



Determination of compressibility factor and fugacity coefficient of hydrogen in studies of adsorptive storage

Li Zhou^{a,*}, Yaping Zhou^b

^aHigh Pressure Adsorption Laboratory, Chemical Engineering Research Center, Tianjin University, Tianjin 300072, People's Republic of China

^bDepartment of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

Abstract

The compressibility factor (z) of hydrogen was evaluated from the experimental p – V – T data and calculated from equations of state, such as the SRK equation and BWR equation as well. The effect of z on the adsorbed amount calculated was demonstrated by the adsorption of hydrogen on 5A-zeolite. The compressibility factor and the fugacity coefficient of hydrogen were formulated based on the experimental p – V – T data for 60–333 K and up to 25 MPa. © 2001 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

The hydrogen fuel cell powered cars will play a major role in urban transportation soon [1]. The storage of hydrogen on board might be the final obstacle for the commercialization of PEMFC cars. Adsorptive storage of gaseous hydrogen has been an attractive technology apart from others [2]. The specially designed activated carbon and carbon nanofiber have been considered the most promising adsorbents, though there still are some conflicting arguments. Appropriate conclusion should be derived from reliable data. However, publications related to the adsorption capacity of adsorbents did not make clear how the factors affecting the adsorption capacity of adsorbents were accounted for. Among other factors, the compressibility factor of hydrogen must be accounted for up to 10 MPa pressures so long as the amount adsorbed was calculated from the p – V – T relation. On the other hand, pressure should be replaced by fugacity at high pressures, if theoretical relations that derived initially for ideal gas were introduced. Unfortunately, the data source for compressibility factor and the fugacity coefficient of hydrogen are not available. Both, the compressibility factor and the fugacity coefficient, can be calculated

from an appropriate equation of state. However, the calculated values should be compared with those evaluated from the experimental p – V – T data before being applied for the determination of adsorption.

The author selected two equations of state to evaluate the compressibility factor of hydrogen. One is the Soave–Redlich–Kwong (SRK) equation, which is a good trade-off between precision and tediousness of calculation and is widely applied in petrochemical processing computations. Another is Benedict–Webb–Rubin (BWR) equation, which contains eight parameters and is recommended especially for hydrogen [3]. The experimental p – V – T data of hydrogen came from Vargaftik [4]. The authors searched the *Journal of Physical and Chemical Reference Data* from the beginning till the latest issue, but no updated data for hydrogen were found. It is hoped that the information presented will help people who are interested in adsorptive storage of hydrogen to facilitate their computation job, especially, those to whom chemistry is not a specific field.

2. Evaluation of compressibility factor from the SRK equation

SRK equation is a three-parameter equation of state. Better results are usually expected than two-parameter equations and are used satisfactorily in the domain of

* Corresponding author. Tel.: +86-22-2740-6163; fax: +86-22-2740-4757.

E-mail address: zhouli@public.tpt.tj.cn (L. Zhou).

petrochemical process engineering. The SRK equation relates the compressibility factor and the fugacity coefficient as follows:

$$\ln \frac{f}{P} = z - 1 - \ln(z - B^*) - \frac{A^*}{B^*} \ln \left(1 + \frac{B^*}{z} \right), \quad (1)$$

where $\phi = f/p$ is the fugacity coefficient, and z is the compressibility factor. A^* and B^* can be determined from three parameters of the gas: critical pressure P_c ; critical temperature T_c and the eccentric factor ω :

$$A^* = 0.4278 \cdot \alpha \cdot \frac{P/P_c}{(T/T_c)^2}, \quad (1a)$$

$$B^* = 0.0867 \cdot \frac{P/P_c}{T/T_c}, \quad (1b)$$

$$\alpha^{0.5} = 1 + m(1 - T_r^{0.5}), \quad (1c)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2. \quad (1d)$$

Since $\omega = -0.216$ for hydrogen [3], it yields

$$m = 0.131805.$$

The critical parameters of hydrogen are

$$T_c = 33.2 \text{ K}; \quad P_c = 1.28 \text{ MPa}.$$

For example, $T = 298.15 \text{ K}$; $T_r = 298.15/33.2 = 8.9804$. By the substitution of m and T_c in Eq. (1c), one obtains

$$\alpha = \left[1 + 0.131805 \left(1 - \left(\frac{298.15}{33.2} \right)^{0.5} \right) \right]^2 = 0.5429.$$

The values of A^* and B^* can thus be determined from Eqs. (1a) and (1b). Compressibility factor z is obtained by solving the following equation:

$$z^3 - z^2 + z(A^* - B^* - B^{*2}) - A^*B^* = 0. \quad (1e)$$

Eq. (1e) was solved by an iteration method. The convergence criterion was set equal to 1×10^{-11} . The values of z and A^* , B^* were substituted in Eq. (1), from which the fugacity coefficient ϕ was determined.

