Greek Letters

η = catalyst effectiveness factor
μ = viscosity
ρ = density, g./cc.
ϕ = fugacity coefficient
ϕ_s = Thiele modulus

LITERATURE CITED

1. Barnett, L. G., R. E. C. Weaver, and M. M. Gilkeson, *AIChE J.*, 7, 211 (1961).
2. Bird, R. B., W. E. Steward, and E. N. Lightfoot, "Transport Phenomena," John Wiley, New York (1960).
3. Chambers, R. P., and M. Boudart, *J. Catalysis*, 3, 141 (1966).
4. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, 26, 1183 (1934).
5. DeAcetis, J., and G. Thodos, *ibid.*, 52, 1003 (1960).
6. Graham, R. R., MS thesis, Texas Tech., Lubbock (1967).
7. Heinemann, H., G. A. Mills, J. B. Hattman, and F. W. Kirsch, *Ind. Eng. Chem.* 45, 130 (1953).
8. Holmes, J. T., and M. G. Baerns, *U. S. Atomic Energy Commission Report ANL-6951*, Argonne Nat. Lab., Argonne, Ill. (1964).
9. Hougen, O. A., and K. M. Watson, "Chemical Process Principles, III." Wiley, New York (1947).
10. Khoobiar, S., R. R. Peck, and B. J. Reitzer, *Proc. Intern. Congr. Catalysis, 3rd*, Amsterdam (1964).
11. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
12. Rossini, F. D., et al. *Am. Petrol. Inst.*, Project 44, 4 (1953).
13. Satterfield, C. N., and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley, Palo Alto, California (1963).
14. Smith, N. L., and N. R. Amundson, *Ind. Eng. Chem.*, 43, 2156 (1951).

Manuscript received May 10, 1967; revision received August 8, 1967; paper accepted September 6, 1967.

A Generalized B-W-R Equation of State

W. C. EDMISTER, J. VAIROGS, and A. J. KLEKERS
Oklahoma State University, Stillwater, Oklahoma

The Benedict-Webb-Rubin Equation of State has been generalized by expressing the eight constants as functions of critical pressure, critical temperature, and acentric factor. An evaluation of the resulting generalization against the observed P-V-T data of thirteen hydrocarbons and carbon dioxide shows 0.3 to 2.0% average deviations of the calculated pressures from the observed, as compared with 0.2 to 1.4% when using the individual (that is, nongeneralized constants for each component. Standard errors of estimate for 1,464 experimental data points were 0.0089 for the proposed generalization vs. 0.0084 for the original B-W-R Equation.

As originally developed and applied to the computation of thermodynamic properties of hydrocarbons and their mixtures, the Benedict-Webb-Rubin (*7, 8*) Equation of State employed a set of eight individual constants for each hydrocarbon. These eight constants were derived empirically by fitting the equation to experimental P-V-T data.

Efforts to develop generalizations for the prediction of these constants have had only limited success (*9, 13, 17, 28*). Canjar, et al. (*9*), correlated the constants with critical temperature. Hansen (*13*) used critical temperature to correlate generalized constants reduced with critical volume. Opfell, et al. (*17*), used critical temperature, critical pressure, critical volume and acentric factor (*19*) in their generalization. Su and Viswanath (*28*) used the critical temperature and critical pressure in a generalization similar to the Su-Chang (*27*) treatment of the Beattie-Bridgeman Equation.

These three generalizations employed one, two, and four properties of the components. In the generalization study reported here, three of these properties, the critical temperature, the critical pressure, and the acentric factor, have been employed in the development of reduced constant relationships for the B-W-R Equation.

