α *vs.* x (Figure 7) occurring at $x \sim 0.98$ are a direct consequence of the assumption that the liquid consists of N_2O_3 and N_2O_4 only. In this model, NO_2 is included in the gas phase, but its possible presence is ignored in the liquid phase.

The fact that a plot of α in Figures 7 and 8 goes over a maximum at any given temperature is not fictitious. The effective separation factor is increased by the addition of nitric oxide to the system, as long as the added NO affects the vapor phase—*i.e.*, decreases the denominator of Equation 16—more than the liquid phase. As the composition of the vapor phase approaches towards that of pure NO, a point is reached where further increase in the relative amount of +2 nitrogen in the system affects the gas phase composition less than the composition of the liquid phase; the numerator of Equation 16 decreases more rapidly than the denominator, and α_{eff} decreases.

LITERATURE CITED

(1) Baume, G., Robert, M., *Compt. rend.* **169**, 970 (1919).
(2) Beattie, I. R., *Progr. Inorg. Chem.* 5, 1 (1963).
(3) Beattie, I. R., Bell, S. W., *J. Chem. Soc.* **1957**, 1681.
(4) Beattie, I. R., Bell, S. W., Ishida, T., Spindel, W., *Ibid.*, in press.
(5) Beattie, I. R., Bell, S. W., Vosper, A. J., *Ibid.*, **1960**, 1496.
(6) Beattie, I. R., Vosper, A. J., *Ibid.*, **1960**, 4799.
(7) *Ibid.*, **1961**, 2106.
(8) Bigeleisen, J., Mayer, M. G., *J. Chem. Phys.* **15**, 261 (1947).
(9) Giauque, W. F., Kemp, J. D., *Ibid.*, **6**, 40 (1938).
(10) Monse, E. U., *Ibid.*, **33**, 312 (1960).
(11) Monse, E. U., Kauder, L. N., Spindel, W., *Ibid.*, **41**, 3898 (1964).
(12) Monse, E. U., Kauder, L. N., Spindel, W., *Z. Naturforsch.* 18a, 235 (1963).
(13) Monse, E. U., Spindel, W., Kauder, L. N., Taylor, T. I., *J. Chem. Phys.* **32**, 1557 (1960).
(14) Monse, E. U., Spindel, W., Stern, M. J., *Advan. Chem. Ser.*, No. 89, 185 (1969).
(15) Monse, E. U., Taylor, T. I., Spindel, W., *J. Phys. Chem.* **65**, 1625 (1961).
(16) Purcell, R. H., Cheesman, G. H., *J. Chem. Soc.* **1932**, 826.
(17) Vosper, A. J., *Ibid.*, **A**, **1966**, 1762.
(18) Whittaker, A. G., Sprague, R. W., Skolnik, S., Smith, G. B. L., *J. Am. Chem. Soc.* 74, 4794 (1952).

RECEIVED for review March 21, 1969. Accepted September 18, 1969. Work supported by the U. S. Atomic Energy Commission under Contract AT(30-1)-3264.

P-V-T Properties of Hydrogen and Mixtures Containing Hydrogen

ARNOLD BRIEF and JOSEPH JOFFE
Newark College of Engineering, Newark, N. J. 07102

The generalized B-W-R equation of state of Edmister, Vairogs, and Klekers has been evaluated by them for a number of hydrocarbons with encouraging results. In the present work, the equation has been applied to hydrogen, which exhibits quantum deviations from the corresponding states principle, and to gas mixtures containing hydrogen. The systems examined in this paper are hydrogen, nitrogen-hydrogen, methane-hydrogen, and ethane-hydrogen.

THE BENEDICT-WEBB-RUBIN equation is an equation of state containing eight constants. These constants are derived empirically by fitting the equation to experimental *P-V-T* data. The equation is given below:

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2)\exp(-\gamma d^2) \quad (1)$$

where the constants of the B-W-R equation for hydrogen are (*8*):

$A_0 = 585.127$
$B_0 = 3.339\,37 \times 10^{-4}$
$C_0 = 482.82 \times 10^4$
$a = -98.597$
$b = 868.2 \times 10^{-4}$
$c = 1423.17 \times 10^3$
$a\alpha = 49.239$
$\gamma = 900.00 \times 10^{-3}$

These constants may be used in the B-W-R equation when T is in degrees Rankine, d in lb. moles per cu. ft., P in p.s.i., and $R = 10.7335$ lb. cu. ft. per (sq. in.) (lb. mole) (°R.).