It is not difficult to find the three parameters of a gas needed by the SRK equation. Besides, no special constraints were appended. Therefore, the SRK equation is quite convenient for users.

3. Evaluation of compressibility factor from the BWR equation

The BWR equation contains eight parameters, therefore is more precise than three-parameter equations especially at above-critical temperatures and not very high pressures. It reads [5]

$$p = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2} \right) \rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^2}{T^2} [(1 + \gamma\rho^2)\exp(-\gamma\rho^2)], \quad (2)$$

where ρ is the density of gas, which relates to the compressibility factor by

$$z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \right) \rho + \left(b - \frac{a}{RT} \right) \rho^2 + \frac{a\alpha}{RT} \rho^5 + \frac{c\rho^2}{RT^3} [(1 + \gamma\rho^2)\exp(-\gamma\rho^2)]. \quad (2a)$$

It is a dimensional equation, where p is in atm, T in K, ρ in mol/l or kmol/m³, $R = 0.08205 \text{ atm l/mol K}$ or $\text{atm m}^3/\text{kmol K}$. The eight parameters of hydrogen take the values that follow for the condition of 0–150°C and $\rho_r < 2.5$:

$$a = -9.2211 \times 10^{-3} \text{ (l/mol)}^3 \text{ atm},$$

$$A_0 = 9.7319 \times 10^{-2} \text{ (l/mol)}^2 \text{ atm},$$

$$b = 1.7976 \times 10^{-4} \text{ (l/mol)}^2,$$

$$B_0 = 1.8041 \times 10^{-2} \text{ l/mol},$$

$$c = -2.4613 \times 10^2 \text{ (l/mol)}^3 \text{ K}^2 \text{ atm},$$

$$C_0 = 3.8914 \times 10^2 \text{ (l/mol)}^2 \text{ K atm},$$

$$\alpha = -3.4215 \times 10^{-6} \text{ (l/mol)}^3,$$

$$\gamma = 1.89 \times 10^{-3} \text{ (l/mol)}^2.$$

By substituting the eight parameters and the value of R in Eq. (2) one obtains

$$p = 0.08205T\rho + \left(1.4803 \times 10^{-3}T - 9.7319 \times 10^{-2} - \frac{389.14}{T^2} \right) \rho^2 + (1.4749 \times 10^{-5}T + 9.2211 \times 10^{-3})\rho^3 + 3.155 \times 10^{-8}\rho^6 - \frac{246.13\rho^3}{T^2} \times [(1 + 0.00189\rho^2)\exp(-0.00189\rho^2)]. \quad (2b)$$

Eq. (2b) can be solved easily by the secant method. A convergence function was formulated based on Eq. (2b):

$$f(\rho) = 0.08205T\rho + \left(1.4803 \times 10^{-3}T - 9.7319 \times 10^{-2} - \frac{389.14}{T^2} \right) \rho^2 + (1.4749 \times 10^{-5}T + 9.2211 \times 10^{-3})\rho^3 + 3.155 \times 10^{-8}\rho^6 - \frac{246.13\rho^3}{T^2} \times [(1 + 0.00189\rho^2)\exp(-0.00189\rho^2)] - p. \quad (2c)$$

The iteration formula is

$$\rho_{k+1} = \frac{\rho_{k-1}f(\rho_k) - \rho_k f(\rho_{k-1})}{f(\rho_k) - f(\rho_{k-1})}. \quad (2d)$$

