Application of the Benedict-Webb-Rubin Equation of State to Argon

DAVID ZUDKEVITCH and THOMAS G. KAUFMANN

Esso Research and Engineering Company, Florham Park, New Jersey

The coefficients of the Benedict-Webb-Rubin equation of state have been developed for argon. By employing these coefficients, the volumetric behavior of argon has been predicted with an average deviation of 0.241% for five hundred ninety-seven smoothed and experimental data points in the superheated region.

At temperatures below the critical, two sets of C_o's, one for the liquid and one for the vapor, were needed to relate the vapor pressure to the densities of saturated argon. However, consistent fugacities for the saturated vapor and liquid argon could not be predicted with these C_o values. Therefore, another set of C_o's was developed by equating the pure component vapor and liquid fugacities along the vapor pressure curve. These values were used to test the applicability of the equation of state to predict derived thermodynamic properties.

The original BWR expression for calculating isothermal pressure effects on enthalpy was modified to include explicitly the temperature dependence of the coefficient C_o. Vapor-liquid equilibrium relations for the argon-nitrogen system predicted by the standard BWR procedure were compared with experimental data.

The empirical equation of state of Benedict, Webb, and Rubin (*3*) was originally developed to correlate and predict the fugacities of light hydrocarbon mixtures. Since its publication, it has been used extensively to represent the volumetric and phase relations of light hydrocarbons and some nonhydrocarbons. Several papers (*3* to *5*, *8*, *13*) have been published describing success in predicting high pressure phase behavior of multicomponent systems. As the BWR technique gained widespread use, more and more shortcomings were reported (*8*, *13*). Most of the difficulties have been observed in predicting P-V-T relationship within the critical region, and predicting vapor-liquid equilibrium ratios at low temperatures. As a result, it is widely believed that the BWR equation is inadequate for systems at low temperatures. Attempts have been made to modify the equation and the combining rules for mixtures in order to use it for low temperature predictions. The limitations of the BWR method and suggested modifications have been summarized by Canjar (*8*), Ellington (*13*), and Lin (*20*). The application of the BWR approach to the cryogenic systems nitrogen-methane (*26*) and nitrogen-carbon monoxide (*24*) at temperatures below 200°R. established that temperature is not a limiting condition for use of the technique. The results of the present work extend the application of the BWR method to another cryogenic material, namely, argon.

As was recently stated by Thodos (*25*), argon is a good substance to test the validity of an equation of state. Its molecule is monatomic and therefore its properties should resemble those expected from a simple fluid as defined by Pitzer (*23*). Furthermore, its relatively high atomic weight provides a good test for any equation employing a high power series in density. Beattie and Bridgeman (*2*) showed that such an equation can apply to argon.

The BWR equation requires the determination of eight coefficients by a lengthy trial and error process. Once the coefficients are established they have to be tested. Application of the equation also requires a complicated trial and error procedure to find the phase densities. Publications concerning the BWR equation and its application describe methods to evaluate the coefficients (*7*) and its various uses (*4*, *5*, *13*, *14*, *20*, *25*, *26*). However, the literature does not give a clear procedure for evaluating the effect of temperature on the coefficient which is necessary for the prediction of vapor pressure. This presentation discusses this aspect of the problem.

The present work involved the following steps:

1. Establish the eight coefficients for the BWR equation by regression analysis of the P-V-T data in the superheated gas phase.
2. Test the accuracy of pressure predictions in the superheated range.
3. Evaluate the temperature effect on the coefficients of the equation at temperatures below the critical and quantitatively account for it by varying one of the coefficients C_o.
4. Test the validity of the above by calculating isothermal pressure effects on enthalpy and vapor-liquid equilibrium ratios (K values).

EVALUATION OF BWR COEFFICIENTS FOR ARGON

The equation of state of Benedict, Webb, and Rubin (*3*) describes the P-V-T properties of both vapors and liquids and therefore is suitable for calculating densities, fugacities, and isothermal effects on enthalpy and entropy. In all its applications the independent variable, at a given temperature, is the density.

