

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE WITH BARTLETT'S P - V - T DATA ON HYDROGEN

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In two previous papers, Bartlett¹ and his co-workers have published compressibility data for hydrogen, nitrogen and their 3:1 mixture to 1000 atmospheres pressure and from -70 to 400° . These included their own measurements and those from other sources. It is desirable to have a formula that will represent this compressibility data over as wide a range as possible in order that thermodynamic properties may be computed analytically. Accordingly the writers have attempted to find values for the constants in the Beattie-Bridgeman² equation of state for these data. The constants for nitrogen have already been published.³ We here present the values of the constants for hydrogen; and in a later article we hope to present those for the 3:1 hydrogen-nitrogen mixture with a discussion of the scheme for combining the constants of the constituents to derive an equation for a mixture.

The method of determining the constants is a modification of that originally given by Beattie and Bridgeman and it was explained in detail in our paper on nitrogen. In the present work we use specific volumes in cc. per mole instead of cc. per gram; and we decided to use Birge's value⁴ 22414.1 cc. for the volume of a mole of an ideal gas at S. T. P., and his value 273.18°K. for the ice point. The "International Critical Tables" (Vol. III, p. 3) give 0.99939 for the ratio of PV at 0° and 0 pressure to PV at 0° and 1 atm. pressure for hydrogen, so we use $22414.1/0.99939 = 22427.8$ cc. as the volume of a mole of hydrogen at S. T. P. This is the factor that converts Bartlett's volumes into cc. per mole. For R we use $22414.1/273.18 = 82.0489$ cc. atm. per mole per degree. In the previous work on nitrogen we used 273.13°K. for the ice point, but we think it is better to adopt Birge's values now. This change is too small to affect the constants in the equation of state because their values are fixed by the positions of certain lines or curves (Fig. 1), and in such work the locations of the curves are often a matter not easy to decide. Further, the ice-point enters mainly through the product RT , that is, through the volume of a mole of an ideal gas at 0° and 0 pressure, for which Birge's value is very

¹ Bartlett, Cupples and Tremearne, *THIS JOURNAL*, **50**, 1275 (1928); Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.*, **52**, 1364 (1930).

² Beattie and Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); *THIS JOURNAL*, **49**, 1665 (1927); and later papers.

³ Deming and Miss Shupe, *ibid.*, **52**, 1382 (1930).

⁴ Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

nearly the same as had commonly been accepted prior to his compilation of physical constants, so the use of 273.18° does not have any discernible effect on the values to be determined for the parameters.

Bartlett and co-workers compiled and published compressibility data from all available sources along with their own. For the determination of the parameters in the equation of state we decided to smooth and average all of these data, and at the same time to interpolate to even temperatures.⁵

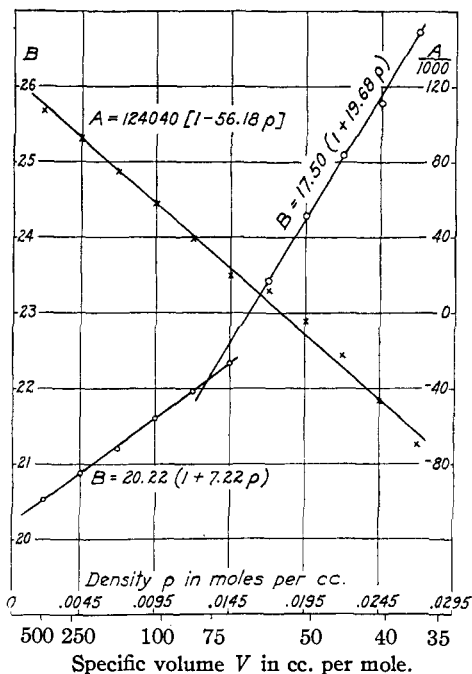


Fig. 1.—Hydrogen, The A and B plots.

computing the D . These compressibility factors, which are shown in Table I, should be the most reliable yet published for hydrogen. Values at 400° are not shown, because, although Bartlett made determinations at 100, 200, 300 and 400 atmospheres at this temperature, he does not consider them to be reliable.

For determining the constants in an equation of state it is better to have the pressures listed at even temperatures and densities than to have volumes listed at even temperatures and pressures. This change can be

⁵ In the first reference to Bartlett and co-workers, some of the temperatures lacked a few tenths of being integral. Further, after the second reference had gone to the publisher, Dr. Kvalnes advised us that a recalibration of their thermocouple showed the temperatures published as -70 , -50 , -25° should have been -69.90 , -49.93 , -24.99° . In our Table I the compressibility factors are computed for integral temperatures.

