

Effect of Equation of States on High Pressure Volumetric Measurements of Methane-Coal Sorption Isotherms - Part 1: Volumes of Free Space and Methane Adsorption Isotherms

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This supporting information for our manuscript titled “*Effect of Equation of States on High Pressure Volumetric Measurements of Methane-Coal Sorption Isotherms - Part 1: Volumes of Free Space and Methane Adsorption Isotherms*” contains the appendices mentioned in the manuscript. It contains (a) appendix A – description of the comparison equations of state (b) appendix B - description of the adsorption steps and (c) appendix C – volume of free space calculated by different equations of state

Appendix A – Description of the Comparison Equations of State

A1. Cubic Equations of State

In terms of molar volume, Van der Waal type cubic equations of state assume the following general mathematical form:

$$P = \frac{RT}{(v_m + \beta)} - \frac{a(T)}{(v_m + \delta)(v_m + \gamma)} \quad A1$$

Where the parameters P , R and T are the pressure, gas constant and temperature respectively; δ and γ are EOS-specific parameters while parameters $a(T)$ and β are similarly defined for all Van der Waal type equations of state as:

$$a(T) = a = \frac{\Omega_a \alpha(T) R^2 T_c^2}{P_c} \quad A2$$

$$\beta = -b \quad A3$$

The parameter b is given as:

$$b = \frac{\Omega_b R T_c}{P_c} \quad A4$$

Where Ω_a , Ω_b EOS-specific constants and T_c , P_c are the critical temperature and critical pressure of the gas respectively. The temperature dependent parameter $\alpha(T)$ is also EOS-specific and is given as:

$$\alpha(T) = \left(1 + m \left(1 - T_r^{\frac{1}{2}}\right)\right)^2 \quad A5$$

Where:

$T_r = \frac{T}{T_c}$ is the reduce temperature and m is EOS-specific.

In terms of the molar volume, the *equation A1* can be expanded to yield

$$v_m^3 + v_m^2 \left(\beta + \delta + \gamma - \frac{RT}{P} \right) + v_m \left(\beta\delta + \beta\gamma + \delta\gamma - \frac{RT}{P}\delta - \frac{RT}{P}\gamma + \frac{a}{P} \right) + \left(\frac{a}{P}\beta - \frac{RT}{P}\delta\gamma + \beta\delta\gamma \right) = 0 \quad A6$$

The molar volume of the gas can be obtained as the lowest root of *equation A6* for a given EOS.

Alternatively, *equation A6* can be expressed in terms of the gas compressibility factor, Z as:

$$Z^3 + Z^2 \left(\frac{P}{RT}(\beta + \delta + \gamma) - 1 \right) + Z \left(\frac{P^2}{R^2T^2}(\beta\delta + \beta\gamma + \delta\gamma) - \frac{P}{RT}\delta - \frac{P}{RT}\gamma + \frac{P}{R^2T^2}a \right) + \left(\frac{P^2}{R^3T^3}a\beta - \frac{P^2}{R^2T^2}\delta\gamma + \frac{P^3}{R^3T^3}\beta\delta\gamma \right) = 0 \quad A7$$

The largest root of *equation A7*, solved iteratively, is the z -factor of the gas for the given EOS parameters a, β, δ and γ .

Also, for use in subsequent subsections, two additional parameters A & B are generally defined as

$$A = \frac{aP}{R^2T^2} \quad A8$$

$$B = \frac{bP}{RT} \quad A9$$

A1.1 Soave-Redlich-Kwong (SRK) Equation of State

The SRK-EOS is given as:

$$P = \frac{RT}{(v_m - b)} - \frac{a(T)}{v_m(v_m + b)} \quad A10$$

Compared to *equation A1*, it can be seen that $\beta = -b$; $\delta = 0$ and $\gamma = b$. The SRK-EOS is also characterized by $\Omega_a = 0.42747$; $\Omega_b = 0.08664$ and the parameter m is given as:

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad A11$$

ω is the acentric factor of the fluid/gas being studied.