The basic formula expresses the pressure P as a function of the molal density d.

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

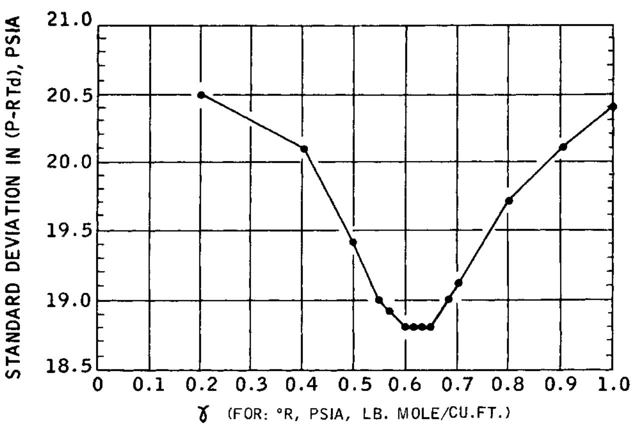

Fig. 1. Standard deviation of pressure vs. assumed γ for argon.

Except for the last term, Equation (1) could be considered as a power series of d. In order to utilize conventional linear regression analysis, a value of γ must be assumed to permit determination of the other seven coefficients: B_o, A_o, C_o, b, a, c, and α. For each assumed value of the γ the standard deviation of the dependent variable, in this case $(P - RTd)$, can then be determined. In selecting the term $(P - RTd)$ as the dependent variable, this work differs from Brough (*7*) and others who utilized $(Z - 1)$ as the dependent variable.

For the evaluation, five hundred ninety-seven P-V-T points for argon in the gaseous phase were used. They contained experimental data which had been published by Michels et al. (*21, 22*), as well as some smoothed values from Din's tabulation (*11*). The data covered the temperature range of 290° to 1,080°R. and the pressure range of 14.7 to 7,500 lb./sq. in. abs.

The calculations were carried out on an IBM-7094 computer, utilizing a multiple regression analysis technique (*12*). The coefficients of the linear terms were evaluated for different values of γ's. In each case the standard deviation was plotted against the corresponding assumed value of γ to establish the one having the minimum standard deviation. The selection of the best value was done graphically as shown in Figure 1 and the corresponding set of coefficients is given in Table 1. Numerically, the minimum standard deviation is 18.8 lb./sq. in. abs.

The ability of the BWR equation of state to represent the P-V-T behavior of argon was tested by comparing pressures calculated from submitted values of temperature and volume. The smoothed values tabulated by Din (*11*) and the experimental data of Whalley (*27*) were used for this comparison. Representative comparisons are shown in Figure 2. The average percentage deviation between Din's values and the predicted pressures was 0.214%. The largest deviations were observed along the isotherm closest to the critical. The maximum error was 4.26%. The same comparison with five isotherms of Whalley (*27*) resulted in a deviation of 0.45%.

TABLE 1. CONSTANTS FOR BWR EQUATION OF STATE FOR ARGON AND NITROGEN

Constant	Argon (present work)	Nitrogen (*20*)
B_o	0.356939	0.733661
A_o	3105.10	4496.95
$C_o \times 10^{-8}$	1.60560	0.719534
b	0.552433	0.508467
a	1741.87	900.069
$c \times 10^{-8}$	1.56230	1.07267
α	0.146285	1.19838
γ	0.60	1.92541

P = lb./sq. in. abs. T = °R. = °F. + 459.688. d = lb.-mole/cu. ft. R = 10.7335 (consistent with references 3 to 5).

