have shown, methods of approximating the acentric factor do not always match the value calculated from the definition.

The exponents of $T_c - T$ do not correlate well because this simple formula is not exact. As can be seen from the figures, the latent heat varies in a manner slightly more complicated than $(T_c - T)^n$.

CONCLUSION

The latent heat equation $L = k\ (T_c - T)^n$ has been fitted for 44 substances with an average value of n of 0.378. This value is little different from 0.38 proposed by Watson (*58*) in 1931. The exponent was found to be a random variable against various parameters that might have been expected to correlate it.

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LITERATURE CITED

(1) Barkelew, C.H., Valentine, J.L., Hurd, C.O., *Trans. Am. Inst. Chem. Engrs.* **43**, 25 (1947).
(2) Benning, A.F., McHarness, R.C., E. I. DuPont de Nemours & Co., Wilmington, Del., *DuPont Bull.* **T-21**, 1939.
(3) *Ibid.*, **T-114B**, 1944.
(4) Bowden, S.T., *J. Chem. Phys.* **23**, 2454 (1955).
(5) Brydon, J.W., Walen, N., Canjar, L.N., *Chem. Eng. Progr. Symp. Ser.* **49**, No. 7, 151 (1953).
(6) Canjar, L.N., Goldman, M., Marchman, H., *Ind. Eng. Chem.* **43**, 1186 (1951).
(7) Christensen, L.D., Smith, J.M., *Ibid.*, **42**, 2128 (1950).
(8) DeWijs, J.C., *Rec. Trav. Chim.* **62**, 449 (1943).
(9) Din, F., "Thermodynamic Functions of Gases," Vol. **1**, pp. 75-89, 122, 164, Butterworths Scientific Publications, London, 1956.
(10) *Ibid.*, Vol. **2**, p. 56, 116.
(11) Dobratz, C.J., *Chem. Eng.* 144, February 10, 1958.
(12) DuPont de Nemours, E. I. & Co., Wilmington, Del., *DuPont Bull.* **T-11A**, 1942.
(13) *Ibid.*, **T-11B**, 1938.
(14) *Ibid.*, **T-11C**, undated.
(15) *Ibid.*, **T-12**, 1956.
(16) *Ibid.*, **T-12S**, 1956.
(17) *Ibid.*, **T-13**, 1959.
(18) *Ibid.*, **T-13B1**, 1963.
(19) *Ibid.*, **T-14**, 1961.
(20) *Ibid.*, **T-22A**, 1945.
(21) *Ibid.*, **T-22D**, 1963.
(22) *Ibid.*, **T-113A**, 1938.
(23) *Ibid.*, **T-113B**, undated.
(24) *Ibid.*, **T-114A**, undated.
(25) *Ibid.*, **T-114C**, undated.
(26) *Ibid.*, **T-115**, 1958.
(27) *Ibid.*, **T-502**, 1963.
(28) DuPont de Nemours, E. I. & Co., Wilmington, Del., *DuPont P-H Diagram for Freon 116*, undated.
(29) DuPont de Nemours, E. I. & Co., Wilmington, Del., *DuPont Tech. Bull.* **B-2**, 1962.
(30) DuPont de Nemours, E.I., & Co., Wilmington, Del., *DuPont P-H Diagram for Freon C-318*, undated.
(31) Goodwin, R.D., Diller, D.E., *et. al.*, *Natl. Bur. Stds. Rept.* **6791**, 1961.
(32) Gosman, A.L., Hust, J.G., McCarty, R.D., *Ibid.*, **8293**, 1964.
(33) "Handbook of Chemistry and Physics," 39th ed. p. 2123, Chemical Rubber Publishing Co., Cleveland, Ohio, 1957.
(34) Hanson, G.H., *Trans. Am. Inst. Chem. Engrs.* **42**, 959 (1946).
(35) Huisman, J., Sage, B.H., J. CHEM. ENG. DATA **9**, 223 (1964).
(36) Jones, W.J., Bowden, S.T., *Phil. Mag.* **37**, 480 (1946).
(37) Kay, W.B., *J. Am. Chem. Soc.* **68**, 1336 (1946).
(38) Keenan, J.H., Keyes, F.G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
(39) Kendall, J., *J. Am. Chem. Soc.* **36**, 1620 (1914).
(40) Lu, B.C., *Can. J. Chem. Eng.* **42**, 123 (1964).
(41) McCarthy, R.D., Stewart, R.B., *Advan. Cryog. Eng.* **9**, (1964).
(42) Matthews, C.S., Hurd, C.O., *Trans. Am. Inst. Chem. Engrs.* **42**, 55 (1946).
(43) Meyers, C.H., Cragoe, C.S., Mueller, E.F., *J. Res. Natl. Bur. Stds.* **39**, 507 (1947).
(44) Mock, J.E., Smith, J.M., *Ind. Eng. Chem.* **42**, 2125 (1950).
(45) Mullins, J.C., Ziegler, W.J., Kirk, B.S., Georgia Institute of Technology, Atlanta, Ga., Project No. A-593, Tech. Rept. **1**, 1961.
(46) Nutting, P.G., *Ind. Eng. Chem.* **22**, 771 (1930).
(47) O'Brien, L.J., Alford, W.J., *Ibid.*, **43**, 506 (1951).
(48) Organick, E.I., Studhalter, W.R., *Chem. Eng. Progr.* **44**, 847 (1948).
(49) Pitzer, K.S., Lippman, D.Z., Curl. R.F., Jr., Huggins, C.M., Peterson, P.E., *J. Am. Chem. Soc.* **77**, 3433 (1955).
(50) Rynning, D.F., Hurd, C.O., *Trans. Am. Inst. Chem. Engrs.* **41**, 265 (1945).
(51) Schnaible, H.W., Smith, J.M., *Chem. Eng. Progr. Symp. Ser.* **49**, No. 7, 159 (1953).
(52) Smith, J.M., *Chem. Eng. Progr.*, **44**, 521 (1948).
(53) Stewart, D.E., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **46**, 2592 (1954).
(54) Stull, D.R., *Ibid.*, **39**, 542 (1947).
(55) Tanner, H.G., Benning, A.F., Mathewson, W.F., *Ibid.*, **31**, 878 (1939).
(56) Thiesen, A., *Verhl. Deut. Phys. Ges.* **16**, 80 (1897).
(57) Thompson, W.H., Braun, W.G., American Petroleum Institute 29th Midyear Meeting, Preprint No. 06-64, St. Louis, Mo., 1964.
(58) Watson, K.M., *Ind. Eng. Chem.* **23**, 362 (1931).
(59) West, J.R., *Chem. Eng. Progr.* **44**, 287 (1948).
(60) Wilson, G.M., Silverberg, P.M., Zellner, M.G., Air Products & Chemicals, Inc., Tech. Documentary Rept. No. **APL-TDR-64-64**, 1964.
(61) Winter, R.M., *J. Phys. Chem.* **32**, 576 (1928).
(62) York, R., Jr., White, E.F., Jr., *Trans. Am. Inst. Chem. Engrs.* **40**, 227 (1944).

