Corrections to C_0 for the Benedict-Webb-Rubin Equation

S. K. SOOD and G. G. HASELDEN
The University of Leeds, Leeds, England

The well-known eight parameter Benedict-Webb-Rubin equation of state was formulated in 1940 (*1, 2*) to specifically describe the behavior of light hydrocarbons and their mixtures for reduced temperatures greater than 0.6. The limitations of this method, however, have been well known and together with suggested modifications have been summarized by Canjar (*4*), Lin (*11*), Ellington (*10*), and Starling et al. (*15*). Difficulties have been experienced in predicting P-V-T relationships within the critical region and vapor-liquid equilibrium K ratios at low temperatures.

While the B-W-R equation has been successfully applied to paraffin and olefin systems, accurate extension to other systems or to the cryogenic region necessitates the introduction of special interaction constants. The work of Benedict and Stotler (*3*) and others indicates that at least one and possibly three or more interaction constants would be required.

If the B-W-R equation is to be used for cryogenic phase-equilibria calculations, it should predict correct vapor pressures as the mixture composition approaches the limit of a pure component. Benedict and Stotler (*3*) suggested that this be done by varying the B-W-R coefficient C_0 at intervals along the vapor pressure curve of the pure component. By making C_0 temperature dependent, Barner and Schreiner (*7*) were able to accurately predict the enthalpy behavior of a 94.9% methane, 5.1% propane mixture for temperatures as low as −160°F. under pressures from 260 to 1,500 lb./sq.in.abs. Barner and Adler (*6*) and Zudkevitch and Kaufmann (*18*) have further testified to the reliability of this modification for phase-equilibria and enthalpy calculations at low temperatures. This approach has also been used by Kaufmann (*12*), Lee et al. (*13*), and McCracken and Mullins (*14*). Wilson (*17*) has also used the same method to modify the constant a for the two-constant Redlich-Kwong equation with good results.

A recent paper by Orye (*22*) has presented C_0 polynomials for eighteen compounds using the variable $\Delta C_0^{1/2}(T) = C_0^{*1/2} - C_0^{1/2}(T)$. The form of this equation is not explained, and the results are presented in pounds per feet per degrees Rankin. He also describes the introduction of a single mixing parameter for the combination of A_0 coefficients for use with wide boiling mixtures.

The authors, equating vapor and liquid fugacities along the vapor-pressure curve, have derived alternative correlations for C_0 using a normalized form in the following way:

$$C_0/C_0^* = A_0 + A_1\phi + A_2\phi^2 + A_3\phi^3 + A_4\phi^4 \qquad (1)$$

where C_0^* is the published high temperature value for C_0 of each substance and $\phi = \dfrac{T_c - T}{T_c}$, where T_c is the critical temperature. The vapor-pressure data required for the fitting procedure has been obtained from Timmermans (*16*) except for nitrogen and argon, where the source was Din (*9*) and for isobutane Canjar et al. (*5*). The authors confirm the view of others (*12, 14*) that a fourth-order polynomial is sufficiently accurate to represent the C_0 curves. Approximately thirty points have been used to fit each polynomial by using a linear least-squares technique.

Making C_0 temperature dependent adds on a derivative term $\rho/T\ (dC_0/dT)$ to the isothermal enthalpy expression originally published (*2*). From Equation (1)

$$\frac{1}{C_0^*} \times \frac{dC_0}{dT} = -\frac{1}{T_c}\left[A_1 + 2A_2\phi + 3A_3\phi^2 + 4A_4\phi^3\right] \qquad (2)$$

Table 1 gives a list of C_0 polynomial coefficients for sixteen industrially important fluids. The table supplements that given by Orye (*22*) in two important respects. Firstly, by using reduced (dimensionless) units it can be employed with any dimensionally consistent set of units, and secondly it includes the additional components argon, nitrogen, carbon monoxide and 1-butene. The temperature range of application is clearly indicated. It is suggested that outside this temperature range C_0^* be used as the value for C_0. Table 1 also shows the standard mean deviation of the normalized C_0 values obtained from the polynomials. It is important to note that these polynomials are specific to the full set of eight B-W-R constants used in obtaining the temperature variant C_0 values. For hydrocarbons only, these constants were obtained from Sherwood and Reid (*21*). They are also available in the tabulation of Cooper and Goldfrank (*20*). For the nonhydrocarbon compounds, except as indicated in Table 1, all the values were obtained from Cooper and Goldfrank (*20*). Where more than one set of constants was presented for one compound, the criterion of selection was applicability of the constants in both the vapor and liquid phases. Of these, the set applicable over the largest pressure and temperature range was chosen.