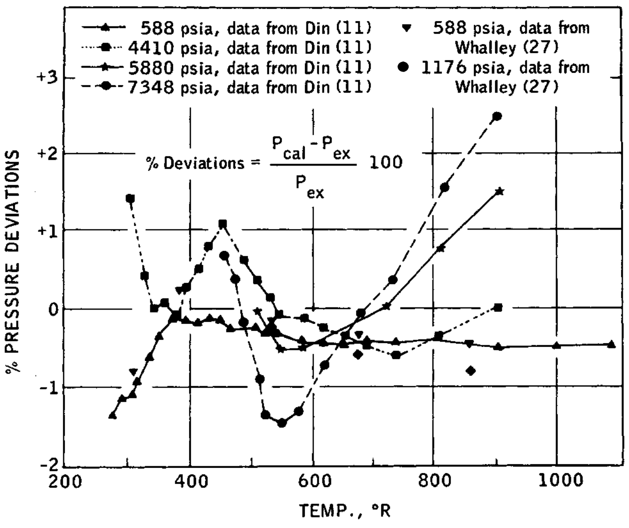

Fig. 2. Deviations in pressure predictions from literature values for argon.

FUGACITY COMPUTATIONS AND FITTING THE BWR EQUATION TO SATURATED ARGON

The original objective in developing the BWR method was to obtain a procedure for calculating the fugacities of components in both their pure state and in mixtures. It follows therefore that the equation of state when applied to either of the phases at equilibrium must predict the same pressure and the same fugacity, that is

$$P_L = P_V \tag{2}$$

and

$$f_L^\circ = f_V^\circ \tag{3}$$

The fugacity of either of the phases, related to the fugacity at unit pressure, is calculated from the following relationship:

$$RT \ln f = RT \ln RTd + 2\,(B_oRT - A_o - C_o/T^2)d + (3/2)(bRT - a)d^2 + (6/5)\,a\alpha d^5 + \frac{cd^2}{T^2}\left[\frac{1}{\gamma d^2} - \left(\frac{1}{\gamma d^2} - \frac{1}{2} - \gamma d^2\right)\exp\,(-\gamma d^2)\right] \tag{4}$$

The variables in Equation (4), including the density d, are the same as those in Equation (1).

For a pure compound, Equation (3) must be satisfied along the vapor pressure curve. Benedict, Webb, and Rubin (*5*) pointed out that the coefficients of Equation (1) vary with the temperature along the vapor pressure curve; but for practicality, they recommended changing only the coefficient C_o with temperature.

Equation (1) can be used to evaluate C_o at each temperature from the vapor pressure and the density of either the saturated vapor or the saturated liquid. Data on the vapor pressure of argon were published by Baly (*1*), Clark et al. (*9*), and Michels et al. (*22*). The properties of saturated argon were smoothed and were tabulated by Din (*11*). These data were utilized to calculate values of C_o along the vapor pressure curve. Two values of C_o rather than the expected single value were obtained at each temperature, one for the vapor and one for the liquid. Furthermore, when these values were used to calculate fugacities, the requirement of Equation (3) could not be met. It was obvious that these C_o's could not be used to calculate phase equilibria and another approach was necessary.

To develop a set of C_o's which can be used in predicting phase equilibria, the following procedure was adopted. At each temperature, a value of C_o was assumed, the densities of the two phases at the vapor pressure were established by trial and error from Equation (1), and the fugacity of the component in each of the phases was calculated via Equation (4). This procedure was repeated until the requirement of Equation (3) was satisfied. The final values of C_o thus established for argon along its vapor pressure curve and the corresponding fugacities are given in Table 2. Fugacities of a saturated simple fluid at the same corresponding state were computed from Pitzer's relationships (*23*); these are also listed in Table 2. The comparison of fugacities obtained with the two methods was needed to verify that the trial and error procedure resulted in coefficients that will yield thermodynamically acceptable fugacities.

It was noticed that at low temperatures and pressures the fugacity of the saturated liquid is sensitive to variations in the fourth decimal place of C_o, while the vapor fugacity is hardly affected. On the other hand, variations in C_o within the vicinity of the critical point equally affect both phases and which make it difficult to zero in on the final values of C_o. Pitzer's fugacities were used as guides for selecting the final values. The above discussion is illustrated in Figure 3. Almost any value of C_o within the segment enclosed by *AB* and *AC* would yield results close to satisfying Equation (3). The solid curve, however, represents the values that yield fugacities close to those calculated by Pitzer's method. The value of $C_o = 1.562 \times 10^8$ at the critical point is somewhat lower than the value established for the superheated region (1.6056×10^8). Extrapolation of the curve *AC* beyond the critical point qualitatively indicated a possibility of improving the utilization of the BWR equations on both sides of the critical point.