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Application of Benedict-Webb-Rubin Equation of State to Ammonia

R. S. RAMALHO[1] and W. G. FRIZELLE[2]
University of Rochester, Rochester, N. Y.

THE BENEDICT-WEBB-RUBIN EQUATION of state (hereafter called BWR equation) has been used primarily in predicting the thermodynamic properties of light hydrocarbons and light hydrocarbon mixtures (*1-7, 13, 15, 18, 19, 21, 23*). Some effort has been extended towards investigation of the applicability of the BWR equation to polar compounds, and successful results have been achieved with nitrous oxide (*16*), carbon dioxide (*9*), sulfur dioxide (*14*), and nitrogen-carbon monoxide (*12*) systems. The objectives of this work are: to determine the coefficients for the BWR equation for ammonia from available pressure-volume-

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[1] Present address: Laval University, Quebec, Canada
[2] Present address: General Motors Institute, Flint, Mich.

The Benedict-Webb-Rubin equation of state has been used primarily in predicting the thermodynamic properties of light hydrocarbons and light hydrocarbon mixtures. In this paper, the applicability of the Benedict-Webb-Rubin equation to a highly polar system, namely ammonia, is evaluated.

temperature data, to study whether this equation represents satisfactorily the volumetric behavior, and to utilize it to calculate thermodynamic properties of ammonia. The properties considered include enthalpy, entropy, isobaric heat capacity, isometric heat capacity, fugacity, and Joule-Thomson coefficients.