CRITICAL TEMPERATURE AND PRESSURE EFFECTS

The first step in the study was to replace the pressure, temperature and density parameters of the original B-W-R Equation with reduced parameters. This was done in the way suggested by Su, et al. (*27, 28*), starting with the original specific form of the B-W-R, namely:

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1 + \gamma d^2)\exp(-\gamma d^2) \quad (1)$$

The P, T, and d terms are replaced by the following

$$P = P_c\pi \qquad T = T_c\theta \qquad d = \rho\frac{P_c}{RT_c}$$

where π, θ, and ρ are reduced parameters, defined by these substitution relationships.

This substitution and rearrangement gives

$$\pi = \theta\rho + (B'_o\theta - A'_o - C'_o/\theta^2)\rho^2 + (b'\theta - a')\rho^3 + (a'\alpha')\rho^6 + \frac{c'\rho^3}{\theta^2}(1 + \gamma'\rho^2)\exp(-\gamma'\rho^2) \qquad (2)$$

TABLE 1. REDUCED B-W-R CONSTANTS FOR TWELVE HYDROCARBONS DERIVED FROM SPECIFIC VALUES OF BENEDICT ET AL. (*8*)

Hydrocarbon	$B'_o = \frac{B_oP_c}{R\,T_c}$	$A'_o = \frac{A_oP_c}{R^2T_c^2}$	$C'_o = \frac{C_oP_c}{R^2T_c^4}$	$b' = \frac{b\,P_c^2}{R^2T_c^2}$	$a' = \frac{a\,P_c^2}{R^3T_c^3}$	$\alpha' = \frac{\alpha\,P_c^3}{R^3T_c^3}$	$c' = \frac{c\,P_c^2}{R^3T_c^5}$	$\gamma' = \frac{\gamma\,P_c^2}{R^2T_c^2}$
Methane	0.1244	0.3456	0.1151	0.02884	0.02690	0.003096	0.03795	0.05120
Ethylene	0.1195	0.3090	0.1109	0.03960	0.05140	0.001757	0.05239	0.04250
Ethane	0.1210	0.3185	0.1050	0.04130	0.05115	0.001742	0.05195	0.04380
Propylene	0.1290	0.3090	0.1660	0.04293	0.05940	0.001585	0.05900	0.04185
Propane	0.1346	0.3135	0.1695	0.04310	0.05880	0.001609	0.05955	0.04210
i-Butane	0.1480	0.3286	0.1637	0.04910	0.06700	0.001337	0.05930	0.03935
i-Butene	0.1339	0.3000	0.1779	0.04605	0.06537	0.001386	0.06070	0.03910
n-Butane	0.1337	0.3107	0.1692	0.04620	0.06240	0.001132	0.05795	0.03925
i-Pentane	0.1394	0.2046	0.1892	0.05063	0.07530	0.001122	0.06560	0.03510
n-Pentane	0.1355	0.2732	0.2160	0.04988	0.07910	0.001169	0.07250	0.03545
n-Hexane	0.1278	0.2490	0.2220	0.05630	0.08820	0.001043	0.07270	0.03443
n-Heptane	0.1210	0.2410	0.2235	0.05630	0.08670	0.000982	0.0708	0.03330

where

$$B'_o = \frac{B_oP_c}{R\,T_c}$$

$$A'_o = \frac{A_oP_c}{R^2T_c^2}$$

$$C'_o = \frac{C_oP_c}{R^2T_c^4}$$

$$b' = \frac{b\,P_c^2}{R^2T_c^2}$$

$$a' = \frac{a\,P_c^2}{R^3T_c^3}$$

$$\alpha' = \frac{\alpha\,P_c^3}{R^3T_c^3}$$

$$c' = \frac{c\,P_c^2}{R^3T_c^5}$$

$$\gamma' = \frac{\gamma\,P_c^2}{R^2T_c^2}$$

Eight reduced constants are defined above in terms of the specific constants and the criticals plus the gas constant. These reduced constants are dimensionless.

Using the values of the specific constants, obtained by Benedict, et al. (*8*), for twelve hydrocarbons and their criticals, the reduced B-W-R constants were computed via the above definitions. These are tabulated in Table 1 for the twelve hydrocarbons included in the Benedict, et al. (*8*), work.