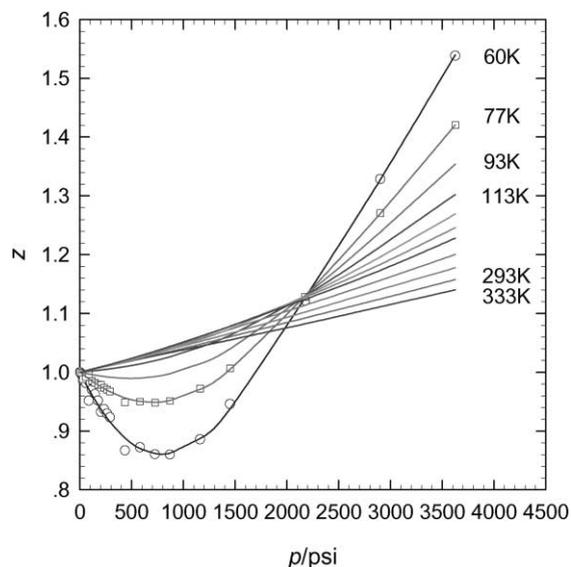


Fig. 1. Compressibility factor of hydrogen.

Two initial values of ρ are needed in iteration. One is set to zero, another is set to the density of ideal gas: p/RT . The compressibility factor z can be calculated from the value of ρ known via Eq. (2a).

4. Evaluation of compressibility factor from the experimental p - V - T data

Any comment on an equation of state must be relied on experimental p - V - T data of real gases. Such tabulated data

of hydrogen came from Ref. [2]. The pressure and temperature increments in the table are not even. To get the data for the conditions of interest, one has to establish the functional relations between molar volume V_m and T for a specified p first, and between V_m and p for a specified T afterwards. The compressibility factor z was calculated from Eq. (3) for the data given in the table

$$z = \frac{pV_m}{14.696 \times 82.056 \times T} \quad (3)$$

The z -values were calculated for selected temperatures from 60 to 333 K up to 25 MPa, which is wide enough to cover the condition of adsorptive storage of hydrogen. The calculated z -values were correlated with pressure by a polynomial function. As a consequence, the effect of experimental errors in the measurement of V_m was alleviated, as shown in Fig. 1 at 60 and 77 K. The coefficients of the correlation are provided in Table 1.

5. Comments on the SRK and BWR equation

Comparison was made between the z -values calculated from the equations of state and those evaluated from the experimental p - V - T data of hydrogen. The root mean square of the deviations between the two kinds of z -values are shown in Fig. 2. The BWR equation seems to be more precise than SRK equation. However, the parameter values available are limited to 273 K and higher. Therefore, the z -value at 253 K is not legally calculated and, no more z -values at lower temperatures was provided. The SRK equation is not bad since only 1% deviation is observed at temperature as low as 113 K.

The effect of precision of z -values on the determination of the amount adsorbed was examined in the adsorption of

Table 1
Coefficients in the z - p correlation

T (K)	C_0	C_1	C_2	C_3	C_4	C_5
60	1	-3.56359×10^{-4}	2.17874×10^{-7}	3.48354×10^{-11}	-3.10679×10^{-14}	4.27166×10^{-18}
77	1	-1.37792×10^{-4}	7.02630×10^{-8}	4.58762×10^{-11}	-2.28420×10^{-14}	2.80464×10^{-18}
93.15	1	-3.84988×10^{-5}	2.18529×10^{-8}	3.18068×10^{-11}	-1.27753×10^{-14}	1.43316×10^{-18}
113.15	1	1.55535×10^{-5}	9.97491×10^{-9}	1.03778×10^{-11}	-3.13014×10^{-15}	2.57149×10^{-19}
133.15	1	3.65001×10^{-5}	7.25818×10^{-9}	2.53471×10^{-12}	-4.59451×10^{-16}	
153.15	1	4.22492×10^{-5}	9.07270×10^{-9}	-9.32954×10^{-13}	1.03267×10^{-16}	
173.15	1	4.22929×10^{-5}	1.17902×10^{-8}	-3.23481×10^{-12}	4.27207×10^{-16}	
193.15	1	4.22528×10^{-5}	1.07812×10^{-8}	-3.15062×10^{-12}	3.96269×10^{-16}	
213.15	1	4.32526×10^{-5}	6.73138×10^{-9}	-1.50426×10^{-12}	1.54717×10^{-16}	
233.15	1	4.48189×10^{-5}	1.41949×10^{-9}	7.13390×10^{-13}	-1.53686×10^{-16}	
253.15	1	4.53115×10^{-5}	-2.21317×10^{-9}	2.12955×10^{-12}	-3.41678×10^{-16}	
273.15	1	4.29422×10^{-5}	-1.38070×10^{-9}	1.52607×10^{-12}	-2.48483×10^{-16}	
293.15	1	3.66664×10^{-5}	5.34991×10^{-9}	-1.66244×10^{-12}	1.94641×10^{-16}	
298.15	1	3.44635×10^{-5}	7.97590×10^{-9}	-2.86657×10^{-12}	3.59834×10^{-16}	
313.15	1	4.20779×10^{-5}	-4.61076×10^{-9}	2.36176×10^{-12}	-3.24542×10^{-16}	
333.15	1	4.08451×10^{-5}	-4.33640×10^{-9}	1.87267×10^{-12}	-2.32438×10^{-16}	