DETERMINATION OF COEFFICIENTS

The BWR equation is commonly written as:

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

After appropriate manipulation, Equation 1 may be rewritten in terms of the compressibility factor, z_{cal} as:

$$z_{\text{cal}} = \frac{PV}{RT} = 1 + \left(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right)\frac{1}{V} + \left(b - \frac{a}{RT}\right)\frac{1}{V^2} + \left(\frac{a\alpha}{RT}\right)\frac{1}{V^5} + \left[\frac{c}{RT^3}\left(1 + \frac{\gamma}{V^2}\right)e^{-\gamma/V^2}\right]\frac{1}{V^2} \tag{2}$$

The problem involves the determination of the BWR constants such that there is a minimum deviation between calculated and experimental compressibility factors:

$$Z_n = z_{\text{cal},n} - z_n \tag{3}$$

The subscript, n, refers to the n_{th} measurements for a particular system under consideration. The minimum error corresponds to the condition for which the sum of the squares of the deviations is a minimum.

The method proposed by Brough (*8*) was used in the determination of the coefficients. The method consists of determining the seven coefficients: A_o, B_o, C_o, a, b, c, and α for assumed values of γ. A seven-by-seven matrix is established for each assumed γ, which is then solved by computer methods for matrix solution. The sum of the squares of the residuals is then calculated for each set of coefficients and plotted against the corresponding γ's. The optimum γ is then taken as the one leading to the minimum value of the sum of the squares of the residuals. All calculations were performed using digital computors. Programs were written in Fortran language.

English units were used throughout the calculations although the input and output data were usually in metric units. The BWR constants are reported here in English units.

COEFFICIENTS FOR AMMONIA

The BWR constants were determined separately for liquid and vapor ammonia using data published by Davies (*10*). Four-hundred and five sets of P-V-T data were used in each instance, with pressure and temperature ranges as shown below:

	Liquid	Vapor
Pressure	20 to 800 atm.	1 to 1100 atm.
Temperature	310° to 400° K.	300° to 580° K.

The computer programs used were tested by recalculation of values for carbon monoxide (*22*) and nitrous oxide (*16*), which are available in the literature.

Serious consideration was given in the selection of the values of γ to be used in the least squares procedure outlined above. Investigation of the literature showed that for all systems studied, only positive values of γ have been reported. However, for a single component system there is no thermodynamic justification for gammas to be either negative or positive (*11*). A possible reason for the fact that negative gammas have not been reported is that only positive values can be used for the calculation of thermodynamic properties of mixtures. Benedict, Webb, and Rubin (*2*) have shown that for mixture calculations, the values of the BWR constants are functions of the values of the corresponding constants for the single components and their mole fractions in the mixture, the value of γ for a mixture being given by:

$$\gamma = \left[\sum_i x_i(\gamma_i)^{1/2}\right]^2 \tag{4}$$

where the subscripts refer to component i.

Equation 4 rules out the possibility of use of negative gammas, since imaginary values would result. Conceivably, however, in the single component systems, a negative γ may lead to a minimum value for the sum of the squares of the residuals mentioned above.

In this investigation, both positive and negative values of γ were considered.

For the vapor region, a value of $\gamma = -1.046$ leads to an absolute minimum for the sum of the squares of the residuals. A positive $\gamma = 5.082$ also results in a minimum for the vapor region as shown by Figures 1 and 3. For the

Table I. B-W-R Constants for Ammonia and Sum of the Squares of Residuals

	Vapor Region		Liquid Region	
Constant	Positive Gamma	Negative Gamma	Positive Gamma	Units
B_o	0.82730548	0.65427773	0.053902442	ft.^{3}/lb. mole
A_o	972.32957	841.30569	519.85938	(ft.^{3}/lb. mole)^2 atm.
C_o	148460950.0	17436490.0	50223701.0	(ft.^{3}/lb. mole)^2 (° R.)^2 (atm.)
b	0.18464544	+0.13664276	0.73166422	(ft.^{3}/lb. mole)^2
a	425.59268	+0.0089864025	0.069045632	(ft.^{3}/lb. mole)^3 (atm.)
α	0.019122334	+0.0089864025	0.069045632	(ft.^{3}/lb. mole)^3
c	2097979.6	+49632.400	22949623.0	(ft.^{3}/lb. mole)^3 (R)^2 (atm.)
	5.082	−1.046	0.170	(ft.^{3}/lb. mole)^2
Sum of the Squares of Residuals	0.44128649	0.083849217	2.9304745	

Table II. Average Absolute Percentage Deviation (A.A.P.D.) of Thermodynamic Properties of Ammonia Computed in this Work