From the values in Table 1, it is obvious that these reduced constants do vary from component to component and that a single value cannot be used for each of the eight constants. The ranges of these variations and the averages are shown in Table 2. The spread between low and high is from 30 to 300%. Average values of these same reduced constants obtained by Su and Viswanath (*28*) by another technique are also given. These two averages are rather far apart, as can be seen. If a set of average values of these reduced constants is desired, those of Su and Viswanath are probably better than those obtained in this work.

The use of average values of the constants is not recommended, however. The $\alpha'a'$ product is more nearly nonvariant than the other constants and might be fixed at an average value. This was done in the present work.

ACENTRIC FACTOR EFFECTS

The next step in this generalization was to find equations that would predict these reduced constants from some physical property of the hydrocarbons. Acentric factor, proposed by Pitzer, et al. (*19*), as a third parameter (critical temperature and pressure, being the first and second) in correlating compressibility factors, was the property chosen in this work.

TABLE 2. RANGES AND AVERAGES OF REDUCED B-W-R CONSTANTS

Constant	Range low	high	Averages Table 1 values	Su et al. (*28*)
B'_o	0.1195	0.1480	0.1306	0.07643
A'_o	0.2410	0.3456	0.3088	0.24180
C'_o	0.1050	0.2235	0.1688	0.21217
b'	0.02884	0.05630	0.04587	0.037152
a'	0.02690	0.08820	0.06430	0.04407
α'	0.000982	0.003096	0.001497	0.002583
c'	0.03795	0.07270	0.06006	0.06448
γ'	0.0333	0.0512	0.03979	0.060
$\alpha'a'$	0.0000706	0.0000941	0.0000875	0.0001137

Seven constants, all except α', were plotted against ω, the acentric factor (*19*), and against Z_c, the critical compressibility factor, to determine if the reduced constants were smooth functions of either of these two variables. Straight line relationships were first derived for both variables and tested for all reduced constants except B'_o and α'. The average values shown in Table 2 for B'_o and $\alpha'a'$ were used in these tests. The results show that straight line functions of ω and Z_c are unsatisfactory with the Z_c correlations giving larger deviations than ω.

Examination of the reduced constant plots shows a better trend for ω than Z_c plots. Correlation with respect to Z_c was set aside in favor of ω. Six of the reduced constants appeared to be higher order functions of ω. The six reduced constants were fitted with quadratic functions of ω by a least squares method giving the following equations

$$\gamma' = 0.052058 - 0.09064\omega + 0.10506\omega^2 \qquad (3)$$

$$c' = 0.035694 + 0.185297\omega - 0.230125\omega^2 \qquad (4)$$

$$a' = 0.0235866 + 0.290284\omega - 0.295413\omega^2 \qquad (5)$$

$$b' = 0.0275404 + 0.131009\omega - 0.134924\omega^2 \qquad (6)$$

$$C'_o = 0.098224 + 0.401236\omega - 0.0397267\omega^2 \qquad (7)$$

$$A'_o = 0.343258 - 0.127521\omega - 0.509131\omega^2 \qquad (8)$$

In this generalization, α' can be found from the constant value of the $\alpha' a'$ product, that is

$$\alpha' a' = 0.0000875 \qquad (9)$$

and the value of a' from Equation (5). These seven equations permit evaluation of all the B-W-R constants except B'_o which is not a clearly defined function of ω.