VALIDITY TESTS BY CALCULATING DERIVED PROPERTIES

The validity of an equation of state undergoes a severe test when its derivatives are used to calculate the enthalpy difference $H^P - H^*$ which results from isothermal pressure effects. The original expression of Benedict, Webb, and Rubin (*3*) for calculating the above difference was modified in the present work to reflect the temperature dependence of the coefficient C_o along the vapor pressure curve.

TABLE 2. C_o OF SATURATED ARGON FROM FINAL TRIAL EQUATING FUGACITIES

$T°$, °R.	$P°$, lb./sq. in. abs.*	$C_o \times 10^{-8}$†	Fugacity, lb./sq. in. abs. Pitzer's (23) $f^{(o)}$	BWR
149.8	9.99	1.319	9.72	9.52
157.1	14.70	1.350	14.2	14.2
170.0	29.39	1.378	27.9	27.6
178.6	44.09	1.399	41.2	40.6
199.8	102.87	1.447	91.6	89.0
210.3	146.96	1.468	127.2	123.3
234.1	293.92	1.517	222.5	224.5
250.3	440.88	1.537	315.4	318.1
263.0	587.84	1.553	403.1	399.5
271.3	705.41	1.561	470.5	457.0

* Vapor pressure data from references 6 and 8.
† For units see Table 1.

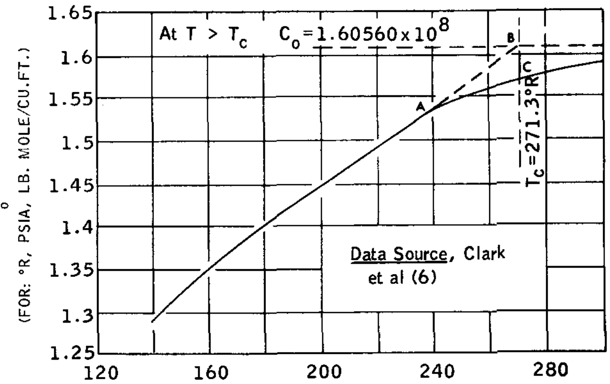

Fig. 3. Values of C_o for argon obtained from fugacity equalization.

Starting with the following expression of the enthalpy departure in terms of the Helmholtz free energy $\tilde{A}$

$$H^p - H^* = A - T\left(\frac{\partial \tilde{A}}{\partial T}\right)_{d,x} + P/d \tag{5}$$

and replacing the various terms by the corresponding derivatives of the BWR equation, one obtains

$$H^p - H^* = \left[B_oRT - 2A_o - \frac{4C_o}{T^2} + \frac{1}{T}\left(\frac{dC_o}{dT}\right)\right] d + (bRT - 1.5a)d^2 + \frac{6}{5}a\alpha d^5 + \frac{cd^2}{T^2}\left[\frac{3}{\gamma d^2}(1 - e^{-\gamma d^2}) - \frac{e^{-\gamma d^2}}{2} + \gamma d^2 e^{-\gamma d^2}\right] \tag{6}$$

Equation (6) is different from the original BWR expression (*3*) as it includes the term $(1/T)/(dC_o/dT)$. An analytical expression relating C_o to the temperature was derived from the values in Table 2 to enable computation of argon enthalpies with Equation (6). In the absence of experimental calorimetric data, computed values of $H^p - H^*$ were compared against literature values that had been obtained by differentiating and integrating P-V-T data. Sample comparisons are shown in Table 3. The comparison would be more significant if calorimetric data were available. With the exception of the value at the critical point, relatively good agreement was observed between enthalpies calculated with Equation (7) and literature values (*11*). The average difference is less than 1.5 B.t.u./lb.