	Pressure Range, Atm.				Pressure Range, Atm.				Pressure Range, Atm.			
Property	1 to 80	90 to 450	500 to 1100	Total 1 to 1100	1 to 80	90 to 450	500 to 1100	Total 1 to 1100	20 to 260	280 to 500	550 to 800	Total 20 to 800
	Vapor ($\gamma = 1.046$)				Vapor ($\gamma = 5.082$)				Liquid ($\gamma = 0.170$)			
Volume iteration $[(V_{i+1} - V_i)/V_i] \times 100$	0.12	0.16	0.07	0.12	0.14	0.11	0.13	0.13	0.18	0.11	0.07	0.14
Volume	0.97	1.72	0.80	1.16	1.03	1.94	1.49	1.38	10.01	5.52	5.19	6.91
Pressure	0.11	0.21	0.22	0.17	0.13	0.20	0.45	0.24	6.54	1.38	0.79	2.90
Enthalpy	3.18	1.35	0.74	1.88	3.15	1.53	0.96	1.99	11.09	11.32	10.87	11.12
Entropy	8.91	10.76	12.07	10.40	8.91	10.83	12.15	10.45	11.21	11.29	11.57	11.30
Isobaric heat capacity	5.94	13.01	24.89	13.37	6.28	10.70	18.10	10.97	5.95	7.22	6.37	6.44
Isometric heat capacity	4.83	16.56	46.12	19.72	5.37	13.59	35.90	16.21	4.92	2.90	2.17	2.92
Fugacity	1.04	3.00	6.66	3.20	1.13	3.37	5.97	3.19	69.30	67.83	70.72	69.01
Joule-Thompson coefficient	67.84	66.71	70.18	55.68	67.96	67.14	75.81	69.68	57.55	61.26	57.18	58.68

liquid region, an optimum positive $\gamma = 0.170$ was found. In calculating the thermodynamic properties of ammonia vapor, both the negative and positive gammas were considered and values are reported for both cases. An attempt was made to fit the data for the vapor and liquid regions with a single set of constants, but the results were extremely poor. Similar difficulty was encountered for the systems sulfur dioxide (*14*) and nitrous oxide (*16*). Values for the BWR constants for ammonia are presented in Table I.

Figures 1, 2, 3, and 4 are plots of the sum of the squares of the residuals against assumed gammas for the vapor and liquid regions.

THERMODYNAMIC PROPERTIES OF AMMONIA DETERMINED BY THE BWR EQUATION

Use of the BWR equation to predict thermodynamic properties requires the knowledge of the equation constants for the system in question and the pressures and specific volumes at any given temperature. In practice, it is convenient to do calculations as function of temperature and pressure over definite intervals. It is then necessary to determine the volume at any given temperature and pressure. Since Equation 1 is implicit in volume (explicit in pressure), volumes were calculated by means of Newton's

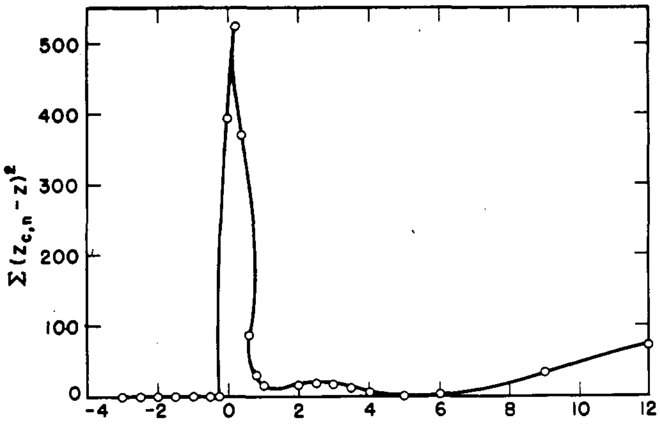

Figure 1. Effect of gammas on sum of squares of residuals over a wide range of gammas (vapor region)

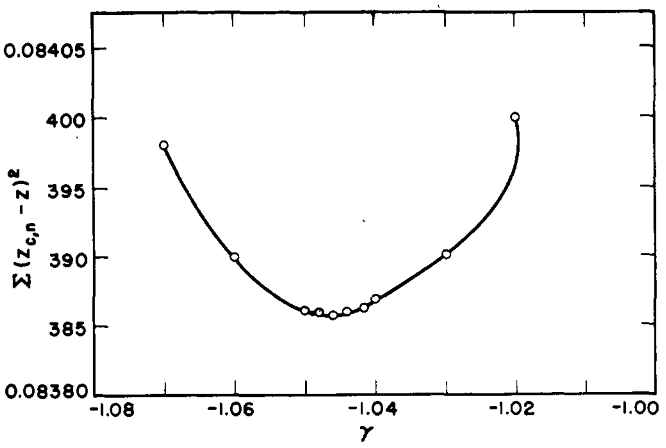

Figure 2. Effect of gammas on sum of squares of residuals in the vicinity of the optimum negative gamma (vapor region)

