Benedict–Webb–Rubin Equation of State Constants for $N_2O_4 \rightleftarrows 2NO_2$, NO, and O_2

D. N. SESHADRI, D. S. VISWANATH, and N. R. KULOOR
Department of Chemical Engineering, Indian Institute of Science, Bangalore, India

Benedict–Webb–Rubin equation of state constants for NO, O_2, and the equilibrium mixture $N_2O_4 \rightleftarrows 2NO_2$ are reported.

THE pressure-volume-temperature $(P\text{-}V\text{-}T)$ relation of hydrocarbons has been represented successfully by the Benedict-Webb–Rubin (BWR) equation of state (1, 2). Recently, this equation has been applied to ammonia— a highly polar gas (9). With the applicability of the BWR equation both to nonpolar and polar gases, the authors thought that the formula could be used in the evaluation of the thermodynamic properties of the equilibrium system,

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2 \qquad (1)$$
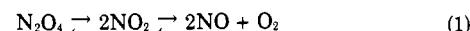
In the past few years, many have been interested in the evaluation of the thermodynamic and transport properties of the above equilibrium system. A direct combination of the constants to utilize the BWR equation for the mixtures may not be fruitful and, therefore, the authors saw fit to report the constants for the individual substances.

Table I. Benedict-Webb-Rubin Equation Constants

Units: Atm., Liters/Gram Mole, ° K.

Constants	$N_2O_4 \rightleftarrows 2NO_2$	NO	NO[a]	O_2
			Substance	
A_0	-340.443548	2.19573852	0.4344693	0.950851963
B_0	-6.8866796	0.0604550814	$9.76280227 \times 10^{-3}$	$0.353285054 \times 10^{-7}$
C_0	1.81095376×10^7	-1.79557089×10^4	2.7441581826×10^4	3.26435918×10^4
a	234.1000080	-0.350821484	0.234879752	0.162689940
b	4.86749901	$-7.53154391 \times 10^{-3}$	$8.623521138 \times 10^{-3}$	$0.358834736 \times 10^{-2}$
c	1.10086892×10^7	-1.15237289×10^4	4.678297612×10^3	1.28273741×10^4
α	$1.309140732 \times 10^{-3}$	$1.563696033 \times 10^{-5}$	$1.24608062 \times 10^{-5}$	-3.927058894
γ	0.041	0.002	0.00195	0.0301
Range of Temperature, ° K.	299 to 444	278 to 378	200 to 378	300 to 1000
Range of pressure, atm.	1 to 68	1 to 170	1 to 204	0.01 to 70.0
Source of data	(10)	(5)	(3, 5, 7)	(6)
Average-absolute deviation, %	1.22	0.065	0.17	0.06

[a] Literature values by Opfell, Schlinger, and Sage (8).

Table II. Average-Absolute and Maximum Deviations

Substance		277.61	294.27	310.94	327.60	344.27	360.94	377.60	394.27	410.93	427.60	444.27
						Isotherms in ° K.						
NO	No. of points	23	...	23	...	23	...	23	...	...	...	...
	Av.-abs. dev., %	0.06	...	0.06	...	0.07	...	0.06	...	...	...	...
	Max. dev., %	0.15	...	0.21	...	0.24	...	0.18	...	...	...	...
	Max. dev. at P(atm.) =	2.27	...	119.08	...	170.11	...	170.11	...	...	...	...
NO[a]	No. of points	23	...	23	...	23	...	23	...	...	...	...
	Av.-abs. dev., %	0.18	...	0.22	...	0.11	...	0.17	...	...	...	...
	Max. dev., %	0.72	...	0.83	...	0.32	...	0.47	...	...	...	...
	Max. dev. at P(atm.) =	170.11	...	170.11	...	170.11	...	170.11	...	...	...	...
N_2O_4 $\rightleftarrows 2NO_2$	No. of points	...	1	3	6	8	10	10	10	17	18	18
	Av.-abs. dev., %	...	3.86	4.30	1.94	0.43	1.82	0.94	0.96	1.25	0.77	1.32
	Max. dev., %	...	3.86	5.70	3.20	0.92	4.51	2.59	2.55	3.92	2.40	5.05
	Max. dev. at P(atm.) =	...	1.00	2.04	4.08	2.04	10.21	10.21	10.21	40.83	54.44	54.44

[a] Values for constants given by Opfell, Schlinger, and Sage (8). Deviation = (Exptl.–calcd.)/Exptl.

METHOD OF EVALUATION OF THE CONSTANTS

The constants in the BWR equation were evaluated by a least-squares technique outlined by Brough, Schlinger, and Sage (4), minimizing the sum of squares of deviations in the calculated pressure values. Details of the method are outlined elsewhere (4, 11). Although the least-squares technique was used, the minimization of maximum and average-absolute deviations was taken into consideration also.