By using C_0 variation, an enthalpy comparison has been carried out on data obtained at the University of Leeds (*8*) by using an isobaric flow calorimeter. A simulated natural gas of nominal composition given in Table 2 was used. The enthalpy differences were measured from an inlet temperature of +100°C. to an outlet temperature from 0° to −120°C., and the data covered two isobars at 400 and 550 lb./sq.in.abs. with most of the results being in the two phase and the all liquid region. The average deviation of all fifty-four enthalpy predictions was only 0.7%, with a largest single deviation of 2% in the all liquid region. An enthalpy comparison for ten sample data points in the two phase and all liquid regions is shown in Table 3.

CONCLUSION

Polynomials have been presented for the C_0 variation of sixteen important compounds in a form which is suitable for computation. The polynomials have been tested for a five-component natural gas mixture and shown to represent low temperature enthalpy data very well.

LITERATURE CITED

1. Benedict, Manson, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940); **10**, 747 (1942).
2. ——————, and Leo Friend, *Chem. Eng. Progr.*, **47**, 419, 449, 571, 609 (1951).
3. Benedict, Manson, and H. H. Stotler, *Chem. Eng. Progr.*

TABLE 1. POLYNOMIAL COEFFICIENTS FOR C_0 ADJUSTMENT EQUATION IN UNITS OF LITRE-ATM. -GM. MOLE-°K

Compound	Standard mean deviation	Temp. range, °K.	A0	A1	A2	A3	A4
Nitrogen*	Not given	Not given	1.00000	-1.689605×10^{-1}	3.606153	−8.621769	5.339828
Nitrogen	9.45×10^{-4}	63 to 126	0.9997103	-2.526856×10^{-3}	4.381323×10^{-2}	-4.726279×10^{-2}	9.256033×10^{-3}
Carbon monoxide	2.02×10^{-2}	64 to 133	1.018458	−2.638971	9.586363	−14.756768	7.603512
Argon	4.82×10^{-3}	70 to 151	0.9987691	−0.7174757	2.651036	−6.601487	5.3088647
Oxygen*	Not given	Not given	1.00000	0.8689789	0.9792821	−1.248256	−2.175794
Methane	1.06×10^{-3}	90 to 191	0.9979814	-3.320010×10^{-2}	2.962412×10^{-1}	−1.932208	1.1346987
Ethylene	3.91×10^{-3}	124 to 280	0.9947091	0.2463640	−1.411671	2.881806	−2.871082
Carbon dioxide	2.73×10^{-2}	139 to 304	1.071528	−2.413171	20.329057	−46.96394	32.152077
Ethane	1.43×10^{-4}	136 to 305	1.000434	0.2715179×10^{-1}	-4.379819×10^{-2}	−0.4433283	−0.2001602
Propylene	2.82×10^{-3}	166 to 363	0.9858207	0.3294600	−1.7105199	3.5640557	−34.42999
Propane	2.73×10^{-4}	145 to 370	0.9965831	1.574242×10^{-2}	0.2005013	−0.8345010	-2.544982×10^{-2}
iso-butane	4.74×10^{-3}	183 to 408	0.9997103	-8.168955×10^{-3}	0.4579070	−1.596897	1.0110428
1-butene	7.51×10^{-3}	216 to 398	1.006835	0.8245186×10^{-1}	−0.3141616	4.366620×10^{-3}	0.430830×10^{-4}
n-butane	2.97×10^{-2}	195 to 403	0.9319580	1.192142	−2.6581867	17.290853	−28.408991
iso-pentane	1.68×10^{-4}	231 to 461	0.9992118	$-0.1386477 \times 10^{-1}$	0.5157715	−1.430737	0.5618867
n-pentane	1.45×10^{-3}	224 to 470	0.9972927	0.3197312×10^{-1}	$-0.5942343 \times 10^{-1}$	0.284999	−1.1674545

* Values from McCracken and Mullins (*14*).