W. C. Edmister and coworkers have generalized the above equation by expressing the eight constants as functions of critical temperature, critical pressure, and acentric factor (*5*):

$$\pi = \theta\rho + (B_0'\theta - A_0' - C_0'/\theta^2)\rho^2 + (b'\theta - a')\rho^3 + a'\alpha'\rho^6 + (c'\rho^3/\theta^2)(1 + \gamma'\rho^2)\exp(-\gamma'\rho^2) \quad (2)$$

where[2] $\pi = P/P_c$
$\theta = T/T_c$
$\rho = dRT_c/P_c$

The constants of Equation 2 are functions of the acentric factor, ω. They are as follows:

$$A_0' = 0.343258 - 0.127521\omega - 0.509131\omega^2 \quad (3)$$

$$B_0' = 0.113747 + 0.127349\omega - 0.243280\omega^2 \quad (4)$$

$$C_0' = 0.098224 + 0.401236\omega - 0.0397267\omega^2 \quad (5)$$

$$a' = 0.0235866 + 0.290284\omega - 0.295413\omega^2 \quad (6)$$

$$b' = 0.0275404 + 0.131009\omega - 0.134924\omega^2 \quad (7)$$

$$c' = 0.035694 + 0.185297\omega - 0.230125\omega^2 \tag{8}$$

$$\gamma' = 0.052058 - 0.09064\omega + 0.10506\omega^2 \tag{9}$$

$$\alpha' a' = 0.0000875 \tag{10}$$

To work with Equation 1, the eight constants for the particular gas must be known; otherwise they must be determined. If Equation 2 is employed, then, in addition to the critical temperature and pressure, only the acentric factor of the gas is needed to calculate the eight constants.

Edmister and coworkers compared their generalized Equation 2 to the original B-W-R Equation 1 by calculating pressures by both methods using observed *P-V-T* data of 13 hydrocarbons and carbon dioxide. Their results indicated that the generalized B-W-R equation is in most cases only moderately less accurate than the original B-W-R equation.

The generalized B-W-R equation has been applied in the present study to hydrogen and gas mixtures containing hydrogen. Quantum gases do not follow the same law of corresponding states as that followed by classical gases. Therefore, Equation 2 may not be used directly for hydrogen, which is a quantum gas, nor for mixtures containing hydrogen, without some modifications of critical constants. Chueh and Prausnitz (*2*) and Gunn *et al.* (*6*) have proposed the following modifications of the critical conditions for quantum gases such as hydrogen:

Effective critical temperature,

$$T_c = \frac{T_c^\circ}{1 + (c_1/mT)} \tag{11}$$

Effective critical pressure,

$$P_c = \frac{P_c^\circ}{1 + (c_2/mT)} \tag{12}$$

Effective critical volume,

$$V_c = \frac{V_c^\circ}{1 + (c_3/mT)} \tag{13}$$

where c_1 = 21.8° K.
c_2 = 44.2° K.
c_3 = −9.91° K.
m = molecular weight of quantum gas, in this case hydrogen
T = absolute temperature of system

Since the acentric factor of quantum gases according to Gunn, Chueh, and Prausnitz should be set equal to zero, the generalized constants of Equation 2 when applied to hydrogen become equal to the constant terms of Equations 3 through 10.