A similar quadratic expression was derived for B'_o by using the values of the other constants from the above seven equations, [Equations (3) through (9)], and using experimental P-V-T data for the 12 original B-W-R hydrocarbons to minimize the average absolute percent deviation in the pressure calculation. A total of 1,112 data points, including the critical point data of n-nonane and n-decane, were used in this determination of the B'_o function. The n-nonane and n-decane critical points were used to extend the correlation to higher ω values since the P-V-T data for these components in the desirable density range is not available. The results of this optimization give the equation

$$B'_o = 0.113747 + 0.127349\omega - 0.243280\omega^2 \qquad (10)$$

No attempt was made to weigh the critical region data or to fit the correlation specifically to the critical point values. If the critical point is to be fitted with high accuracy, then the reduced constants cannot be obtained from the original B-W-R constants. This procedure would involve regression of all reduced constants using all of the experimental P-V-T data points with special weighing at the critical values. This is an extension project beyond the scope of this work.

If B'_o had been optimized, as in this work, with heavy emphasis at all the critical points, the average deviation for all other experimental P-V-T points would suffer by giving a more restricted generalization that would be better near the critical point, but would give larger deviations in other regions. The present generalization is believed to give the best results over the entire range of the equation's applicability. Modification of the generalization to include Z_c in the reduced constants failed to improve the correlation while introducing an extra variable.

EVALUATIONS

This proposed generalized B-W-R Equation has been tested against two data compilations: 1. available P-V-T data for thirteen hydrocarbons and carbon dioxide, and 2. the Pitzer, et al. (*19*), generalized correlation of compressibility factors, $Z(P_r, T_r, \omega)$. In each of these evaluations comparisons are made with other prediction methods.

In the first evaluation, pressures were calculated from density and temperature values and compared with experimentally observed pressures. Similar calculations were made with the original B-W-R (*7*) and with the Su-Viswanath (*28*) generalization of the B-W-R. The results of these calculations are summarized in Table 3. Absolute average deviations in pressure are given in Table 3 and deviations in pressure at the critical points are given in Table 4. Data sources are indicated.

From the results given in Table 3 it is obvious that the proposed generalization is superior to the Su-Viswanath (*28*) generalization but slightly inferior to the original (*7*) equation. Standard errors of estimate $\left(\left[\frac{\Delta Z^2}{n-1}\right]^{1/2}\right)$ for the prediction of compressibility factors by these three equations for the 1,464 data points were also found, as follows:

Original B-W-R	0.0084
Proposed Generalized B-W-R	0.0089
Su-Viswanath Generalized B-W-R	0.0208

The worst deviations were in the critical region where errors up to 6%, with the exception of methane, in pressure prediction are encountered. At the higher densities in the $T_r < 1.2$ and $P > P_c$ region, deviations up to 10% are found. The corresponding maximum deviations for the Su-Viswanath (*28*) equation are 9% and up to 50%, the latter being for the higher molecular weight hydrocarbons.

In the second evaluation of the proposed generalized B-W-R equation, compressibility factors were computed

TABLE 3. COMPARISON OF PROPOSED GENERALIZED B-W-R EQUATION WITH SU GENERALIZATION AND ORIGINAL FORM, USING INDIVIDUAL CONSTANTS, FOR PREDICTION OF PRESSURE

			Original BWR (*8*)		Su's Generalized BWR (*28*)		This Generalized BWR	
Hydrocarbon	Number of points	Ref.	Avg. Abso. Dev. %	Max. Dev. %	Avg. Abso. Dev. %	Max. Dev. %	Avg. Abso. Dev. %	Max. Dev. %
Methane	89	15	0.376	+ 2.25	2.43	− 8.85	1.97	+16.76
Ethylene	110	16	0.143	+ 1.04	1.65	+ 8.87	0.531	+ 6.86
Ethane	180	3	0.322	+ 1.02	1.43	+ 8.78	0.574	+ 5.55
Propylene	154	29	0.219	− 2.92	1.55	+ 8.92	0.318	+ 3.97
Propane	109	5	0.361	+ 1.39	2.72	−14.98	1.35	− 9.11
i-Butane	30	23	1.15	+ 1.56	1.58	−18.15	1.67	−13.98
i-Butene	62	4	0.330	+ 2.41	2.40	+ 8.91	1.49	−10.65
n-Butane	95	6	0.372	+ 1.60	2.91	+15.80	1.53	−10.35
i-Pentane	66	2, 25	1.43	+10.56	3.28	+14.66	1.67	+ 7.66
n-Pentane	31	24	0.961	− 8.99	2.03	− 9.71	0.611	− 7.82
n-Hexane	13	14	0.769	− 2.14	13.2	+59.51	0.964	+ 2.77
n-Heptane	29	26	0.402	+ 1.11	6.45	+40.53	1.84	+ 3.44
n-Nonane	1	1	No Values		8.24	+ 8.24	0.905	− 0.91
n-Decane	1	1	No Values		7.55	+ 7.55	2.575	− 2.58
Benzene	142	12, 18	0.367	− 1.58	2.81	+ 8.92	0.484	+ 2.42
Carbon Dioxide	352	10, 11	0.482	+21.30	1.08	−31.25	0.494	−24.34