TABLE 2. NOMINAL COMPOSITION OF SIMULATED NATURAL GAS MIXTURE

Component	Mole %
Nitrogen	4.00
Methane	90.83
Ethane	3.76
Propane	1.07
iso-butane	0.34
	100.00

TABLE 3. ENTHALPY PREDICTION OF SIMULATED NATURAL GAS MIXTURE

Outlet temp., °K.	Pressure, atm.	Predicted vapor fraction, V	Measured enthalpy change, cal./g. mole	Predicted enthalpy change, cal./g. mole
192.95	27.99	0.936	1941.8	1941.4
181.33	28.13	0.763	2324.7	2319.2
177.61	27.40	0.628	2495.8	2507.3
170.93	28.15	0.207	3293.7	3298.4
156.50	28.15	Liquid	3563.0	3542.8
201.86	38.28	0.953	1891.0	1891.3
193.16	38.43	0.847	2161.4	2132.0
187.98	38.47	0.598	2452.2	2456.2
186.61	38.62	0.452	2605.1	2604.1
179.93	38.62	Liquid	3121.7	3102.7

Symposium Ser. No. 6, **49**, 25 (1953).
4. Canjar, L. N., *Petrol. Ref.*, **35**, 113 (1956).
5. ———, D. Nahmias, and F. S. Manning, *ibid.*, **42**, No. 8, 127 (1963).
6. Barner, H. E., and S. B. Adler, *Hydrocarbon Process.*, **47**, No. 10, 150 (1968).
7. Barner, H. E., and W. C. Schreiner, *ibid.*, **45**, No. 6, 161 (1966).
8. Banks, R., Ph.D. thesis, Univ. Leeds, England (1968).
9. Din, F., ed., "The Thermodynamic Functions of Gases," Vols. 1, 2, Butterworth, London, England (1959).
10. Ellington, R. T., "Notes for Conference on Thermodynamic Properties of Mixtures," Okla. State Univ., Stillwater (Apr. 13, 14, 1964).
11. Lin, M. S., and L. M. Naphtali, *AIChE J.*, **9**, No. 5, 580 (1963).
12. Kaufmann, T. G., *Ind. Eng. Chem. Fundamentals*, **7**, 155 (1968).
13. Lee, T. W., S. B. Wyatt, S. H. Desai, and K. C. Chao, Chicago Bridge and Iron Co., Oakbrook, Ill. (May, 1968).
14. McCracken, T. A., and J. C. Mullins, *Final Rept. No. 012.*, Contract No. GK-1016, National Science Foundation, Washington, D. C.
15. Starling, K. E., J. L. Bono, N. F. Carnahan, Y. C. Kwok, paper presented at proc. of 47th, convn. of NGPA, New Orleans, La. (Mar. 19-21, 1968).
16. Timmermans, J., "Physiochemical Constants of Pure Organic Compounds," Vols. 1, 2, Elsevier, New York (1950).
17. Wilson, G. M., *Advan. Cryog. Eng.*, **9**, 168 (1964).
18. Zudkevitch, David, and T. G. Kaufmann, *AIChE J.*, **12**, No. 3, 577 (1966).
19. Prausnitz, J. M., and P. L. Chueh, "Computer Calculations for High-Pressure Vapor-Liquid Equilibria, Prentice-Hall, Englewood Cliffs, N. J. (1968).
20. Cooper, H. W., and J. C. Goldfrank, *Hydrocarbon Process*, **46**, No. 12, 141 (1967).
21. Sherwood, T. K., and R. C. Reid, "The Properties of Gases and Liquids, 2 ed., McGraw-Hill, New York (1966).
22. Orye, R. V., *Ind. Eng. Chem., Process Design Develop.*, **8**, No. 4, 579 (Oct., 1969).