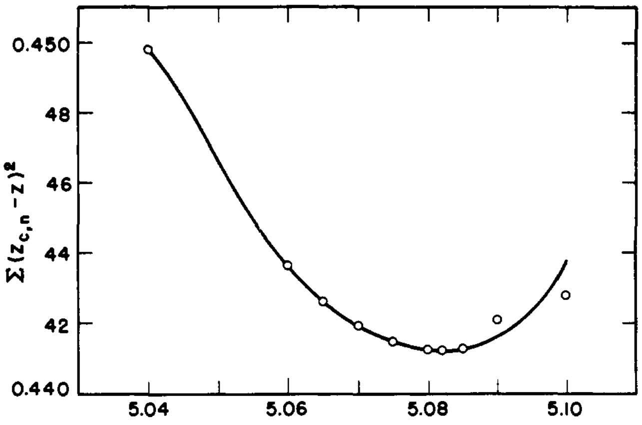

Figure 3. Effect of gammas on sum of squares of residuals in the vicinity of the optimum positive gamma (vapor region)

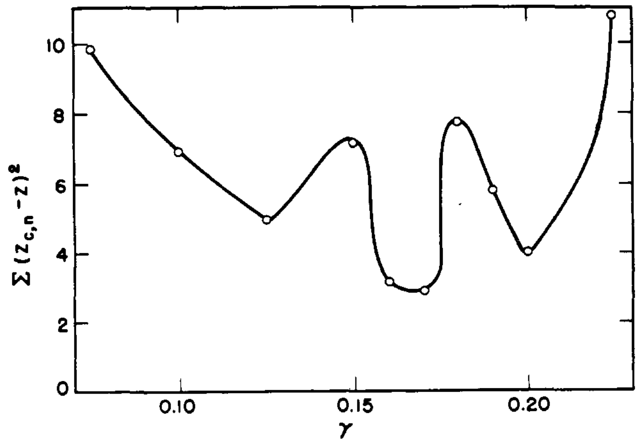

Figure 4. Effect of gammas on sum of squares of residuals in the vicinity of the optimum gamma (liquid region)

iteration method. The volume is defined as:

$$V_{i+1} = V_i + \frac{P - P(V_i)}{\mathrm{d}P(V_i)/\mathrm{d}V} \qquad (5)$$

where $\mathrm{d}P(V_i)/\mathrm{d}V$ is the rate of change in pressure at V_i with change in volume. V_{i+1} was accepted as a final volume when the absolute value of its relative deviation from V_i, $|(V_{i+1} - V_i)/V_i|$ was less than 0.005. A comparison of the calculated volumes with those reported by Davies (*10*) is given in Table II.

The calculation of thermodynamic properties was then performed using *P-V-T* data established by the iteration process. The data were arbitrarily broken down into three groups: low pressure range—0.1 to 80 atm. for the vapor region and 20 to 260 atm. in the liquid region; intermediate pressure range—90 to 450 atm. for the vapor region, 280 to 500 atm. for the liquid region; and high pressure range—50 to 1100 atm. for the vapor region, 550 to 800 atm. for the liquid region.

The average absolute percentage deviation defined as:

$$\text{A.A.P.D.} = \left(\frac{\text{Davies' Value } (10) - \text{Calcd. value, this work}}{\text{Davies' Value}}\right) \times 100 \qquad (6)$$

Reference conditions in the vapor and liquid state were chosen as follows:

	Vapor	Liquid
T_o	240° K.	240° K.
P_o	1.0124 atm.	1.0124 atm.
H_o	8856 cal./gram mole	3291 cal./gram mole
V_o	18,905 cm.^{3}/gram mole	24.99 cm.^{3}/gram mole
S_o	43.95 cal./(gram mole)(° K.)	20.76 cal./(gram mole)(° K.)

All data used for reference conditions were taken from the tables compiled by Davies (*10*). In these tables, the enthalpy and entropy were taken as zero at absolute zero temperature. Since zero could not be tolerated in the denominator of certain terms of the BWR equation the above values were chosen as reference conditions. They are approximately the same reference state of other published data for ammonia (*20*) (233° K., 0.696 atm.).