If the generalized B-W-R equation is to be applied to gas mixtures, then pseudocritical constants must be used to obtain reduced pressure, temperature, and density values in Equation 2. Gunn, Chueh, and Prausnitz have proposed a method for calculating a pseudo-critical temperature and pressure in a gas mixture containing quantum gases (*6*):

$$T_{cM} = \frac{\Sigma y_i T_{ci}^\circ}{1 + (c_1/m_M T)} \tag{14}$$

$$P_{cM} = \frac{R(\Sigma y_i z_{ci}^\circ)\,(\Sigma y_i T_{ci}^\circ)}{(\Sigma y_i V_{ci}^\circ)\,(1 + c_2/m_M T)} \tag{15}$$

$$\frac{1}{m_M} = \left[\Sigma\left(\frac{y_i}{(m_i)^{1/2}}\right)\right]^2 \tag{16}$$

$$\omega_M = \Sigma y_i\, \omega_i \tag{17}$$

In this paper the Gunn-Chueh-Prausnitz method, described by Equations 14 through 17, is compared with an earlier method proposed by Prausnitz and Gunn for classical gases (*9*) which is a variation of Kay's rule:

$$T_{cM} = \Sigma y_i T_{ci} \tag{18}$$

$$V_{cM} = \Sigma y_i V_{ci} \tag{19}$$

$$z_{cM} = \Sigma y_i z_{ci} \tag{20}$$

$$P_{cM} = \frac{R T_{cM} z_{cM}}{V_{cM}} \tag{21}$$

$$\omega_M = \Sigma y_i\, \omega_i \tag{22}$$

In this current work, it is proposed to use Equations 18 through 22 with gas mixtures containing hydrogen, with the following modifications: T_c and V_c for hydrogen are obtained from Equations 11 and 13, while z_c for hydrogen is taken as 0.291. The proposed method, based on Equations 18 through 22 along with Equations 11 and 13, is a simpler procedure for establishing pseudocritical constants of gas mixtures than the Gunn-Chueh-Prausnitz method and, at least for mixtures containing hydrogen, appears to be equally accurate.

Table I. Hydrogen[a]

No. of Points	Temp. Range, ° K.	Pressure Range, Atm.	Original B-W-R Average % deviation	Original B-W-R Max. % deviation	Gener. B-W-R Average % deviation	Gener. B-W-R Max. % deviation
171	30–55	1–100	40.25	252.57	16.41	119.19
252	60–100	1–100	1.65	10.61	0.87	5.25
280	105–150	1–100	0.038	0.16	0.59	1.19
280	155–200	1–100	0.011	0.037	0.42	0.82
280	205–250	1–100	0.011	0.031	0.30	0.59
280	255–300	1–100	0.017	0.044	0.20	0.42
70	310–400	1–100	0.027	0.12	0.098	0.29
70	410–500	1–100	0.052	0.18	0.036	0.12
70	510–600	1–100	0.067	0.23	0.025	0.11
66	198.16–323.16	100–1200	1.42	11.98	4.90	12.02
55	373.16–773.16	100–1200	0.89	2.90	4.00	12.21

[a] Data taken from references (*3, 4, 7*).

Table II. Nitrogen-Hydrogen System[a]

No. of Points	Temp., ° C.	Pressure Range, Atm.	Gunn *et al.* (*6*)		Prausnitz *et al.* (*9*)	
			Average % deviation	Max. % deviation	Average % deviation	Max. % deviation
			12.56 mole % N_2			
8	0.0	25–1000	3.12	8.56	3.09	8.54
8	25.0	25–1000	3.19	8.99	3.17	8.99
7	50.0	50–1000	3.74	9.43	3.72	9.44
7	100.0	50–1000	3.63	9.54	3.64	9.56
7	200.0	50–1000	3.63	9.74	3.65	9.77
7	300.0	50–1000	3.48	9.32	3.64	9.35
			24.44 mole % N_2			
7	0.0	50–1000	3.07	7.35	3.03	7.29
7	25.0	50–1000	3.25	7.95	3.22	7.91
7	50.0	50–1000	3.39	8.47	3.37	8.45
7	100.0	50–1000	3.34	8.63	3.34	8.63
7	200.0	50–1000	3.29	8.91	3.30	8.93
7	300.0	50–1000	3.28	8.90	3.29	8.92
			48.26 mole % N_2			
8	0.0	25–1000	1.82	4.66	1.78	4.57
8	25.0	25–1000	2.07	5.31	2.05	5.25
8	50.0	25–1000	2.19	5.81	2.16	5.76
8	100.0	25–1000	2.35	6.56	2.34	6.54
7	200.0	50–1000	2.80	7.58	2.80	7.59
7	300.0	50–1000	2.82	7.72	2.82	7.74
			73.88 mole % N_2			
8	0.0	25–1000	0.77	1.49	0.70	1.30
8	25.0	25–1000	1.04	2.17	0.98	2.01
7	50.0	50–1000	1.45	2.91	1.39	2.78
7	100.0	50–1000	1.78	3.82	1.75	3.73
7	200.0	50–1000	2.22	5.43	2.20	5.38
6	300.0	50–1000	2.59	6.13	2.21	6.11

[a] Data taken from reference (*11*).