Substituting for the parameters β , δ and γ in *equation A7* and simplifying with *equations A8 & A9*, the SRK-EOS can be written in terms of gas compressibility as:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad A12$$

A1.2 Peng-Robinson (PR) Equation of State

The PR-EOS is given as:

$$P = \frac{RT}{(v_m - b)} - \frac{a(T)}{(v_m^2 + 2bv_m - b^2)} = \frac{RT}{(v_m - b)} - \frac{a(T)}{[(v_m + (1 - \sqrt{2})b)][(v_m + (1 + \sqrt{2})b)]} \quad A13$$

Compared to *equation A1*, it can be seen that $\beta = -b$; $\delta = (1 - \sqrt{2})b$ and $\gamma = (1 + \sqrt{2})b$. The PR-EOS is also characterized by $\Omega_a = 0.457535$; $\Omega_b = 0.077796$ and m is given as:

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad A14$$

Substituting for the parameters β , δ and γ in *equation A7* and simplifying with *equations A8 & A9*, the PR-EOS can be written in terms of gas compressibility as:

$$Z^3 + (B - 1)Z^2 + Z(A - 2B - 3B^2) + (B^3 + B^2 - AB) = 0 \quad A15$$

A1.3 SRK-Peneloux Equation of State

The SRK-Peneloux EOS is given as:

$$P = \frac{RT}{(v_m - b)} - \frac{a(T)}{(v_m + c)(v_m + b + 2c)} \quad A16$$

Compared to *equation A1*, it can be seen that $\beta = -b$; $\delta = c$ and $\gamma = b + 2c$. Parameter c is the volume shift factor introduced by Peneloux et al, to modify the SRK-EOS and given as:

$$c = 0.40768 \frac{RT_c}{P_c} (0.29441 - Z_{RA}) \quad A17$$

Where Z_{RA} is known as the Rackett compressibility factor [1] given as:

$$Z_{RA} = 0.29056 - 0.08775\omega \quad A18$$

Introducing a parameter C defined as:

$$C = \frac{cP}{RT} \quad A19$$

Substituting for the parameters β , δ and γ in *equation A7* and simplifying with the definitions of A, B & C, the SRK-Peneloux EOS can be written in terms of gas compressibility as:

$$Z^3 + (3C - 1)Z^2 + [A - B - B^2 - 2BC - 3C + 2C^2]Z - (AB + BC + B^2C + 2BC^2 + 2C^2) = 0 \quad A20$$

A1.4 PR-Peneloux Equation of State

The PR-Peneloux EOS is given as:

$$P = \frac{RT}{(v_m - b)} - \frac{a(T)}{\{v_m + [b(1 - \sqrt{2}) + c(2 - \sqrt{2})]\}\{v_m + [b(1 + \sqrt{2}) + c(2 + \sqrt{2})]\}} \quad A21$$

Comparing *equation A21* to *equation A1*, it can be seen that $\beta = -b$; $\delta = b(1 - \sqrt{2}) + c(2 - \sqrt{2})$ and $\gamma = b(1 + \sqrt{2}) + c(2 + \sqrt{2})$. The volume shift factor, c is defined in *equation A17* above. With these and the definition of C given in *equation A19*, the PR-Peneloux EOS can be written in terms of Z-factor as:

$$Z^3 + (B + 4C - 1)Z^2 + [A - 2B - 3B^2 - 4BC - 2C + 2C^2]Z - (AB - B^2 - B^3 + 2BC^2 + 2C^2) = 0 \quad A22$$

A2. Non-Cubic Equations of State

Two virial-type equations of state have been selected for comparison with the cubic equations presented in [section A1](#).