The integrals for heat capacity were evaluated by integration of the general equation published by Obert (*17*):

$$C_p^* = a' + b'(10^{-3})T + c'(10^{-6})T^2 + d'(10^{-9})T^3 \qquad (9)$$

where for ammonia in the temperature range 273° to 1500° K.: $a' = 6.5846$, $b' = 6.1251$, $c' = 2.3663$, $d' = 1.5981$. Isobaric heat capacities were calculated from:

$$C_p = \frac{T\left[R + \frac{B_oR}{V} + \frac{2C_o}{T^3V} + \frac{bR}{V^2} - \frac{2c}{V^2T^3}\left(1 + \frac{\gamma}{V^2}\right)e^{-\gamma/V^2}\right]^2}{RT + \frac{2(B_oRT - A_o - C_o/T^2)}{V} + \frac{3(bRT - a)}{V^2} + \frac{6a\alpha}{V^5} + \frac{ce^{-\gamma/V^2}}{V^2T^2}\left(3 + \frac{3\gamma}{V^2} - \frac{2\gamma^2}{V^4}\right)} +$$

$$\frac{C_o\gamma}{T^3V} + \frac{6c(e^{-\gamma/V^2} - 1)}{\gamma T^3} + \frac{3ce^{-\gamma/V^2}}{T^3V^2} + a' + b'T + c'T^2 + d'T^3 - R \qquad (10)$$

is presented for each property calculated in Table II. Extensive tabulations of predicted and experimental values are available (*12*). Detailed derivation of all equations used as well as complete listing of computer output are also available (*12*).

Enthalpy calculations were carried out using the equation:

$$H = \Delta H^{VAP}_{T_o,P_o} - P_oV_o + RT_o + \frac{3C_o}{V_oT_o^2} + \frac{A_o}{V_o} + \frac{a}{2V_o^2} - \frac{a\alpha}{5V_o^5} +$$

$$\frac{3ce^{-\gamma/V_o^2}}{T_o^2} + \frac{3ce^{-\gamma/V_o^2}}{2T_o^2V_o^2} \quad \frac{3c}{T_o^2} + \int_{T_o}^{T} C_p^*\,\mathrm{d}t + PV - RT - \frac{3C_o}{VT^2} -$$

$$\frac{A_o}{V} - \frac{a}{2V^2} + \frac{a\alpha}{5V^2} - \frac{3ce^{-\gamma/V^2}}{T^2\gamma} - \frac{3ce^{-\gamma/V^2}}{2T^2\gamma^2} + \frac{3c}{T^2\gamma} \qquad (7)$$

where $\Delta H^{VAP}_{T_o,P_o}$ is the enthalpy of vaporization at the reference conditions. Entropy calculations were performed using the equation:

$$S = \frac{\Delta H^{VAP}_{T_o,P_o}}{T_o} + \frac{B_oR}{V_o} + \frac{2C_o}{T_o^3V_o} + \frac{bR}{2V_o^2} + \frac{2ce^{-\gamma^2/V_o^2}}{\gamma T_o^3} +$$

$$\frac{ce^{-\gamma/V_o^2}}{T_o^3V_o^2} - \frac{2c}{T_o^3} + \int_{T_o}^{T} \frac{C_p^*}{T}\,\mathrm{d}T + R\ln\frac{V}{V_o} - \frac{B_oR}{V} -$$

$$\frac{2C_o}{T^3V} - \frac{bR}{2V^2} - \frac{2ce^{-\gamma/V^2}}{\gamma T^3} - \frac{ce^{-\gamma/V^2}}{T^3V^2} + \frac{2c}{\gamma T^3} \qquad (8)$$

Isometric heat capacities were calculated from:

$$C_v = \frac{6C_o}{T^3V} + \frac{6c(e^{-\gamma/V^2} - 1)}{\gamma T^3} + \frac{3ce^{-\gamma/V^2}}{T^3V^2} -$$

$$b'T - c'T^2 - d'T^3 - R \qquad (11)$$

Fugacity values were determined using the following relationship:

$$RT\ln f = RT\ln\frac{RT}{V} + 2\left(\frac{B_oRT - A_o - C_o/T^2)}{V}\right) + \frac{3(BRT - a)}{2V^2} +$$

$$\frac{6a\alpha}{5V^5} + \frac{c}{T^2V^2}\left[V^2\frac{(1 - e^{-\gamma/V^2})}{\gamma} + \frac{e^{-\gamma/V^2}}{2} + \frac{e^{-\gamma/V^2}}{V^2}\right] \qquad (12)$$

Fugacity data for the vapor were compared with the values obtained by graphical integration of:

$$\ln\frac{f}{P} = \int_{P_o}^{P} \frac{z - 1}{P}\,\mathrm{d}P \qquad (13)$$

utilizing the compressibility factors calculated from tabulated Davies (*10*) *P-V-T* data.