Our method for smoothing and averaging the observations of the different observers listed by Bartlett was to plot $D \equiv mT - PV + I$ against T . m and I are constants for each isobar; I is the intercept and m the slope of a line chosen to approximate PV plotted against T . There is a PV and hence a D for each observation in Bartlett's tables. Smooth isobars were drawn to the graphs of D vs. T . Bartlett's points were given the most weight because his observations extend over the greatest range. Values of D were read off these curves at even temperatures; and from them $PV = mT + I - D$ was computed at each temperature and pressure, using the same values of m and I for each isobar that were used in

TABLE I

AVERAGED AND SMOOTHED COMPRESSIBILITY FACTORS, PV , FOR HYDROGEN. $PV = 1$

AT 1 ATMOSPHERE AND 0°

| T , °K. | 203.18 | 223.18 | 248.18 | 273.18 | 293.18 | 323.18 | 373.18 | 473.18 | 573.18 |
|----------------|-------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| T , °C. | -70 | -50 | -25 | 0 | 20 | 50 | 100 | 200 | 300 |
| Pressure, atm. | Compressibility factors | | | | | | | | |
| 1 | 0.7437 | 0.8170 | 0.9085 | 1.0000 | 1.0732 | 1.1830 | 1.3661 | 1.7321 | 2.0981 |
| 25 | .7562 | .8295 | .9218 | 1.0145 | 1.839 | | | | |
| 50 | .7699 | .8448 | .9380 | 1.0311 | 1.1054 | 1.2166 | 1.4016 | 1.7692 | |
| 75 | .7848 | .8604 | .9543 | 1.0476 | 1.1221 | | | | |
| 100 | .7993 | .8755 | .9701 | 1.0642 | 1.1391 | 1.2510 | 1.4366 | 1.8036 | 2.1662 |
| 125 | .8139 | .8930 | .9906 | 1.0864 | 1.1610 | | | | |
| 150 | .8310 | .9081 | 1.0034 | 1.0979 | 1.1726 | | | | |
| 200 | .8616 | .9394 | 1.0358 | 1.1317 | 1.2082 | 1.3226 | 1.5121 | 1.8856 | 2.2545 |
| 300 | .9319 | 1.0115 | 1.1095 | 1.2056 | 1.2821 | 1.3959 | 1.5844 | 1.9581 | 2.3274 |
| 400 | 1.0069 | 1.0848 | 1.1814 | 1.2772 | 1.3535 | 1.4676 | 1.6568 | 2.0313 | 2.4011 |
| 500 | 1.0796 | 1.1572 | 1.2540 | 1.3507 | 1.4280 | | | | |
| 600 | 1.1516 | 1.2330 | 1.3300 | 1.4257 | 1.5017 | 1.6152 | 1.8033 | 2.1764 | 2.5438 |
| 800 | 1.2989 | 1.3775 | 1.4732 | 1.5692 | 1.6451 | 1.7583 | 1.9462 | 2.3196 | 2.6803 |
| 1000 | 1.4439 | 1.5218 | 1.6172 | 1.7123 | 1.7878 | 1.9008 | 2.0877 | 2.4586 | 2.8158 |

effected by the following method.⁶ $\Delta \equiv (PV - RT)V/RT$ is plotted against $\rho = 1/V$ for each temperature and smooth isotherms are drawn. Then Δ is read off at even densities from each isotherm, and $P = RT(\rho - \rho^2\Delta)$ is computed for each temperature and volume. In this process the data are further smoothed. Pressures thus derived are listed in Table II at even temperatures and densities. The family of ρ, Δ isotherms were so regular that extrapolations beyond the highest observed densities seemed justified and, since they are to be desired, were made. We write

$$P + \Gamma = \psi T - \phi \tag{1}$$

Beattie and Bridgeman put

$$\left. \begin{aligned} \Gamma T^2 &= \psi c/V \\ B &= B_0(1 - b/V) \end{aligned} \right\} \psi = R(V + B)V^{-2} \quad \left. \begin{aligned} A &= A_0(1 - a/V) \\ \phi &= AV^{-2} \end{aligned} \right\} \tag{2}$$

with A_0, V_0, a, b, c constants, mentioning the possibility of extending the expressions for A and B to include higher powers of $1/V$. The method that we used for finding the constants was described in the paper on nitrogen.

For the four highest densities, the best values of c are 10.4, 19.7, 18.9, 23.9×10^6 . They evidently increase as the density decreases. We adopted $c = 20 \times 10^6$ as the best average value. We then determined what values of ψ and ϕ with $c = 20 \times 10^6$ render the mean square per cent. deviations of the calculated pressures a minimum for each isochore. The values thus found were used to compute $A = \phi V^2$ and $B = (\psi V^2 - RV)/R$ for each density. A and B were then plotted against ρ .