RESULTS AND DISCUSSION

Table I gives the values of the constants, the range of temperature and pressure used in the evaluation of the constants, and other information. A set of constants for NO is reported earlier by Opfell, Schlinger, and Sage (8). Table I shows the two sets of constants for NO. A comparison of the degree of fit for the two sets of constants is shown in Table II. Although the disagreement between the two sets of constants is large, Opfell, Schlinger, and Sage have used wider temperature and pressure ranges. However, in the limited range considered in the present work, the set of constants obtained gives a better representation of the P-V-T data. Further, Opfell, Schlinger, and Sage minimized the sum of the squares of the deviations in compressibility as compared with pressure used in this work. The accuracy of any fit depends on several things such as the primary data used, the number of points used, the weight put on the points, the range of temperature and pressure used, the criterion on which the fit is obtained, the dependent and the independent variables chosen, etc. Therefore, each set of constants should be judged by its own merit depending on its use and not solely by some criterion such as standard deviation, as this has no reflection on the accuracy of the fit.

In the case of oxygen and nitric oxide, although the principle of least-squares was used, both average-absolute and maximum deviations were minimized, also, and the maximum deviation for different values of γ was 1%. Included in Table II are the maximum and average-absolute deviations for each isotherm, and the values of the pressures

Table III. Effect of γ on Various Deviations for $N_2O_4 \rightleftarrows 2NO_2$

γ	Av.-Abs. Dev., %	Max. Dev., %	Sum of the Squares of Dev.
0.0380	2.95	17.72	46.45
0.0400	1.25	8.20	20.76
0.0405	1.75	10.15	18.00
0.0410	1.21	5.70	19.04
0.0420	1.27	6.23	18.77
0.0440	1.36	7.00	18.40

at which the maximum deviations occurred. In the case of $N_2O_4 \rightleftarrows 2NO_2$, the γ value chosen was the one which gave a minimum value for the maximum and average-absolute deviations, and for which the sum of the squares of the deviations was close to the minimum value also. This is shown in Table III.

LITERATURE CITED

(1) Benedict, M., Webb, G.W., Rubin, L.C., J. Chem. Phys. 8, 334 (1940).
(2) Benedict, M., Webb, G.W., Rubin, L.C., Chem. Eng. Progr. 47, 419, 449, 571, 609 (1951).
(3) Brinner, E., Biedermann, H., Rothen, A., J. chim. phys. 23, 157 (1926).
(4) Brough, H.W., Schlinger, W.G., Sage, B.H., Ind. Eng. Chem. 43, 2442 (1951).
(5) Golding, B.H., Sage, B.H., Ibid., 43, 160 (1951).
(6) Hilsenrath, J., "Tables of Thermodynamic and Transport Properties," pp. 369-436, Pergamon Press, London, 1960.
(7) Johnston, H.L., Weimer, H.R.; J. Am. Chem. Soc. 56, 625 (1934).
(8) Opfell, J.B., Schlinger, W.G., Sage, B.H., Ind. Eng. Chem. 46, 189 (1954).
(9) Ramalho, R.S., Frizelle, W.G., J. CHEM. ENG. DATA 10, 366 (1965).
(10) Schlinger, W.G., Sage, B.H., Ind. Eng. Chem. 42, 2158 (1950).
(11) Viswanath, D.S., Ph.D. thesis, University of Rochester, Rochester, N. Y., 1962.

Solid-Liquid Solubility Determination by Variable Heating Rates

E. L. HERIC
Department of Chemistry, University of Georgia, Athens, Ga.

IN a recent paper Satterfield and Houlard (3) have shown that the visual determination of solid solubility in liquids by static methods avoids errors due to overshoot of the true solubility temperature in the dynamic method. The existence of such an overshoot has been well recognized in the literature of solubility determination. Unfortunately, the static method frequently involves considerable time in the location of the precise temperature at which the last crystal of solid dissolves only after prolonged isothermal agitation. (This is especially true in the case of highly viscous solutions.) Satterfield and Houlard recommend 3 hours of isothermal agitation at the solubility temperature. Heric and Posey (2) have made isothermal solubility determinations from the direction of undersaturation, and they considered 12 hours of agitation advisable to assure saturation of the solution by the solid solute. The uncertainty

of the results of the latter work was estimated to be 0.0005 in mole fraction solute at saturation.

In presenting an argument for the greater accuracy of the static method, Satterfield and Houlard have provided at least tentative evidence that the dynamic method may also be suited, with proper usage, to precise solubility determination. This communication points out this evidence, with the hope that the method may prove to be a useful technique.

Table I, taken from the publication of Satterfield and Houlard (3), presents the argument proposed here. Listed there for each system are the ratios of the saturation temperature overshoot to the heating rate—i.e., the overshoot per unit heating rate—both for each heating rate and the average for all heating rates in a system. [The two values in parentheses there have been omitted in averaging because