Fugacity data for the liquid were determined by the method outlined by Smith and Van Ness (*24*). Vapor pressure data were obtained from Davies' wall-sized chart and specific volumes for the liquid were those tabulated by Davies (*10*). Then, for the liquid fugacities:

$$\ln\frac{f_L, P_2}{f_L, P_1} = \frac{1}{\mathrm{RT}}\int_{P_1}^{P_2} V_L\mathrm{d}P \qquad (14)$$

Joule-Thomson coefficients were calculated from:

$$\mu_{JT} = -\frac{1}{C_p}\left[V + \frac{\frac{T}{V}\left\{\frac{RT}{V} + \frac{B_oR}{V} + \frac{2C_o}{T^3V} + \frac{bR}{V^2} - \frac{2c}{V^2T^3}\left(1 + \frac{\gamma}{V^2}\right)e^{-\gamma/V^2}\right\}}{-\frac{1}{V^2}\left\{RT + \frac{2}{V}\left(B_oRT - A_o\,\frac{C_o}{T^2}\right) + \frac{3}{V^2}(BRT - A) + \frac{6a\alpha}{V^5} + \frac{ce^{-\gamma/V^2}}{V^2T^2}\left(3 + \frac{3\gamma}{V^2} - \frac{2\gamma^2}{V^4}\right)\right\}}\right] \qquad (15)$$

DISCUSSION

The volume differences for the vapor region were very small as shown in Table II, so they are adequate for engineering calculations. Liquid data showed considerably higher deviation thus giving an indication that subsequent calculated values of other thermodynamic properties for the liquid region would not be of much engineering use.

The range of conditions investigated in this work was quite wide. Pressure range was from 1 to 1100 atm. over a temperature range of 300° to 580° K. Previous investigations of polar materials covered considerably smaller ranges. Maxwell (*16*), in investigating the applicability of the BWR equation to nitrous oxide considered only the pressure range from 10 to 4000 p.s.i.a. over a temperature range of −200° to 422° K. Kang and McKetta (*14*), for sulfur dioxide, considered a pressure range from 1 to 315 atm. over a temperature range of 283° to 523° K.

Davies (*10*) states that the error in the published data does not exceed ±2% in any case. On this basis, the calculated vapor enthalpy data are as accurate as the observed values on an over-all average. The maximum error for the case of both positive and negative gammas occurred at 140 atm. and 420° K. These errors were 9.4 and 9.6%, respectively. Since the critical temperature and pressure (*10*) are, respectively, 405.6° K. and 111.5 atm., this pattern of deviation is comprehensible, as it is very difficult for any equation of state to represent the *P-V-T* data accurately near the critical region.

For the fugacity calculation, the maximum deviation for both positive and negative gammas occurred at 1100 atm. and 420° K. These deviations were 20.9 and 22.2%, respectively.

The isometric heat capacities for the liquid showed a maximum deviation of 28.6% at 120 atm. and 400° K., conditions that are very close to the critical temperature and pressure.

The maximum deviation of calculated pressures from those tabulated by Davies occurs for the vapor region, using the positive gamma, at 500 atm. and 420° K. This deviation was 1.66%. For the negative gamma, the maximum deviation of 1.83% occurred at 260 atm. and 420° K.

The calculations mentioned above are considered to be the most useful in terms of applicability of the BWR equation of state. In all cases, the maximum error in these calculations occurs at temperatures near the critical, but not necessarily at pressures near the critical pressure.

The calculation of thermodynamic properties with the BWR equation does not give results which are as accurate as those obtained from graphical and numerical methods. The amount of error that results with its use depends generally upon the type of operation performed on it. In particular, differentiation followed by integration may lead to large errors. If the errors in representing the data are completely random, then integration over a large interval will smooth them out. However, if they show a definite trend, the error in calculating thermodynamic properties grows as the interval of integration is widened.