A2.1 LK-EOS

Lee and Kesler [2] presented a modification of Benedict-Webb-Rubin (BWR) EOS following the principle of corresponding states [2, 3]. In terms of the reduced parameters (P_r , T_r & v_r), the LK-EOS is given as:

$$1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{c_4}{T_r v_r^2} \left(\beta + \frac{\gamma}{v_r^2} \right) \exp\left(-\frac{\gamma}{v_r^2}\right) - \frac{P_r v_r}{T_r} = 0 \quad A23$$

The values of the variables B, C & D are given by the following auxiliary equations:

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}; \quad C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}; \quad D = d_1 + \frac{d_2}{T_r}$$

The compressibility, Z of any fluid of known acentric factor (ω) is given in terms of the compressibility Z^0 of a simple fluid ($\omega = 0$) and the compressibility Z^{ref} of a reference fluid ($\omega = \omega^{ref}$) as follows:

$$Z = Z^0 + \frac{\omega}{\omega^r} (Z^{ref} - Z^0) \quad A24$$

Where:

$$Z^0 = \frac{P_r v_r^0}{T_r} \quad A25a$$

$$Z^{ref} = \frac{P_r v_r^{ref}}{T_r} \quad A25b$$

v_r^0 & v_r^{ref} are respective the reduced specific molar volumes of the simple fluid (rare gas) and reference fluid (n-octane) determined by solving the *equation A23* for v_r using the corresponding values of the coefficients $b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, \beta$ and γ from *table A1* below.

Table A1: Numerical Values of the coefficients of the LK-EOS [2]

Coefficient	Simple fluid	Reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.15479	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0	0.016901
c_4	0.042724	0.041577
d_1	1.55488×10^{-5}	4.87360×10^{-5}
d_2	6.23689×10^{-5}	74.0336×10^{-5}
β	0.65392	1.226
γ	0.060167	0.03754

A2.2 SBWR-EOS

Soave [4]'s modification represented an attempt to reduce the number of terms while improving the accuracy of the BWR-EOS. The SBWR-EOS is given in terms of the 3 parameters (P_r, T_r & v_r) as:

$$1 + \frac{B}{v_r} + \frac{D}{v_r^4} + \frac{E}{v_r^2} \left(1 + \frac{F}{v_r^2} \right) \exp \left(-\frac{F}{v_r^2} \right) - \frac{P_r v_r}{T_r} = 0 \quad A26$$

The variables B, D, E and F are defined as given in the following auxiliary equations:

$$B = \frac{RT_c}{P_c} \left[bZ_c + 0.422 \left(1 - \frac{1}{T_r^{1.6}} \right) + 0.234\omega \left(1 - \frac{1}{T_r^3} \right) \right] \quad A27a$$

$$D = d \left(\frac{RT_c Z_c}{P_c} \right)^4 \left[1 + d_1 \left(\frac{1}{T_r} - 1 \right) + d_2 \left(\frac{1}{T_r} - 1 \right)^2 \right] \quad A27b$$

$$E = \left(\frac{RT_c}{P_c} \right)^2 \left[eZ_c^2 + e_1 \left(\frac{1}{T_r} - 1 \right) + e_2 \left(\frac{1}{T_r} - 1 \right)^2 + e_3 \left(\frac{1}{T_r} - 1 \right)^3 \right] \quad A27c$$

$$F = f \left(\frac{RT_c Z_c}{P_c} \right)^2 \quad A27d$$

P_c , T_c and Z_c are respectively the critical pressure, critical temperature and critical z-factor of a given fluid whose acentric factor is ω . The critical z-factor can be calculated from the Rackett equation [4] given as:

$$Z_c = 0.2908 - 0.099\omega + 0.04\omega^2 \quad A28a$$

The coefficients in *equations 2.27a-d* can be obtained as follows:

$$b = Z_c - 1 - d - e(1 + f) \exp(-f) \quad A28b$$

$$d = \frac{1 - 2Z_c - e(1 + f - 2f^2) \exp(-f)}{3} \quad A28c$$

$$e = \frac{2 - 5Z_c}{(1 + f + 3f^2 - 2f^3) \exp(-f)} \quad A28d$$

$$f = 0.77 \quad A28e$$

$$d_1 = 0.4912 + 0.6478\omega \quad A28f$$

$$d_2 = 0.3000 + 0.3619\omega \quad A28g$$

$$e_1 = 0.0841 + 0.1318\omega + 0.0018\omega^2 \quad A28h$$

$$e_2 = 0.0750 + 0.2408\omega - 0.0140\omega^2 \quad A28i$$

$$e_3 = -0.0065 + 0.1798\omega - 0.0078\omega^2 \quad A28j$$

The compressibility of any fluid of known acentric factor can then be calculated from *equation A29* below once the reduced specific molar volume is obtained from *equation A26* above.