The applicability of the BWR coefficients of argon to vapor-liquid equilibrium calculations was tested by comparing predicted *K* values with the experimental argon-

TABLE 3. ENTHALPY DEVIATIONS FROM THE IDEAL STATE FOR LIQUID ARGON AT SATURATION

$T°$, °R.	P, lb./sq. in. abs.	$(H^p - H^*)_T$, B.t.u./lb. $\Delta H_{\text{Din}\,(11)}$	ΔH_{BWR}
157.10	14.70	−70.15	−67.52
170.00	29.29	−68.45	−66.59
178.70	44.09	−67.19	−65.57
199.80	102.87	−62.76	−62.16
210.30	146.96	−61.29	−60.11
234.10	293.92	−55.73	−54.53
250.30	440.88	−50.25	−49.77
263.00	587.84	−45.66	−45.34
271.30	705.41	−33.27	−41.68

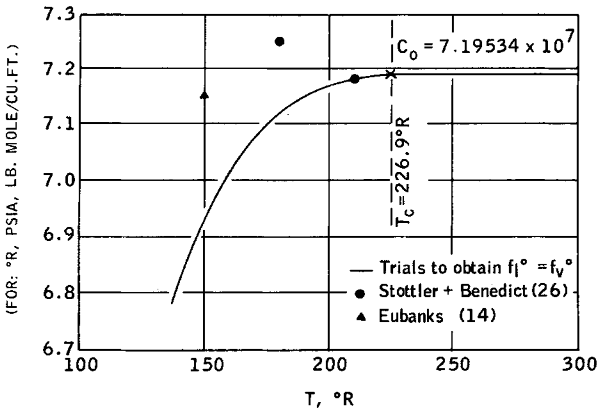

Fig. 4. Values of C_0 for nitrogen obtained from fugacity equalization.

nitrogen data of Holst (*18*) and Wilson et al. (*28*). For this purpose a set of temperature dependent C_o for nitrogen was obtained by the fugacity equalization procedure described previously, since the few points in the literature (*14, 26*) could not be interpolated. These are shown in Figure 4. Predicted equilibrium constants in the temperature range 135° to 233°R. agreed within ±5% with the experimental data. However, the comparisons also indicated certain trends. Most of the predicted values were larger than Wilson's data (*28*) and a maximum deviation of 25% was observed.

CONCLUSIONS

1. The BWR equation of state with the coefficients developed for argon accurately represent the volumetric behavior of this substance in the superheated region. However, two different values of C_o at each temperature, one for the vapor and one for the liquid, are necessary if the equation of state is to be used to calculate the volumetric behavior of the saturated phases along the vapor pressure curve.
2. When the BWR procedure with the above values of C_o is used to calculate the fugacities of saturated vapor and liquid, different values are obtained for each phase; consequently, another set of C_o's had to be obtained by trial-and-error matching the fugacities of the saturated vapor and liquid. The set thus obtained is more useful in calculating phase equilibria and enthalpies.
3. Predicted liquid enthalpies of argon, calculated by the modified BWR expression which takes into account the temperature dependence of the coefficient C_o, were in good agreement with the experimental data. Although vapor-liquid equilibrium constants can be predicted with an average deviation of 5% from the experimental data, additional studies on mixing rules and mixing effects in the argon-nitrogen system are recommended.

ACKNOWLEDGMENT

The authors thank Esso Research and Engineering Company for releasing this work for publication. Also, the authors are indebted to Robert H. Johnston and Lawrence N. Canjar for their helpful suggestions.

NOTATION

$A_o, a, B_o, b, C_o, c, \alpha, \gamma$ = constants of the BWR equation of state

$\tilde{A}$ = Helmholtz free energy, B.t.u./lb.-mole

d = molal density, lb.-mole/cu. ft.

f = fugacity, lb./sq. in. abs.

H = enthalpy, B.t.u./lb.

K = equilibrium constant, dimensionless

P = pressure, lb./sq. in. abs.