Table III. Methane-Hydrogen System[a]

No. of Points	Temp., ° C.	Pressure Range, P.S.I.	Gunn *et al.* (*6*)		Prausnitz *et al.* (*9*)	
			Average % deviation	Max. % deviation	Average % deviation	Max. % deviation
			9.03 mole % CH_4			
6	−210.0	172.7–1160.9	0.54	1.37	0.71	1.69
6	−180.0	200.0–1331.4	0.45	1.14	0.59	1.39
7	−150.0	214.9–1770.5	0.59	0.99	0.72	1.16
7	−120.0	235.0–1968.3	0.33	0.63	0.43	0.79
7	− 90.0	257.0–2162.9	0.35	0.56	0.44	0.64
7	− 60.0	278.0–2358.5	0.38	0.61	0.45	0.70
7	− 30.0	300.0–2548.2	0.29	0.46	0.34	0.52
7	0.0	319.0–2739.8	0.25	0.44	0.30	0.50
7	30.0	340.0–2937.5	0.15	0.44	0.19	0.47
7	60.0	360.4–3126.1	0.12	0.20	0.15	0.23
7	90.0	381.2–3313.2	0.11	0.23	0.12	0.26
6	120.0	401.7–2909.0	0.12	0.21	0.14	0.23
6	150.0	422.3–3063.3	0.14	0.20	0.14	0.21
6	180.0	442.7–3214.8	0.16	0.36	0.15	0.32
5	210.0	461.0–2732.9	0.11	0.18	0.12	0.15
5	240.0	482.9–2853.6	0.11	0.32	0.11	0.30
5	270.0	502.0–2976.5	0.14	0.37	0.14	0.35
5	300.0	523.4–3095.6	0.14	0.49	0.13	0.47

[a] Data taken from reference (*10*).

PROCEDURE AND RESULTS FOR HYDROGEN

The generalized B-W-R equation, Equation 2, was applied to hydrogen using the effective critical constants of Equations 11 and 12. The study covered temperatures from 30° to 773° K. and pressures up to 1200 atm. Pressures were computed for 1874 points from literature data (*3, 4, 7*) and per cent deviations from observed pressures were found. Average absolute per cent deviations were computed for several temperature and pressure ranges. Similar calculations were carried out with the original B-W-R equation for hydrogen and the results compared in Table I.

A careful analysis of the results leads to the following conclusions: The generalized equation is superior to the original B-W-R below 100° K. Over most of the range studied, the deviations are small for both methods. At high temperatures and pressures, the original equation is superior to the generalized form.

PROCEDURE AND RESULTS FOR MIXTURES

The generalized B-W-R equation was used for all mixtures. Mixture densities were obtained from literature data and the pressures calculated with the equation. The pseudocritical constants were calculated by two methods, the Gunn-Chueh-Prausnitz method (*6*) and the proposed method of the current study, based on Equations 18 through 22, and Equations 11 and 13 for hydrogen.

The nitrogen-hydrogen system (*11*), for which the results are shown in Table II, was studied for four different compositions covering a total of 175 points, temperatures from 0° to 300° C., and pressures up to 1000 atm. Average absolute per cent deviations in this system range from 1.54 to 3.48%, being almost the same for the two pseudocritical methods.