$$Z = \frac{P_r v_r}{T_r} \quad A29$$

Appendix B – Description of the Adsorption Steps

B1. Adsorption Steps

Consider two consecutive adsorption steps $i - 1$ & i as illustrated in *figure B1* below. Each adsorption step involves 3 processes discussed as follows:

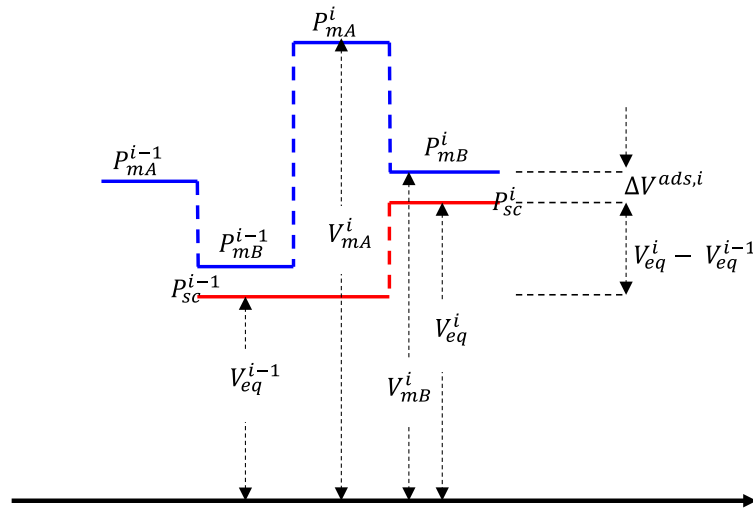


Figure B1: Schematic of 2 consecutive adsorption pressure steps

- Filling the manifold with the adsorbate:* The amount of gas that enters into the manifold at pressure, P_{mA}^i and temperature, T_{mA}^i (where $i = 1, 2, 3, \dots, n$) is given as:

$$N_{mA}^i = \frac{P_{mA}^i}{T_{mA}^i Z_{mA}^i} \times \frac{V_{man}}{R} \quad B1$$

The equivalent volume at STP is given as:

$$V_{mA}^i \approx \frac{P_{mA}^i V_{man}}{T_{mA}^i Z_{mA}^i} \times \frac{V_{STP}}{R} \quad B2$$

Where V_{man} is the volume of the manifold, R = gas constant, Z is the gas compressibility factor and V_{STP} is the molar gas volume at STP (≈ 22400 cc).

- b. *Expanding gas from the manifold to the sample cell:* The final pressure and temperature in the manifold are P_{mB}^i and T_{mB}^i respectively. Hence, the amount of gas expanded/dosed into the sample cell and the equivalent volume at STP can be calculated as:

$$N_{dosed}^{ads,i} = \Delta \left(\frac{P}{ZT} \right)_{man}^i \times \frac{V_{man}}{R} \quad B3$$

$$V_{dosed}^i \approx \left(\frac{P_{mA}^i V_{man}}{T_{mA}^i Z_{mA}^i} - \frac{P_{mB}^i V_{man}}{T_{mB}^i Z_{mB}^i} \right) \times \frac{V_{STP}}{R} \quad B4$$

- c. *Equilibrating the gas in the system:* The volume, at STP, of gas in equilibrium is given as:

$$V_{free}^i = (V_{eq}^i - V_{eq}^{i-1}) \quad B5$$

The free space available to gas is composed of three parts, the lower stem of volume, V_{ls} , the upper stem of volume, $V_{us} = 7$ cc [5] and the sample cell of volume, V_{sc} . Therefore:

$$V_{free}^i = \frac{V_{STP}}{R} \left[\left(\frac{P_{sc}^i V_{sc}}{T_{sc}^i Z_{sc}^i} + \frac{P_{us}^i V_{us}}{T_{us}^i Z_{us}^i} + \frac{P_{ls}^i V_{ls}}{T_{ls}^i Z_{ls}^i} \right) - \left(\frac{P_{sc}^{i-1} V_{sc}}{T_{sc}^{i-1} Z_{sc}^{i-1}} + \frac{P_{us}^{i-1} V_{us}}{T_{us}^{i-1} Z_{us}^{i-1}} + \frac{P_{ls}^{i-1} V_{ls}}{T_{ls}^{i-1} Z_{ls}^{i-1}} \right) \right] \quad B6$$