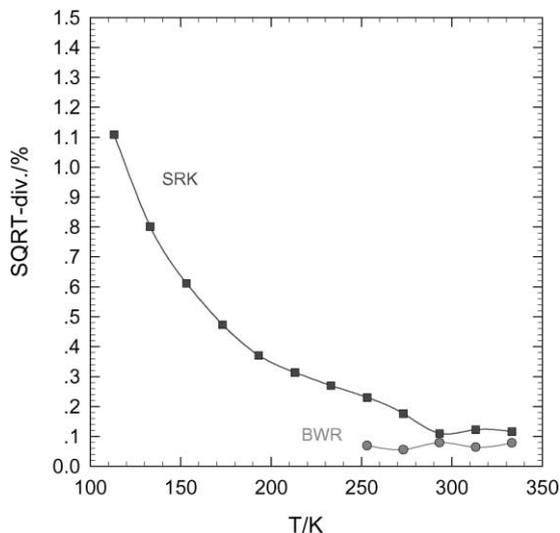


Fig. 2. The square root mean deviations of z -values from the equations of state to that from the experimental data.

hydrogen on 5A-zeolite. It can hardly notice the difference between the isotherms of Fig. 3. However, the root mean square of the deviations between the isotherms yielded, from different sources of z are shown clearly in Fig. 4. Although the BWR equation yielded more precise z -values than the SRK equation, it did not yield more “correct” adsorption isotherms than the other. Because z -values were used three times in the calculation of the amount adsorbed for a volumetric measurement, the effect of uncertainty in z -values was considerably amplified in the determination of adsorption. Therefore, the best way to evaluate z -values is based on the experimental p - V - T data of hydrogen. Because of such consideration, only the fugacity coefficient evaluated from the experimental p - V - T data is proposed in the subsequent section.

6. The fugacity coefficient of hydrogen

Fugacity should replace pressure for real gases in the application of laws or theoretical formulations that are defined for ideal gases. For example, fugacity has to be used in evaluating adsorption potential at high pressures and/or low temperatures. The fugacity of a pure gas is a physical quantity that complies with the following relation:

$$\mu(g, T, p) = \mu^0(g, T) + RT \ln \left(\frac{f}{p^0} \right), \quad (4)$$

where g denotes gas, f is the fugacity, and the superscript “0” denotes a standard pressure (10^5 Pa). However, the fugacity coefficient defined as $\phi \equiv f/p$, which is independent

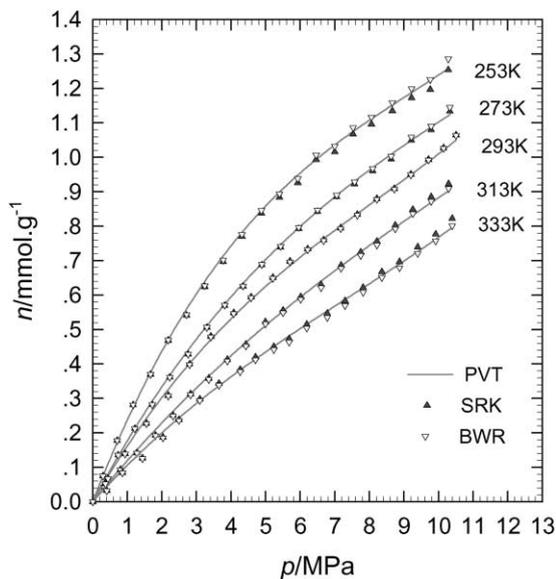


Fig. 3. Adsorption isotherms of hydrogen on 5A-zeolite evaluated from different sources of z -values.