The methane-hydrogen system (*10*), with results entered in Table III, was studied for only one composi-

Table IV. Ethane-Hydrogen System[a]

			Gunn *et al.* (*6*)		Prausnitz *et al.* (*9*)	
No. of Points	Temp. °F.	Pressure Range, P.S.I.	Average % deviation	Max. % deviation	Average % deviation	Max. % deviation
		89.96 mole % C_2H_6				
6	90.0	350–1049	5.72	8.56	5.19	7.76
6	120.0	377–1298	4.14	6.01	3.72	5.38
6	150.0	402–1547	3.25	4.59	2.92	4.08
6	180.0	428–1794	2.56	3.54	2.28	3.12
6	210.0	453–2039	2.13	2.90	1.88	2.53
6	240.0	479–2282	1.81	2.59	1.59	2.27
6	270.0	503–2524	1.63	2.41	1.43	2.13
6	300.0	527–2764	1.49	2.25	1.33	1.99
		79.97 mole % C_2H_6				
6	90.0	387–1395	5.02	6.82	4.49	6.02
6	120.0	415–1637	4.17	5.43	3.75	4.64
6	150.0	442–1878	3.56	4.63	3.16	3.97
6	180.0	469–2118	3.01	3.98	2.68	3.42
6	210.0	496–2355	2.61	3.62	2.33	3.14
6	240.0	522–2589	2.41	3.43	2.16	3.00
6	270.0	548–2822	2.19	3.31	1.98	2.93
6	300.0	575–3055	2.03	3.20	1.84	2.86
		50.17 mole % C_2H_6				
6	70.0	512–2153	4.14	5.96	3.65	5.17
6	90.0	534–2302	3.75	5.48	3.32	4.82
6	120.0	568–2520	3.25	5.03	2.88	4.41
6	150.0	603–2739	2.85	4.58	2.52	4.04
6	180.0	635–2956	2.54	4.22	2.25	3.74
6	210.0	669–3168	2.32	4.04	2.07	3.62
6	240.0	701–3379	2.17	3.91	1.95	3.54
6	270.0	734–3586	2.03	3.80	1.85	3.47
6	300.0	766–3793	1.93	3.79	1.76	3.49
		20.10 mole % C_2H_6				
6	70.0	214–2347	1.71	3.11	1.56	2.83
6	90.0	222–2451	1.61	3.01	1.47	2.76
6	120.0	235–2606	1.51	2.93	1.39	2.70
6	150.0	246–2760	1.47	2.89	1.36	2.69
6	180.0	259–2916	1.36	2.74	1.27	2.56
6	210.0	271–3071	1.29	2.63	1.21	2.47
6	240.0	283–3220	1.29	2.70	1.22	2.56
6	270.0	295–3368	1.28	2.80	1.21	2.66
6	300.0	307–3514	1.26	2.91	1.21	2.79

[a] Data taken from reference (*10*).

tion of 9 mole % methane. A total of 113 points were tested over a temperature range from −210° to +300° F. and for pressures up to 3100 p.s.i.a. The results obtained by both methods were essentially equivalent, with over-all average absolute per cent deviations of 0.30% or less.

The ethane-hydrogen system (*10*) was tested for four compositions covering 204 points over a temperature range from 70° to 300° F. and for pressures as high as 3800 p.s.i.a. The results are presented in Table IV. Once again, the results obtained by the two pseudocritical methods are essentially equivalent, the over-all average absolute per cent deviations ranging from 1.21 to 3.13%.

A summary of all results is presented in Table V. All computations were carried out with the help of a digital computer. A more detailed description of the procedure is given elsewhere by Brief (*1*).

ALTERNATIVE PROCEDURE FOR MIXTURES

There is an alternative but less direct way in which the generalized B-W-R equation may be used in calculations with mixtures. The specific B-W-R constants of each component of the mixture are calculated from the reduced constants with the help of Equations 3 to 10 and the additional equations relating the reduced constants to the specific constants, as presented in the work of Edmister, Vairogs, and Klekers (*5*). The resulting constants of the individual components are then combined in accordance with the standard B-W-R combining rules (*10*) to yield constants for the mixture. Calculations are then carried out with Equation 1, rather than the generalized Equation 2.

