Application of Benedict-Webb-Rubin Equation of State to Sulfur Dioxide

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THE BENEDICT-WEBB-RUBIN equation of state has been used extensively to represent the volumetric behavior of hydrocarbons (*1-3, 5, 12-14*). After Maxwell (*11*) succeeded in applying the equation to a nonpolar inorganic compound, nitrous oxide, there was an interesting question as to whether or not it could be used to represent the volumetric behavior of a highly polar gas such as sulfur dioxide (*15*). The purpose of this work was to determine the specific coefficients for the BWR equation from the experimental pressure-volume-temperature data of gaseous sulfur dioxide (*7, 10*) and to study whether this equation would represent satisfactorily the volumetric behavior of sulfur dioxide in the gas phase.

EVALUATION OF COEFFICIENTS

For the present purpose, the BWR equation is written as

$$Z = 1 + \frac{B_o}{V} - \frac{A_o}{VRT} - \frac{C_o}{VRT^3} + \frac{b}{V^2} - \frac{a}{V^2RT} + \frac{a\alpha}{V^5RT} + \frac{c}{V^2RT^3}\left(1 + \frac{\gamma}{V^2}\right) e^{-\gamma/V^2} \quad (1)$$

and

$$P = \frac{RT}{V} + \frac{(B_oRT - A_o - C_o/T^2)}{V^2} + \frac{(bRT - a)}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right) e^{-\gamma/V^2} \quad (2)$$

The methods proposed by Brough (*4*), Selleck and others (*16*), and Hobby (*8*) to determine the coefficients were followed closely. The conventional method of least squares was used to determine the seven coefficients—B_o, A_o, C_o, b, a, c, and α—for each assumed value of γ. A sum of the squares of residuals was then computed for each set of coefficients and plotted against γ. That set of coefficients, whose γ corresponded to the minimum value of the sum of the squares of residuals, was accepted as the proper set for the BWR equation.

In the previous method (*4, 8, 16*), the sums of the squares of residuals were approximate, as they were computed from an equation whose solution, at best, was not exact. But in this work, these sums were exact, as they were computed without any simplifying assumptions.

The calculations were carried out using an IBM 650 digital computer with floating-point device, indexing registers, tape units, and core storage. The program was first written in the language of 650 Fortran coding system. To solve the set of seven linear simultaneous equations, the program of double precision matrix inversion written by Chappell (*6*) was used.

A total of 1 hour and 50 minutes was required to read in the deck of object program and 784 *P-V-T* data cards, and to finish the first trial of γ value. After that, because the elements in the last row of the 7 × 8 matrix had to be calculated again, the time for a complete trial was cut down to 75 minutes.

SPECIFIC COEFFICIENTS FOR SULFUR DIOXIDE

In following the procedure described above, 784 points of *P-V-T* data of sulfur dioxide in the gaseous phase, comprising Hirth's (*7*) and Kang's (*10*) experimental results, were fitted to a BWR equation. The experimental data, which were in c.g.s. units, were converted to the proper units and used for equation fitting.

Table I and Figure 1 show the sums of the square of the residuals calculated for various values of γ.

Graphically it was determined that the minimum sum of the squares of the residuals occurred at $\gamma = 1.52$. The values of the specific coefficients in the BWR equation of state, corresponding to this value of γ, are

$B_o = 0.41940430$
$A_o = 7{,}996.1667$
$C_o = 9{,}699{,}183{,}200$
$b = 3.7600940$
$a = 51{,}003.485$
$\alpha = 0.29576565$
$c = 22{,}185{,}348{,}000$
$\gamma = 1.5200$

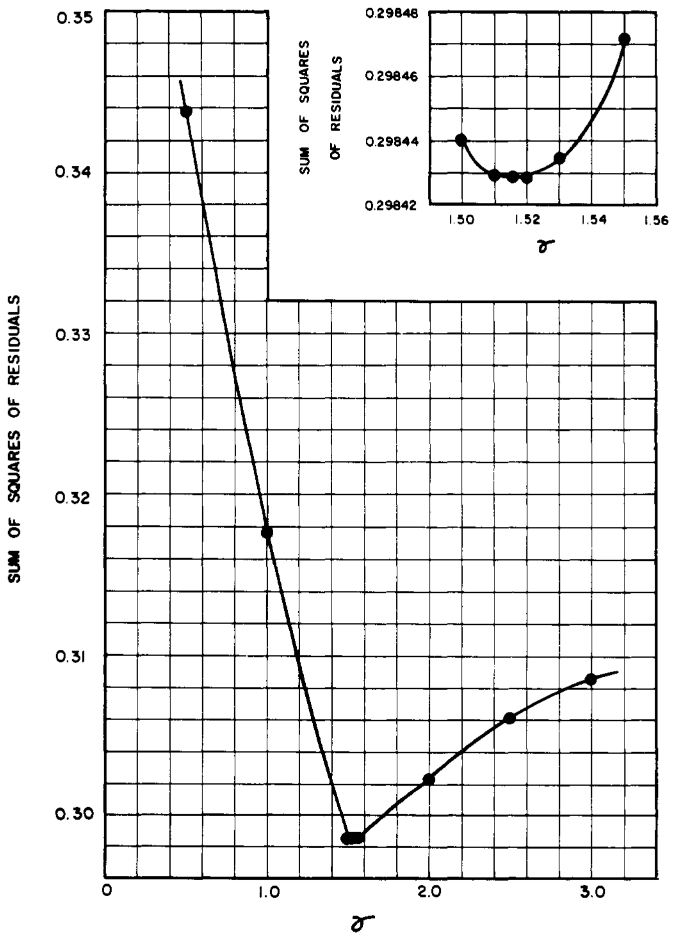

Figure 1. Sum of squares of residuals vs. γ

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Table I. Sum of Squares of Residuals