R = universal gas constant

T = temperature, °R.

x = mole fraction of liquid

y = mole fraction of vapor

Subscripts

L = liquid

V = vapor

i = indexing of components

Superscripts

$*$ = ideal gas behavior

$^\circ$ = pure compound property

p = property at system pressure

LITERATURE CITED

1. Baly, C. C., and F. G. Donan, *J. Chem. Soc.*, **81**, 907 (1902).
2. Beattie, J. A., and O. C. Bridgeman, *J. Am. Chem. Soc.*, **49**, 1665 (1927).
3. Benedict, M., G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 337 (1940).
4. *Ibid.*, **10**, 747 (1942).
5. Benedict, M., G. B. Webb, and L. C. Rubin, *Chem. Eng. Progr. Symposium Ser.*, **47**, 419 (Aug. 1951).
6. Bridgeman, O. C., *Proc. Am. Acad. Art Sci.*, **70**, 1 (1935).
7. Brough, H. W., W. G. Schlinger, and B. H. Sage, *Ind. Eng. Chem.*, **43**, 2442 (1951).
8. Canjar, L. N., *Petrol. Ref.*, **35**, 113 (February, 1956).
9. Clark, A. M., F. Din, J. Robb, and A. Michels, T. Wassenaar, and Zweitering, *Physica*, **XVII**, No. 10, 876 (1951).
10. Crommelin, C. A., *Commun. Phys. Lab. Univ. Leiden*, 118a (1910).
11. Din, R., ed., "The Thermodynamic Functions of Gases," Vol. 2, Butterworth, London (1959).
12. Efroymson, M. A., in "Mathematical Methods for Digital Computers," A. Ralston and H. S. Wilf, eds., Sect. 17, Wiley, New York (1960).
13. Ellington, R. T., "Notes for Conference on Thermodynamic Properties of Mixtures," Oklahoma State Univ., Stillwater (April 13 and 14, 1964).
14. Eubanks, L. S., Ph.D. thesis, Rice Univ., Houston, Tex. (May, 1957).
15. Fastowskii, V. G., and Y. V. Petrovskii, *Zhur. Phys. Khim*, **30**, 76 (1956).
16. Gyorog, D. A., and E. F. Obert, *A.I.Ch.E. J.*, **10**, No. 5, 621 (1964).
17. Holborn, L., and H. Schutze, *Ann. Phys.*, **47**, 1089 (1915).
18. Holst, G., and L. Hamburger, *Z. Phys. Chem.*, **10**, 513 (1916).
19. Latimer, R. E., *A.I.Ch.E. J.*, **3**, No. 1, 75 (1957).
20. Lin, M. S., and L. M. Naphtali, *ibid.*, **9**, No. 5, 580 (1963).
21. Michels, A., H. Wijker, and H. Wijker, *Physica*, **15**, 627 (1949).
22. Michels, A., J. M. Levelt, and W. de Graff, *ibid.*, **24**, 659 (1958).
23. Pitzer, K. S., and R. J. Curl, Jr., *Ind. Eng. Chem.*, **50**, 265 (1958).
24. Schiller, F. C., and L. N. Canjar, *Chem. Eng. Progr. Symposium Ser. No. 7*, **49**, 67 (1953).
25. Shah, K. K., and George Thodos, *Ind. Eng. Chem.*, **57**, No. 3, 30 (1965).
26. Stottler, H. H., and M. Benedict, *Chem. Eng. Progr. Symposium Ser. No. 6*, **49**, 25 (1953).
27. Whalley, E., Y. Lupien, and Schnider, *Can. J. Chem.*, **33**, 633 (1955).
28. Wilson, G. M., P. M. Silverberg, and M. G. Zellner, paper presented at Cryogenic Eng. Conf., Philadelphia, Pa. (August 17-21, 1964).

Manuscript received July 23, 1965; revision received January 18, 1966; paper accepted January 21, 1966. Paper presented at A.I.Ch.E. San Francisco meeting.