}{T}\right) \tag{9}$$

where p is the hydrogen pressure (MPa) and T is the hydrogen temperature (K). The linear error of the Eq.(9) is less than 0.55%. However, the compressibility factor curve at each temperature diverges significantly when $(p/T) < $ 1MPa/K, as shown in Fig. 8.
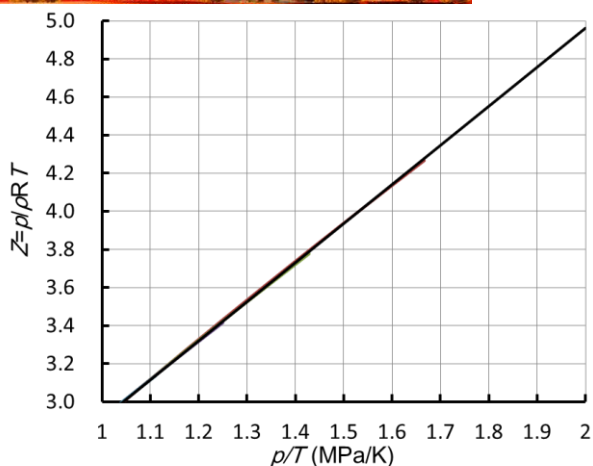
Figure 7: Linear regression curve of compressibility factor of high- pressure hydrogen from NIST data ($p / T > 1$).
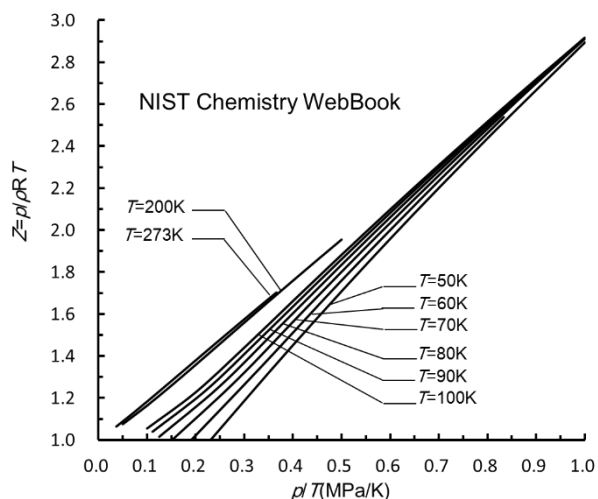

Figure 8: Hydrogen compressibility factor curve from NIST data ($p / T < 1$)[3].

5. Conclusions

The present paper discusses several models for calculating the compressibility factor of gases, especially high-pressure hydrogen.

(1) Higher computational accuracy can be obtained by using Virial Equation to calculate the compressibility factor of high-pressure hydrogen when the condition $T > 200K$. The computational results show that the maximum error is less than 0.9% when $T>200K$,p=10~70MPa.

(2) Van der Waals Equation and Redlich-Kwong's Equation are the equations of state of real gas derived from the corresponding law of state of thermodynamics. When $p_r<7$， T_r=1~2, using the Van der Waals Equation to calculate the compressibility factors of CH_4, C_mH_n, CO_2, N_2, natural gases and other real gases shows higher consistency [7].

(3) Redlich-Kwong's Equation of state can predict the real gas effects of high-pressure hydrogen gas comparatively well. The computational accuracy is less than 1% in a wide range of temperature and pressure.

(4) The density data of high-pressure hydrogen gas in NIST WebBook was converted to compressibility factor. Z-(p/T) can be fitted into a linear equation only when (p/T) $\geq$ 1MPa/K, as shown in Eq. (9), where linear error is less than 0.55%. However, when (p/T) < 1MPa/K, it cannot be fitted into any form of linear equation due to the large linear error.

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