Part II. Generalized Benedict-Webb-Rubin Equation of State for Real Gases

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By use of a least-squares technique, a set of parameters for the generalized Benedict-Webb-Rubin equation is determined. The generalization of the equation is based on the modified theorem of corresponding states. The generalized equation shows a grand average absolute deviation of 1.6% in predicting the observed values of reduced pressure. The set of constants has been determined for densities up to twice the critical density in the reduced pressure range of 0 to 40.0 and a reduced temperature range of 1.0 to 15.0. The recommended generalized constants are $A_o' = 0.24180980$, $a_o' = 0.04407059$ $a'\ \alpha' = 0.11369478 \times 10^{-3}$, $B_o' = 0.07643101$, $b' = 0.03715171$, $C_o' = 0.21217005$, $c' = 0.06448001$ and $\gamma' = 0.06$.

An equation of state in the reduced or generalized form has several advantages. The classical theory of the equation of state first formulated by van der Waals has not only shown that a universal relation among pressure, volume, and temperature exists (perhaps a very complicated one as compared with that of van der Waals), but it has also stimulated thought and interest leading to a better understanding of the behavior of fluids.

One of the present authors proposed a generalized Beattie-Bridgeman equation of state (*22*) and a modified law of corresponding states (*21*). A pseudo critical volume term was defined as $V_{ci} = RT_c/P_c$ to be used in place of the critical volume term, the latter being difficult to measure accurately and unknown for many gases. Accordingly the compressibility factor Z can be written as

$$Z = f(P_r, T_r) \tag{1}$$

instead of

$$Z/Z_c = F(P_r, T_r) \tag{2}$$

The advantages of these correlations have been shown by several authors (*12, 13, 15, 20*).

Apart from other equations of state (*8, 4, 24, 1*) the Benedict-Webb-Rubin equation of state (*2*) has been shown (*3, 10, 19*) to be a good representation of PVT data. Hence it was thought that further investigation of the potentialities of the Benedict-Webb-Rubin equation coupled with the pseudo critical volume was needed, and accordingly the work of this paper was undertaken.

The method of determining the values of the constants for Benedict-Webb-Rubin equation has been outlined by several authors (*1, 6, 9*). In the present work a least-squares technique is used. The principle here is to differentiate the Benedict-Webb-Rubin equation with respect to each one of the constants and to set the derivatives to zero, thus yielding as many equations as there are unknowns. Such a procedure is used by Brough, Schlinger, and Sage (*5*). To circumvent the difficulty arising out of the nonlinear term a value for the constant occurring in the nonlinear term is assumed and the remaining seven constants evaluated. The Benedict-Webb-Rubin equation of state is

$$P = \frac{RT}{V} + \frac{B_o RT - A_o - C_o/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{C}{V^3\,T^2}\,(1 + \gamma/V^2)\, e^{-\gamma/V^2} \tag{3}$$

The reduced generalized Benedict-Webb-Rubin equation can be written as

$$\pi = \theta\rho + \rho^2 \{\theta\, B'(\rho) - A'(\rho) - C'(\rho)/\theta^2\} \tag{4}$$

where

$$A'(\rho) = A_o' + a'\rho\,(1 - \alpha'\,\rho^3)$$

$$B'(\rho) = B_o' + b'\rho$$

$$C'(\rho) = C_o' - C'\rho\,(1 + \gamma'\,\rho^2)\, e^{-\gamma'\rho^2}$$

The constants in Equations (3) and (4) have the same meaning. One can write Equation (4) as

$$\pi = \theta\rho + \sum_{i=1}^{i=7} \psi_i\,(\rho, \theta)\, K_i \tag{5}$$

where K_i's are constants and $\psi_i = g(\rho, \theta)$. If π_o is the observed value, then one can write the deviation squared as

$$X^2\,(\gamma', K_i) = \Sigma\,(\pi - \pi_o)^2 \tag{6}$$

One has the relationships

$$\frac{\partial X^2(\gamma', K_i)}{\partial K_i} = 0 \tag{7}$$

and

TABLE 1. VALUES OF CONSTANTS FOR BENEDICT-WEBB-RUBIN EQUATION FOR DIFFERENT VALUES OF γ'

γ'	A_o'	a'	$a'\alpha' \times 10^3$	B_o'	b'	C_o'	c'
0.100	3.6002659	−0.52371919	1.0860390	0.81622561	−0.12868716	3.8513410	2.7304250
0.075	0.28457292	0.031870456	0.092577307	0.080358782	0.036177011	0.13600591	0.043665163
0.060	0.24180980	0.044070594	0.11369478	0.076431013	0.037151710	0.21217005	0.064480014
0.047	0.15765868	0.065279544	0.13638740	0.065606444	0.039710663	0.33309835	0.092199894
0.0447	0.14545119	0.067646074	0.13489319	0.063251162	0.040244410	0.33986599	0.091337463
0.044	0.14346855	0.067849720	0.13344020	0.062672791	0.040371281	0.33820593	0.089923728
0.040	0.15017823	0.064094012	0.11770803	0.061249147	0.040641092	0.29386392	0.072111447

TABLE 2. DETERMINATION OF THE BEST VALUE OF γ'

γ'	Grand average absolute deviation, %
0.075	2.1004
0.060	1.7389
0.047	1.8699
0.0447	2.0181
0.044	2.0557
0.040	2.2000

$$\frac{\partial^2 X^2 (\gamma', K_i)}{\partial K_i^2} > 0 \qquad (8)$$

for a minimum with respect to K_i's for a given γ'. So

$$\frac{\partial X^2(\gamma', K_i)}{\partial K_i} = 2 \Sigma (\pi - \pi_o) \frac{\partial \pi}{\partial K_i}; \ \frac{\partial \pi}{\partial K_i} = \Sigma \psi_i(\rho, \theta) \qquad (9)$$

$$\frac{\partial X^2(\gamma', K_i)}{\partial K_i} = 2 \Sigma (\pi - \pi_o) \Sigma \psi_i(\rho, \theta) \qquad (10)$$

$$\therefore \Sigma \{\theta \rho + \Sigma \psi_i(\rho, \theta) K_i - \pi_o\} \Sigma \psi_i(\rho, \theta) = 0 \qquad (11)$$