for 2,772 points (22 reduced temperature, 0.8 to 4.0; 21 reduced pressure, 0.2 to 9; and 6 acentric factors, 0 to 0.5) (*20*). Similar calculations were made with the original Redlich-Kwong (*22*) Equation and with its recent extension proposed by Redlich, et al. (*21*). The last equation is an empirical correlation, using 43 constants that are built into the program, the tables of Pitzer, et al. (*20*), and other information in the development of the program and evaluation of the constants. Two of the constants are those of the original Redlich-Kwong, while the remaining 41 appear in the new parts of the equation.

Overall standard deviations obtained in applying these three equations to the 2,772 (*20*) compressibility factors are:

Redlich, et al. (*21*), New Equation	0.013
Proposed Generalized B-W-R	0.025
Original Redlich-Kwong (*22*)	0.054

These comparisons indicate that the proposed generalized B-W-R Equation is superior to the original Redlich-Kwong Equation and almost as reliable as the new modification of the Redlich-Kwong Equation.

TABLE 4. PERCENT DEVIATION* IN PRESSURE CALCULATION AT CRITICAL POINT

Hydrocarbon	Original BWR	Su generalization	Our generalization
Methane	2.25	8.64	12.35
Ethylene	0.70	8.86	6.86
Ethane	0.41	8.78	5.55
Propylene	1.32	8.92	3.97
Propane	0.66	8.90	3.60
i-Butane	0.77	8.82	2.40
i-Butene	2.41	8.91	2.20
n-Butane	0.08	8.92	2.26
i-Pentane	—3.41	8.92	2.15
n-Pentane	—1.48	8.18	1.64
n-Hexane	0.89	8.79	1.07
n-Heptane	—0.64	8.74	0.51
n-Nonane	—	8.24	—0.90
n-Decane	—	7.55	—2.57
Benzene	0.61	8.92	1.97
Carbon Dioxide	0.18	8.75	1.63

$$\text{* Percent Deviation} = \frac{P_{c_{\text{calc}}} - P_{c_{\text{obs}}}}{P_{c_{\text{obs}}}} \times 100$$

CONCLUSIONS

A generalized B-W-R Equation of State is presented. The reduced constants for this equation are functions of acentric factor. Further work might improve the accuracy of this generalized equation but the next major step should be to investigate the combination relationships for mixtures.

NOTATION

A_o = constant in BWR Equation of State
a = constant in BWR Equation of State
B_o = constant in BWR Equation of State
b = constant in BWR Equation of State
C_o = constant in BWR Equation of State
c = constant in BWR Equation of State
d = density
n = number of points
P = pressure
R = gas constant
T = temperature
Z = compressibility factor

Greek Letters

α = constant in BWR Equation of State
γ = constant in BWR Equation of State
π = reduced pressure
ρ = reduced density
θ = reduced temperature
ω = acentric factor