This alternative procedure has been tried with one of the systems previously treated by the pseudocritical method, the four ethane-hydrogen mixtures. In the case of hydrogen, effective critical constants were employed, as in the pseudocritical method. The results of these calculations are presented in Table VI, which may be compared with the results of the pseudocritical method, Table IV. The alternative procedure based on the standard B-W-R combining rules is quite satisfactory for the system tested and is on the whole more accurate than the procedures based on the pseudocritical method.

Table V. Summary of Results

Hydrogen

No. of Points	Temp. Range, ° K.	Press. Range, Atm.	Average % Deviation	
			Original	Gener.
171	30.0– 55.0	1–100	40.25	16.41
1582	60.0– 600.0	1–100	0.23	0.31
121	198.16–773.16	100–1200	1.15	4.45

Mixtures

No. of Points	System	Concn., Mole %	Average % Deviation	
			Gunn *et al.* (*6*)	Prausnitz *et al.* (*9*)
113	CH_4-H_2	9.03/90.97	0.25	0.30
48	C_2H_6-H_2	89.96/10.04	2.85	2.55
48	C_2H_6-H_2	79.97/20.03	3.13	2.80
54	C_2H_6-H_2	50.17/49.83	2.78	2.48
54	C_2H_6-H_2	20.10/79.90	1.42	1.21
44	N_2-H_2	12.56/87.44	3.47	3.48
42	N_2-H_2	24.44/75.56	3.28	3.27
46	N_2-H_2	48.26/51.74	2.34	2.33
43	N_2-H_2	73.88/26.12	1.64	1.54

CONCLUSIONS

The generalized B-W-R equation of Edmister and coworkers may be applied to hydrogen if effective critical constants are used in place of true critical constants. Good results were obtained with this equation for hydrogen over a wide range, from 60° to 773° K. and for pressures up to 500 atm., with a maximum deviation of about 5%.

The generalized B-W-R equation may also be used with gas mixtures containing hydrogen, over a wide range of conditions, provided pseudocritical constants are used. The latter may be computed by a method proposed in this paper which is an extension of an earlier proposal by Prausnitz and Gunn.

In an alternative approach to mixtures, the reduced constants of the generalized B-W-R equation have been used to compute specific B-W-R constants for each component, and the specific constants have been combined by means of standard combining rules to yield B-W-R mixture constants. This also appears to be a satisfactory way of handling gas mixtures containing hydrogen.

NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = constants of original B-W-R equation

$A_0', B_0', C_0', a', b', c', \alpha', \gamma'$ = constants of generalized B-W-R equation

Table VI. Ethane-Hydrogen System[a, b]

No. of Points	Temp., ° F.	Press. Range, P.S.I.	Av. % Dev.	Max. % Dev.
		89.96 mole % C_2H_6		
6	90.0	350–1049	2.62	4.24
6	150.0	402–1547	1.38	2.07
6	210.0	453–2039	0.87	1.22
6	270.0	503–2524	0.73	1.20
6	300.0	527–2764	0.72	1.20
		79.97 mole % C_2H_6		
6	90.0	387–1395	1.66	2.20
6	150.0	442–1878	1.28	1.68
6	210.0	496–2355	1.05	1.51
6	270.0	548–2822	1.05	1.69
6	300.0	575–3055	1.05	1.75
		50.17 mole % C_2H_6		
6	90.0	534–2302	1.24	2.18
6	150.0	603–2739	1.28	2.28
6	210.0	669–3168	1.30	2.39
6	270.0	734–3586	1.32	2.58
6	300.0	766–3793	1.35	2.72
		20.10 mole % C_2H_6		
6	70.0	214–2347	1.37	2.51
6	150.0	246–2760	1.37	2.67
6	210.0	271–3071	1.30	2.57
6	270.0	295–3368	1.35	2.84
6	300.0	307–3514	1.35	2.99

[a] Data taken from reference (*10*).
[b] Alternative procedure based on Equation 1 and standard B-W-R combining rules was used in the calculations.