γ	Sum of Squares of Residuals	γ	Sum of Squares of Residuals
0.5000	0.34366775	1.5300	0.29843483
1.0000	0.31763938	1.5500	0.29847157
1.5000	0.29844044	2.0000	0.30229146
1.5100	0.29842948	2.5000	0.30615942
1.5155	0.29842923	3.0000	0.30860092
1.5200	0.29842909		

To calculate the compressibility factors at definite pressure intervals, volumes were calculated from Equation 2 at the desired pressures by means of the Newton-Raphson method. In this iteration process, V_{i+1} was accepted as the final answer when it was equal to V_i or its absolute deviation, $|(V_{i+1} - V_i)/V_i|$, was less than 10^{-7}.

Two complete statistical studies of the ability of the BWR equation with the above coefficients to represent the volumetric behavior of gaseous sulfur dioxide were made—(1) to find out how well the equation represented the 784 points of experimental data, and (2) to compare the compressibility factors calculated from Equation 1 with the smoothed compressibility factors of sulfur dioxide (*10*), which were spaced at pressure intervals of 1 atm. up to either its vapor pressure or 315 atm. for the isotherms from 10° to 250° C. Table II shows the deviations and Table III the mean absolute relative deviations of the calculated compressibility factors from the smoothed ones for each isotherm.

DISCUSSION

The 0.574% mean absolute relative deviation, as shown in Table III, is greater than the reproducibility of the experimental compressibility data, which is claimed to be 0.2% (*9*). Benedict, Webb, and Rubin (*1*), applying the BWR equation to represent the volumetric behaviors of light hydrocarbons, reported deviations of 0.31, 0.40, 0.31, and 0.34% for *n*-butane, propane, ethane, and methane, respectively, with an average deviation of 0.34%. Canjar and others (*5*) reported average deviations of 0.35% for butane, 0.78% for pentane, 0.61% for *n*-hexane, and 0.58% for heptane. Opfell and Sage (*12*) did not give average deviations but reported deviations ranging from 0.8 to 1.7% for *n*-butane, *n*-heptane, *n*-nonane, and *n*-decane.

Therefore, it is concluded that the BWR equation, with the above coefficients, represents the volumetric behavior of sulfur dioxide reasonably well.

Generally, deviation increases with increase of temperature to a maximum value at the critical temperature (157.5° C.), and then decreases as the temperature continues to increase, with the exception of the 10° and 20° C. isotherms (Table III). This general pattern of deviation is comprehensible, because it is very difficult for any equation of state to represent the *P-V-T* data very well in the critical region.

Table II. Deviations of Compressibility Factors Calculated with the BWR Equation

	From Experimental Data	From Smoothed Results
Sum of squares of residuals, $\Sigma\Delta_n^2$	0.29842909	0.046813436
Standard deviation, $\left(\frac{\Sigma\Delta_n^2}{N}\right)$	0.19510235	0.0051471520
Mean deviation, $\frac{1}{N}\Sigma\Delta_n$	0.00058150995	0.0010794250
Mean absolute deviation, $\frac{1}{N}\Sigma\vert\Delta_n\vert$	0.0041194388	0.0030707430
Mean absolute relative deviation, % $\frac{1}{N}\Sigma\left\vert\frac{\Delta_n}{Z_n}\right\vert$	0.65013277	0.57407453

Table III. Mean Absolute Relative Deviations

Isotherm, ° C.	Mean Abs. Rel. Dev., %	Isotherm, ° C.	Mean Abs. Rel. Dev., %
10	0.40790735	150	0.53025156
20	0.26391402	157.5	0.89004952
30	0.14374229	175	0.63245708
40	0.17800161	200	0.64625413
50	0.21833406	225	0.52058206
75	0.17104415	250	0.33405156
100	0.10295821		
125	0.28113843	Av.	0.57407453

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NOMENCLATURE

N = total number of data points
P = absolute pressure, p.s.i.a.
R = gas constant, 10.731469 (p.s.i.a.)(cu. ft.)/(lb. mole)(° R.)
T = absolute temperature, ° R.
V = volume, cu. ft./lb. mole
Z = compressibility factor
Δ = residual
$B_o, A_o, C_o, a, b, c, \alpha, \gamma$ = constants

Subscripts *i* and *n* are running indices, indicating number of iteration and number of data point, respectively.

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