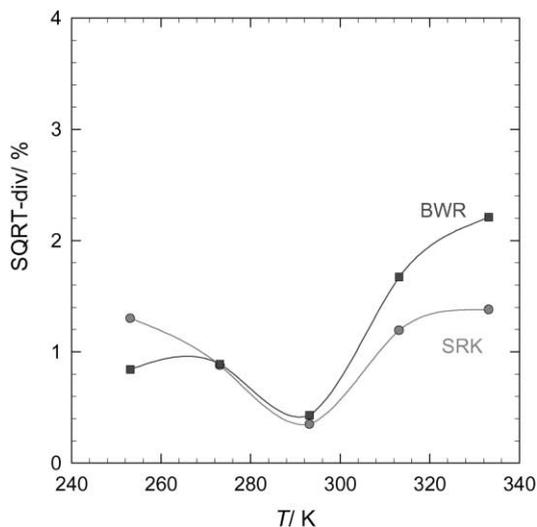


Fig. 4. Deviations of adsorption caused by z -values.

of the standard pressure is of more use. It was derived from the definition of fugacity that

$$\ln \phi = \frac{1}{RT} \int_0^p \left(V_m - \frac{RT}{p} \right) dp, \quad (5)$$

because

$$z = \frac{pV_m}{RT},$$

$$\ln \phi = \int_0^p \left(\frac{pV_m}{pRT} - \frac{1}{p} \right) dp = \int_0^p \frac{(z-1)}{p} dp. \quad (6)$$

Table 2
Coefficients in the ϕ - p correlation

$T(K)$	C_0	C_1	C_2	C_3	C_4	C_5
60	1	-3.54561×10^{-4}	1.66337×10^{-7}	-2.99498×10^{-11}	2.42574×10^{-15}	
77	1	-1.38130×10^{-4}	4.67096×10^{-8}	5.93690×10^{-12}	-3.24527×10^{-15}	3.54211×10^{-19}
93.15	1	-3.86094×10^{-5}	1.23153×10^{-8}	9.00347×10^{-12}	-2.63262×10^{-15}	2.40671×10^{-19}
113.15	1	1.32755×10^{-5}	1.01021×10^{-8}	4.43987×10^{-13}		
133.15	1	3.59307×10^{-5}	5.40741×10^{-9}	4.34407×10^{-13}		
153.15	1	4.24489×10^{-5}	5.03665×10^{-9}	8.93238×10^{-14}		
173.15	1	4.29174×10^{-5}	5.56911×10^{-9}	-2.11366×10^{-13}		
193.15	1	4.47329×10^{-5}	3.91672×10^{-9}	-4.92797×10^{-14}		
213.15	1	4.34505×10^{-5}	3.91417×10^{-9}	-1.50817×10^{-13}		
233.15	1	4.45773×10^{-5}	2.18237×10^{-9}	5.85180×10^{-14}		
253.15	1	4.48069×10^{-5}	8.98684×10^{-10}	2.03650×10^{-13}		
273.15	1	4.25722×10^{-5}	9.50702×10^{-10}	1.44169×10^{-13}		
293.15	1	3.69294×10^{-5}	2.83279×10^{-9}	-1.93482×10^{-13}		
298.15	1	3.49641×10^{-5}	3.60045×10^{-9}	-3.22724×10^{-13}		
313.15	1	4.16186×10^{-5}	-5.28484×10^{-10}	2.73571×10^{-13}		
333.15	1	4.05294×10^{-5}	-7.21562×10^{-10}	2.52962×10^{-13}		

Since

$$z = 1 + \sum_{i=1} c_i p^i \quad (7)$$

as shown in Table 1, the integration is a polynomial function of pressure:

$$\ln \phi = \sum_{i=1} c_i p^i / i. \quad (8)$$

The coefficients of the ϕ - p function for selected temperatures are listed in Table 2. The p - f transformation can be easily completed by

$$f = \phi \cdot p. \quad (9)$$

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