Writing a volume balance for the system,

$$V_{dosed}^i = V_{free}^i + \Delta V^i \quad B7$$

Putting *equations B4 and B6 in B7*, the differential adsorbed volume per unit mass of the adsorbent can be obtained as follows:

$$\begin{aligned}
\Delta \tilde{V}^i &= \frac{V_{STP}}{RM_s} \\
&\left[\left(\frac{P_{mA}^i V_{man}}{T_{mA}^i Z_{mA}^i} - \frac{P_{mB}^i V_{man}}{T_{mB}^i Z_{mB}^i} \right) - \left(\frac{P_{sc}^i V_{sc}}{T_{sc}^i Z_{sc}^i} + \frac{P_{us}^i V_{us}}{T_{us}^i Z_{us}^i} + \frac{P_{ls}^i V_{ls}}{T_{ls}^i Z_{ls}^i} \right) + \left(\frac{P_{sc}^{i-1} V_{sc}}{T_{sc}^{i-1} Z_{sc}^{i-1}} + \frac{P_{us}^{i-1} V_{us}}{T_{us}^{i-1} Z_{us}^{i-1}} + \frac{P_{ls}^{i-1} V_{ls}}{T_{ls}^{i-1} Z_{ls}^{i-1}} \right) \right]
\end{aligned}$$

B8

The cumulative volume adsorbed per unit mass at any pressure step is given as:

$$\tilde{V}_r^{ads} = \sum_{i=1}^r (\Delta \tilde{V}^i) \quad B9$$

For the first adsorption step, it can be safely assumed that $P_{sc}^0 = 0$ since the system is expected to be in fully evacuated prior to this step.

B2. Ambient Free space Volume Calculation

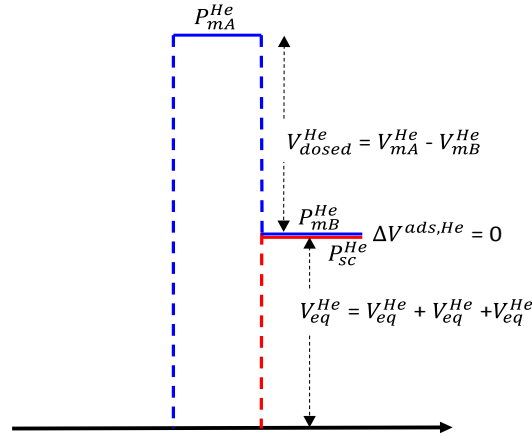


Figure B2: Schematic of helium expansion step measurement of free-space volume

As shown in *figure B2*, free space measurement follows the adsorption processes described in [section B1](#) above except that helium gas is used in this case. It is arguably assumed that helium adsorption is negligible ($\Delta V^{ads, He} \approx 0$) [5, 6]. Therefore:

$$V_{dosed}^{He} = V_{eq}^{He} \quad B10$$

$$\frac{P_{mA}^{He} V_{man}}{T_{mA}^{He} Z_{mA}^{He}} - \frac{P_{mB}^{He} V_{man}}{T_{mB}^{He} Z_{mB}^{He}} = \frac{P_{sc}^{He} V_{sc}}{T_{sc}^{He} Z_{sc}^{He}} + \frac{P_{us}^{He} V_{us}}{T_{us}^{He} Z_{us}^{He}} + \frac{P_{ls}^{He} V_{ls}}{T_{ls}^{He} Z_{ls}^{He}} \quad B11$$