NOMENCLATURE

A_o, B_o, C_o, a, b, c, α, γ = BWR equation constants, units indicated in Table I.
a', b', c', d' = coefficients in heat capacity equations, Equation 9.
C_p^* = ideal gas state heat capacity at constant pressure, cal./(gram mole)(° K.).
C_p = constant pressure heat capacity, cal./(gram mole)(° K.).
C_v = constant volume heat capacity, cal./(gram mole)(° K.).
e = natural logarithm base, 2.7182818.
f = fugacity, atmospheres
f_{L,P_2} = fugacity of the liquid under the pressure in question (P_2), atm.
H = enthalpy, cal./gram mole
P = pressure, atm. Subscript o (P_o) refers to pressure at reference state for enthalpies and entropies.
$P(V_i)$ = pressure predicted by Equation 1, using V_i, atm.
R = universal gas constant, 82.07(cm.^{3})(atm.)/(gram mole)(° K.).
S = entropy, cal./(gram mole)(° K.).
T = absolute temperature, ° K. Subscript o (T_o) refers to temperature at reference state for enthalpies and entropies.
V = volume, cm.^{3}/gram mole. Subscript o (V_o) refers to volume at reference state for enthalpies and entropies.
V_i = the i^{th} approximation to the volume, Equation 5.
V_{i+1} = the $(i+1)^{st}$ approximation to the volume, Equation 5.
V_L = liquid volume, cm.^{3}/(gram mole).
x_i = mole fraction of component i in mixture.
z_{cal} = compressibility factor calculated from Equation 2, dimensionless.
z = experimental compressibility factor, dimensionless.
Z = error in calculated compressibility factor, Equation 3.
μ_{JT} = Joule-Thomson coefficient, ° K./atm.

LITERATURE CITED

(1) Benedict, M., Webb, G.B., Rubin, L.C., *Chem. Eng. Progr.* **47**, 419 (1951).
(2) *Ibid.*, p. 449.
(3) *Ibid.*, p. 571.
(4) *Ibid.*, p. 609.
(5) Benedict, M., Webb, G.B., Rubin, L.C., *Ind. Eng. Chem.* **37**, 55 (1945).
(6) Benedict, M., Webb, G.B., Rubin, L.C., *J. Chem. Phys.* **8**, 334 (1940).
(7) *Ibid.*, p. 747.
(8) Brough, H., Schilinger, W., Sage, B.H., *Ind. Eng. Chem.* **43**, 2442 (1951).
(9) Cullen, E., Kobe, K., *A.I.Ch.E. J.* **1**, 452 (1955).
(10) Davies, P., "Thermodynamic Function of Gases," F. Din, Ed., Vol. 1, p. 33, Butterworths Scientific Publications, London, 1965.
(11) Friend, Leo, M.W. Kellog, Co., Jersey City, private communication, May 1963.
(12) Frizelle, W.G., M.S. thesis, Dept. of Chemical Engineering, University of Rochester, Rochester, N. Y., 1964.
(13) Gornowski, E.J., Amick, E.H., Jr., Hixson, A.N., *Ind. Eng. Chem.* **38**, 1348 (1947).
(14) Kang, K., McKetta, J., J. Chem. Eng. Data **6**, 227 (1961).
(15) Marchman, H., Prengle, H.W., Jr., Motard, R.L., *Ind. Eng. Chem.* **41**, 2658 (1949).
(16) Maxwell, H.C., M.S. thesis, Dept. of Chemical Engineering University of Texas, Austin, Tex., 1960.
(17) Obert, E., "Concepts of Thermodynamics," McGraw-Hill, New York, 1960.
(18) Opfell, J.B., Schlinger, W.G., Sage, B.H., *Ind. Eng. Chem.* **46**, 1286 (1954).
(19) Organick, E.I., Studhaltn, W.R., *Chem. Eng. Progr.* **44**, 847 (1948).
(20) Perry, J.H., "Chemical Engineering Handbook," 4th ed., McGraw-Hill, New York, 1950.
(21) Prengle, H.W., Jr., Marchman, H., *Ind. Eng. Chem.* **42**, 2371 (1950).
(22) Schiller, F., Canjar, L., *Chem. Eng. Progr. Symp. Ser.* **49**, 7, 67 (1953).
(23) Selleck, F.T., Opfell, J.B., Sage, B.H., *Ind. Eng. Chem.* **45**, 1350 (1953).
(24) Smith, J.M., Van Ness, H.C., "Introduction to Chemical Engineering Thermodynamics," McGraw-Hill, New York, 1959.

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