Subscripts

c = property at critical point
r = reduced property

Superscripts

$'$ = generalized constant for BWR equation

LITERATURE CITED

1. American Petroleum Institute Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds,* Texas A&M University, College Station, Texas (Loose-Leaf Data Sheets).
2. Arnold, E. W., D. W. Liou, and J. W. Eldridge. *J. Chem. Eng. Data,* **10,** 88 (1965).
3. Beattie, J. A., C. Hadlock, and N. Poffenberger. *J. Chem. Phys.,* **3,** 93 (1935).
4. Beattie, J. A., H. G. Ingersoll, and W. H. Stockmayer. *J. Am. Chem. Soc.,* **64,** 548 (1942).
5. Beattie, J. A., W. Kay, and J. Kaminski. *ibid.,* **59,** 1589 (1937).
6. Beattie, J. A., G. L. Simard, and G. -J. Su. *ibid.,* **61,** 26 (1939).
7. Benedict, M., G. B. Webb, and L. C. Rubin. *J. Chem. Phys.,* **8,** 334 (1940).
8. Benedict, M., G. B. Webb, L. C. Rubin, and L. Friend *Chem. Eng. Progr.,* **47,** 419, 449, 571, 609 (1951).
9. Canjar, L. N., R. F. Smith, E. Volianitis, J. F. Galluzzo, and M. Carbarcor. *Ind. Eng. Chem.,* **47,** 1028 (1955).
10. Cullen, E. J., and K. A. Kobe. *AIChE J.* **1,** 452 (1955).
11. Din, F. "Thermodynamic Functions of Gases," Vol. 1, p. 102, Butterworth Scientific Publications, London (1950).
12. Gornowski, E. J., E. H. Amick, Jr., and A. N. Hixson. *Ind. Eng. Chem.,* **39,** 1348 (1947).
13. Hansen, R. E. *Chem. Eng. Progr., Symp. Ser. No. 4,* **60,** 49 (1964).
14. Kelso, E. A., and W. A. Felsing. *J. Am. Chem. Soc.,* **62,** 3132 (1940).
15. Kvalnes, H. M., and V. L. Gaddy. *ibid,* **53,** 394 (1931).
16. Michels, A., J. DeGruyter, and F. Niesen. *Physica,* **3,** No. 5, 347 (1936).
17. Opfell, J. B., B. H. Sage, and K. S. Pitzer. *Ind. Eng. Chem.,* **48,** 2069 (1956).
18. Organick, E. I., and W. R. Studhalter. *Chem. Eng. Progr. Symp. Ser. No. 11,* **44,** 847 (1948).
19. Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson. *J. Am. Chem. Soc.,* **77,** 3427 (1955).
20. Pitzer, K. S., G. N. Lewis, M. Randall, and L. Brewer. "Thermodynamics," Appendix 1, McGraw-Hill, New York, (1961).
21. Redlich, O., F. J. Ackerman, R. D. Gunn, M. Jacobson, and S. Lau. *Ind. Eng. Chem. Fundamentals,* **4,** 369 (1965).
22. Redlich, O., and J. N. S. Kwong. *Chem. Rev.,* **44,** 233 (1949).
23. Sage, B. H., and W. N. Lacey. *Ind. Eng. Chem.,* **30,** 673 (1938).
24. *Ibid.,* **34,** 730 (1942).
25. Silberberg, I. H., J. J. McKetta, and K. A. Kobe. *J. Chem. Eng. Data,* **4,** 323 (1959).
26. Smith, L. J., J. A. Beattie, and W. Kay. *J. Am. Chem. Soc.,* **59,** 1587 (1937).
27. Su, G.-J, and C. H. Chang. *ibid.,* **68,** 1080 (1946).
28. Su, G. -J., and D. S. Viswanath. *AIChE J.,* **11,** 205 (1965).
29. Vaughn, W. E., and N. R. Graves. *Ind. Eng. Chem.,* **32,** 1252 (1940).

Manuscript received July 29, 1967; revision received September 29, 1967; paper accepted October 2, 1967. Paper presented at AIChE Mexico City Meeting.