P = pressure
P_c = critical pressure
P_c° = critical pressure in the classical (high-temperature) limit
P_{cM} = pseudocritical pressure of mixture
R = universal gas constant
T = absolute temperature
T_c = critical temperature
T_c° = critical temperature in the classical (high-temperature) limit
T_{cM} = pseudocritical temperature of mixture
V_c = critical volume
V_c° = critical volume in the classical (high-temperature) limit
V_{cM} = pseudocritical volume of mixture
c_1, c_2, c_3 = constants given by Equations 11, 12, and 13
d = density, moles per unit volume
m = molecular weight
y = mole fraction
z = compressibility factor
θ = reduced temperature
π = reduced pressure
ρ = reduced density
ω = acentric factor

Subscripts

c = critical
i = component i
M = mixture

LITERATURE CITED

(1) Brief, A., M.S. thesis, Newark College of Engineering, Newark, N. J., 1969.
(2) Chueh, P. L., Prausnitz, J. M., *A.I.Ch.E. J.* **13**, 896 (1967).
(3) Dean, J. W., U. S. National Bureau of Standards, Technical Note No. 120, 1961.
(4) Deming, W. E., Shupe, L. E., *Phys. Rev.* **40**, 848 (1932).
(5) Edmister, W. C., Vairogs, J., Klekers, A. J., *A.I.Ch.E. J.* **14**, 479 (1968).
(6) Gunn, R. D., Chueh, P. L., Prausnitz, J. M., *Ibid.*, **12**, 937 (1966).
(7) Hilsenrath, J., U. S. National Bureau of Standards, Circular 564, 1955.
(8) Motard, R. L., Organick, E. I., *A.I.Ch.E. J.* **6**, 39 (1960).
(9) Prausnitz, J. M., Gunn, R. D., *Ibid.*, **4**, 430 (1958).
(10) Solbrig, C. W., Ellington, R. T., *Chem. Eng. Progr., Symp. Ser.* 44, 59, 127 (1963).
(11) Wiebe, R., Gaddy, V. L., *J. Am. Chem. Soc.* **60**, 2300 (1938).

RECEIVED for review April 2, 1969. Accepted October 27, 1969.

Isothermal Compressibility of Liquid Water at 1 Atm.

G. S. KELL
Division of Applied Chemistry, National Research Council, Ottawa, Canada

Recent measurements of the velocity of sound in distilled ordinary water give the isothermal compressibility with a standard error of 0.002 $\times$ 10^{-6} bar^{-1}, one tenth that of direct determinations. At least at low temperatures, isothermal compressibilities from the velocity of sound should have fewer systematic errors than direct determinations. Interpolating equations represent the temperature dependence of the velocity of sound, u, of $1/u^2$, and of the isentropic and isothermal compressibilities. Acoustic and direct measurements together give an equation for the isothermal compressibility valid from 0° to 150° C. and to be considered a best estimate of the isothermal compressibility; a table is given to 110° C. The change of temperature of maximum density with pressure is -0.0200 ± 0.0003 deg. bar^{-1}.

THREE RELIABLE DETERMINATIONS of the velocity of sound in ordinary water (*1, 2, 8*) agree well and supersede previous measurements. The velocity of sound, u, is related to the isentropic compressibility, κ_S,

$$\kappa_S = -(\partial \ln V/\partial p)_S = (\partial \ln \rho/\partial p)_S$$

by the relation

$$\left(\frac{\partial \rho}{\partial p}\right)_S = \frac{1}{u^2} \qquad (1)$$

where V is volume, ρ density, and p pressure, and the differentiation is made at constant entropy S. Equation 1 gives the static value of $(\partial \rho/\partial p)_S$, provided u is measured with waves of small amplitude at frequencies sufficiently below the region of dispersion that absorption is small. As absorption is proportional to the square of the frequency, f, in this range, the numerical requirement (*7*) is that $\alpha^2u^2/4\pi^2f^2 << 1$, where α is the attenuation coefficient, given for water at 25° C. by $\alpha/f^2 = 2.3 \times 10^{-16}$ neper sec.^{2} cm.$^{-1}$ (*10*). The measurements used were in the frequency range 10 to 70 MHz.; at 70 MHz. absorption was troublesome for the longest path length (*2*), but the value of u had not shifted.

The isothermal compressibility, κ_T,

$$\kappa_T = -(\partial \ln V/\partial p)_T = (\partial \ln \rho/\partial p)_T$$

may be calculated from κ_S by