The HPVA-II 200® uses 2 temperature-point steps to determine the volume of free-space and the corresponding values V_{ls} , the volume of the lower stem of the sample holder and V_{sc} , the volume of the sample cell. Note that the volume of the upper stem $V_{ls} \approx 7cc$ [5]. For the first step, it is assumed that $T_{sc}^{He} = T_{ls}^{He} = \text{Ambient temperature}$. In this case *equation 3.3* can be written as [6]:

$$V_{Amfs} = V_{sc} + V_{ls} + V_{us} = V_{lsc} + V_{us} \quad B12a$$

Which means:

$$V_{lsc} = V_{sc} + V_{ls} = V_{Amfs} - V_{us} \quad B12b$$

Equation A11 can now be written as:

$$V_{Amfs} = \frac{T_{sc}^{He} Z_{sc}^{He}}{P_{sc}^{He}} \left(\frac{P_{mA}^{He} V_{man}}{T_{mA}^{He} Z_{mA}^{He}} - \frac{P_{mB}^{He} V_{man}}{T_{mB}^{He} Z_{mB}^{He}} - \frac{P_{sc}^{He} V_{us}}{T_{us}^{He} Z_{us}^{He}} + \frac{P_{sc}^{He} V_{us}}{T_{sc}^{He} Z_{sc}^{He}} \right) \quad B13$$

The second step proceeds at the experimental temperature such that $T_{sc}^{He} \neq T_{ls}^{He}$. In this case, *equations B11* & *B12a* are solved for the values of V_{sc} and V_{ls} using the value of V_{Amfs} determined from the previous step [6].

Appendix C – Volume of Free Space for the Different EOS tested

C1. Ambient Volumes of Free Space Calculated by Different EOS

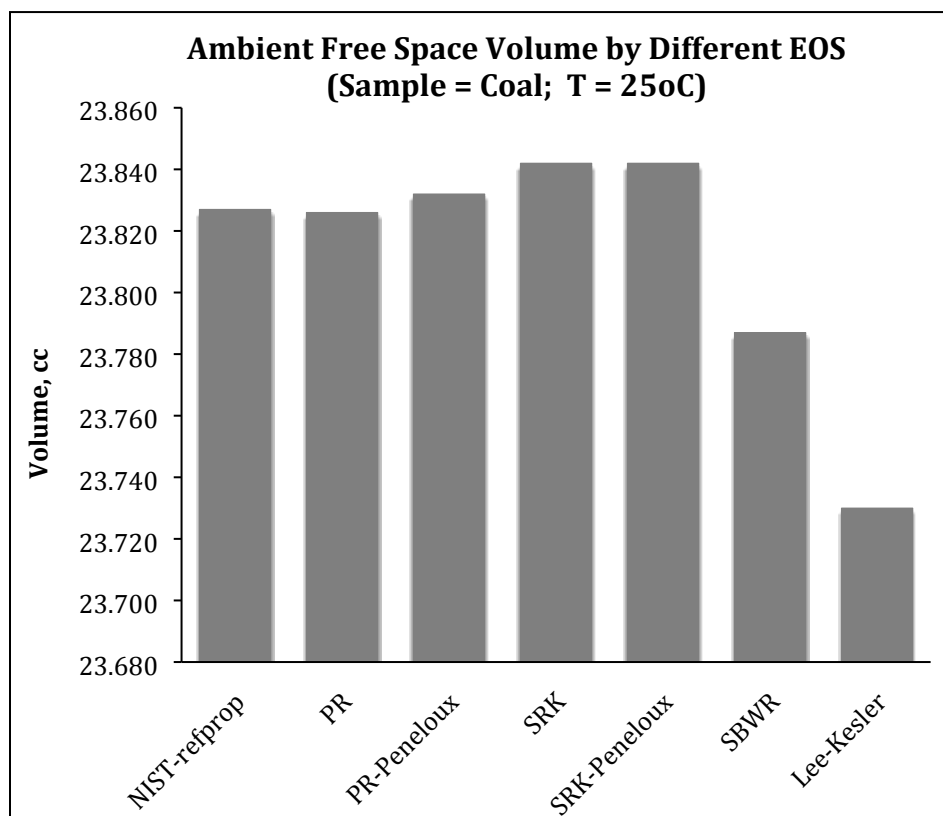


Figure C1: Effect of Equation of State on ambient volume of free space

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