⁶ Andrews, *Phil. Trans. Roy. Soc.*, 166, 421 (1876); O. C. Bridgeman, *THIS JOURNAL*, 49, 1130 (1927).

calculated with the constants of Equations 4 do not agree with the pressures of Table II as well as do the constants in Equations 3, as is shown by the following tabulation of root mean square deviations at the five lowest densities. The second column is anticipated from Table II.

| Density | R. M. S. per cent. deviations using | |
|---------|-------------------------------------|-------------|
| | Equations 3 | Equations 4 |
| 0.0020 | 0.040 | 0.129 |
| .0045 | .048 | .398 |
| .0070 | .058 | 1.30 |
| .0095 | .100 | 2.63 |
| .0120 | .166 | 4.25 |

At higher densities the disparity becomes still more pronounced. On the other hand, the constants of Equations 3 give larger deviations than Equations 4 at the extremely low temperatures at which observations have been made at the Leiden Laboratory. Over the range of density and temperature of Table II the constants in Equations 3 seem to be the best that can be obtained.

Table II lists the smoothed pressures at even temperatures and densities and the comparison with the calculated pressures.

Consideration of the deviations in Table II shows that the constants given in Equations 3 reproduce pressures for hydrogen very well up to 0.0245 mole per cc. inclusive, and with a root mean square error of 1.4% for the five lowest temperatures at 0.0270 mole per cc.

These calculations were made with the two sets of values for B_0 and b , corresponding to the two lines for the B points in the figure. No single set of constants (*i. e.*, no single straight line) will give anywhere near as good agreements between observed and calculated pressures. A parabola cannot be fitted satisfactorily to the B points. The only solution seems to be the two straight lines.

PV values at 400° were calculated and compared with those observed and published by Bartlett, and we find deviations of -1.04 , -0.47 , -0.62 , -0.37% at 100, 200, 300, 400 atm., respectively. This probably confirms Bartlett's suspicion that his observations at 400° may not be reliable, because these are larger deviations than one would expect from an extrapolation of 100° above the interval -70 to 300° at comparatively low pressures. The negative sign of the deviations probably indicates that his measured values of V were too small—perhaps due to gas escaping from or diffusing through the pipet at this high temperature, as was suspected by Bartlett and co-workers.⁷

We have had the willing coöperation of the staff of the Fixed Nitrogen Research Laboratory and of the authors of the equation of state throughout the course of this work.

⁷ Bartlett, Cupples and Tremearne, THIS JOURNAL, 50, 1275 (1928).

TABLE II

OBSERVED PRESSURES AT EVEN DENSITIES AND TEMPERATURES AS SMOOTHED FROM THE COMPILATIONS OF BARTLETT AND CO-WORKERS.
HYDROGEN

Comparison with pressures calculated from the Beattie-Bridgeman equation of state, using the constants of Equation 3. Volumes are in cc. per mole, densities in moles per cc., pressures in normal atmospheres. R. M. S. denotes root mean square deviation.