Using the subscript n to identify a particular observed value of π_o one can write Equation (11) as

$$\sum \left\{ \theta_n \rho_n + \sum_{\substack{i=1\\n=1}}^{\substack{n=n\\i=7}} \psi_{i,n}(\rho, \theta) K_i - \pi_{o,n} \right\} \sum_{\substack{i=1\\n=1}}^{\substack{n=n\\i=7}} \psi_{i,n}(\rho, \theta) = 0 \qquad (12)$$

The error sum of squares

$$X^2(\gamma', K_i) = \sum_{n=1}^{n=n} (\pi_n - \pi_{o,n})^2 \qquad (13)$$

Equation (12) gives seven equations in seven unknowns. Computer programs, written for an IBM-650, are given in reference 23. The set of simultaneous equations generated from Equation (12) is ill-conditioned. The Gaussian elimination method considered as a foolproof method (*18*) under these conditions is used. No exact mathematical way exists to measure the degree of ill-conditioning. Computer program for the Gaussian elimination method is given in reference 23.

The authors have presented a set of generalized compressibility charts in Part I of this series. These charts were used in the evaluation of the generalized constants in this paper.

The values of parameters for different γ' values for pseudo reduced densities of 0.25 to 6.00 and reduced temperatures of 1.0 to 15.0 are given in Table 1.

A fourth program (*23*) written for an IBM-650 Fortransit compiler calculates the values of reduced pressure with Equation (4), compares with observed values, calculates the deviation and square of the deviation for each value, calculates average absolute deviation and the sum of squares of deviation for each isotherm. Table 2 gives the average absolute deviation and total sum of equares of deviation for a particular value of γ'. A value of γ' corresponding to 0.06 was taken as the best value, and the constants corresponding to this value are used.

The recommended generalized constants are:

$A_o' = 0.24180980$, $a' = 0.04407059$, $a'\alpha' = 0.11369478 \times 10^{-3}$, $B_o' = 0.07643101$, $b' = 0.03715171$, $c_o' = 0.21217005$, $c' = 0.06448001$, $\gamma' = 0.06$.

The condition of Equation (8) is fulfilled as only real numbers are involved. It should be noted that the observed values referred to in this work were obtained from the compressibility charts (*23*). These compressibility charts were constructed with the compressibility value of Lydersen-Greenkorn-Hougen (*14*), Soparkar (*17*), Nelson-Obert (*16*), and Su (*20*). In addition to these values actual experimental data of several gases, n-butane, hydrogen, ammonia, nitrogen, sulfur dioxide, nitric oxide, and others, were also used.

The generalized equation shows a grand average absolute deviation of 1.6% in predicting the observed pressure values. A total of 240 points were compared in the reduced pressure range of 0 to 40 and a reduced temperature range of 1.0 to 15.0, covering densities up to twice the critical density.*

By the use of these generalized constants certain derived thermodynamic properties have been calculated and presented in Parts III and IV of this series.

NOTATION

$A, B, C, a, b, c, \alpha, \gamma$ = constants in the Benedict-Webb-Rubin equation of state

$A', B', C', a', b', c', \alpha', \gamma'$ = dimensionless constants in the generalized Benedict-Webb-Rubin equation

P = pressure

R = gas constant

T = temperature

V = volume

Z = compressibility factor = PV/RT

V_{ci} = pseudo critical volume = RT_c/P_c

P_r = reduced pressure $= P/P_c$

π_c = calculated reduced pressure with Benedict-Webb-Rubin equation

θ = reduced temperature = T/T_c

ρ = pseudo reduced density = V_{ci}/V

Subscript

c = critical state except in π_c

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* Tabular material has been deposited as document 8056 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

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The Friction Factor–Reynolds Number Relation for the Steady Flow of Pseudoplastic Fluids Through Rectangular Ducts

Part I. Theory

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A finite difference technique is used to calculate the velocity profile, maximum shear stress, and friction factor-Reynolds number product for a power-law, pseudoplastic fluid flowing through a cylindrical duct of rectangular cross section. It is assumed that the motion is rectilinear. A very simple friction factor-Reynolds number correlation is obtained for the special case of a square duct.

Scientific interest in the flow of non-Newtonian fluids has increased steadily in the last few decades. This growth of interest has been motivated by technical requirements in industry and by the desire of rheologists to fill the gap in knowledge between the classical theories of Hookean elasticity and Newtonian flow. Although some very general formulations of the equations of motion for non-Newtonian fluids have been presented in the literature, the physical systems for which these equations have been solved to yield results that can be compared with experimental measurements have been characterized by a high degree of geometric symmetry. In these systems, which include the pipe, the circular annulus, parallel plates, rotating concentric cylinders, and approximately the cone and plate, there exist coordinate systems such that there is only one nonzero component of velocity and the strain-rate tensor has only two nonzero elements. Since the irrotational strain-rate tensor is symmetric, the constituitive equations relating the corresponding elements of the stress and strain-rate tensors reduce to rather simple expressions.

Hence, the problem becomes one of solving a nonlinear ordinary differential equation for which an analytical solution can often be obtained. The square duct, on the other hand, possesses less symmetry than the previously mentioned systems, and it is impossible to find a coordinate system for which there are fewer than four nonzero ele-