| Density Volume | T, °K. T, °C. | 203.18 -70 | 223.18 -50 | 248.18 -25 | 273.18 0 | 293.18 20 | 323.18 50 | 373.18 100 | 473.18 200 | 573.18 300 | R. M. S. devia- tions, % |
|-----------------------|------------------|---------------|---------------|---------------|-------------|--------------|--------------|---------------|---------------|---------------|--------------------------------|
| 0.0270 | <i>P</i> obs. | 775.81 | 860.45 | 961.88 | 1064.50 | 1145.76 | | | | | |
| 37.0370 | % dev. | 2.10 | 1.60 | 1.02 | 0.90 | 0.86 | | | | | 1.384 |
| 0.0245 | <i>P</i> obs. | 655.40 | 727.49 | 815.46 | 902.72 | 970.83 | 1072.24 | | | | |
| 40.8163 | % dev. | -0.24 | -0.26 | -0.28 | -0.20 | -0.24 | -0.27 | | | | 0.251 |
| 0.0220 | <i>P</i> obs. | 550.48 | 611.58 | 686.59 | 760.20 | 817.66 | 904.09 | 1048.55 | | | |
| 45.4545 | % dev. | -0.53 | -0.48 | -0.39 | -0.34 | -0.41 | -0.38 | -0.19 | | | 403 |
| 0.0195 | <i>P</i> obs. | 458.04 | 509.50 | 572.14 | 633.53 | 682.29 | 754.78 | 874.40 | | | |
| 51.2821 | % dev. | -0.61 | -0.44 | -0.35 | -0.34 | -0.31 | -0.29 | -0.29 | | | 390 |
| 0.0170 | <i>P</i> obs. | 376.29 | 418.73 | 470.13 | 520.89 | 561.25 | 621.67 | 720.07 | 914.70 | | |
| 58.8235 | % dev. | -0.52 | -0.30 | -0.24 | -0.18 | -0.13 | -0.02 | -0.10 | -0.30 | | 267 |
| 0.0145 | <i>P</i> obs. | 304.03 | 338.21 | 379.26 | 420.48 | 452.73 | 501.74 | 582.06 | 740.40 | 892.28 | |
| 68.9655 | % dev. | -0.20 | 0.03 | -0.01 | 0.10 | 0.07 | 0.21 | 0.24 | 0.10 | -0.65 | 257 |
| 0.0120 | <i>P</i> obs. | 239.44 | 266.04 | 298.04 | 330.29 | 355.43 | 394.03 | 457.38 | 582.40 | 703.92 | |
| 83.3333 | % dev. | -0.12 | 0.07 | -0.02 | 0.07 | -0.01 | 0.16 | 0.23 | 0.14 | -0.35 | 166 |
| 0.0095 | <i>P</i> obs. | 181.20 | 200.83 | 224.84 | 248.98 | 267.82 | 296.75 | 344.49 | 438.80 | 531.62 | |
| 105.263 | % dev. | -0.08 | -0.02 | -0.09 | -0.02 | -0.12 | 0.02 | 0.12 | 0.06 | -0.21 | 100 |
| 0.0070 | <i>P</i> obs. | 128.13 | 141.66 | 158.40 | 175.21 | 188.45 | 208.58 | 242.01 | 308.15 | 374.10 | |
| 142.857 | % dev. | 0.01 | -0.03 | -0.09 | -0.05 | -0.11 | -0.03 | 0.07 | 0.02 | -0.02 | 058 |
| 0.0045 | <i>P</i> obs. | 79.38 | 87.55 | 97.72 | 107.92 | 116.06 | 128.28 | 148.67 | 189.13 | 229.57 | |
| 222.222 | % dev. | 0.09 | 0.01 | -0.06 | -0.05 | -0.05 | -0.02 | 0.05 | 0.02 | 0.02 | 048 |
| 0.0020 | <i>P</i> obs. | 34.13 | 37.56 | 41.84 | 46.13 | 49.56 | 54.70 | 63.29 | 80.37 | 97.50 | |
| 500.000 | % dev. | 0.09 | 0.04 | -0.01 | -0.02 | -0.01 | 0 | 0.04 | 0.01 | 0.05 | 040 |
| R. M. S. deviations % | | .706 | .537 | .366 | .321 | .318 | .193 | .163 | .135 | .315 | |

Summary

Bartlett and his collaborators have recently extended their P - V - T measurements on hydrogen to include nine temperatures in the interval -70 to 300° , up to 1000 atmospheres. Their measurements and compilation of data from other sources have been smoothed and averaged and placed in a table (Table I) showing PV at even temperatures and pressures over that range. It is now possible to subject an equation of state for hydrogen to a severe test and to ascertain its limitations. The writers find the constants for hydrogen to be

| | | |
|-----------------------------|----------------|----------------------|
| Below the critical density: | $A_0 = 124040$ | $B_0 = 20.22$ |
| $a = 56.18$ | $b = -7.22$ | $c = 20 \times 10^6$ |
| Above the critical density: | $A_0 = 124040$ | $B_0 = 17.50$ |
| $a = 56.18$ | $b = -19.68$ | $c = 20 \times 10^6$ |

in units of moles, atmospheres and cubic centimeters, for the Beattie-Bridgeman equation of state

$$PV^2 = RT(V + B_0(1 - b/V))(1 - c/VT^3) - A_0(1 - a/V)$$

A method of curve fitting was used which insures that trends and measurements be reproduced as faithfully as the formula is capable of doing. With the constants given above, over the temperature range -70 to 300° , the equation reproduces pressures with a root mean square error of 0.251% at 0.0245 mole per cc., the maximum being -0.28% at -25° ; and with a root mean square error of 1.38% at 0.0270 mole per cc., the maximum being 2.10% at -70° ; and almost perfectly at densities lower than these two. Thus the equation with the above constants reproduces trends and measurements satisfactorily at temperatures as low as -70° up to 0.0270 mole per cc. At densities greater than 0.0270 mole per cc. the calculated pressures (not shown in the table) are invariably too small and the deviations become quite large.

A break between high and low densities comes at about the critical density and is indicated by the intersection of the two lines in the graph of B vs. ρ . It may signify some sort of a change in the properties of hydrogen at this density.

The negative values of ϕ that occur at densities above 0.0180 mole per cc. are evidence for the predominance of repulsive forces between molecules at high densities.

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