the volume of a given gas mass of carbon monoxide is a linear function of the absolute temperature.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

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

BY W. EDWARDS DEMING AND LOLA E. SHUPE

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In connection with recent work in high pressure on gases it has been deemed advisable to test some of the recently proposed equations of state. Bartlett has extended his $P-V-T$ measurements on nitrogen and several other gases to include -25, -50, and $-70°$ up to 1000 atmospheres pressure. At pressures below 100 atmospheres data were obtained by Bartlett at this laboratory only sufficient to check the work of other investigators in this low pressure range. The low pressures in Table III were compiled from data furnished by the Reichsanstalt, the Leiden laboratory, and the Massachusetts Institute of Technology. With this complete set of data an equation of state can now be tested throughout a wider range of pressure, volume, and temperature than has hitherto been possible. The Beattie-Bridgeman[1] equation of state was chosen because its propounders have indicated that it reproduces the trends and measurements very well, and because its utility is great, once the constants have been determined, due to its relatively simple algebraic form.

In this discussion P denotes pressures in atmospheres, v denotes specific volumes in cc. per g., and r, the gas constant in cc. atm. per g. per degree. The gas that Bartlett used for these measurements contained 0.07% argon and 99.93% nitrogen. The presence of the argon makes the value of r slightly different from that for pure nitrogen, but ought to have no discernible effect on any of the other constants in the equation of state. The value of r for this gas is 2.92861 cc. atm. per g. per degree.

Since Bartlett's data[2] are listed in the form of isotherms, they were first converted into isochores, by Andrews' method,[3] because this form is better adapted to the determination of the constants in an equation

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

[2] Bartlett, Cupples, and Tremearne, *ibid.*, **50**, 1275 (1928). Bartlett and his collaborators have since interpolated these data to even temperatures, and their observations have been extended to include -70, -50, -25, and 20°. These are published in the preceding article.

[3] Andrews, *Phil. Trans. Roy. Soc.*, **166**, 421 (1876). This method is clearly explained by O. C. Bridgeman, THIS JOURNAL, **49**, 1130 (1927).

of state that is solved explicitly for P. The observed pressures at even volumes are listed in Table III, the digit in the last decimal place being doubtful. Interpolated pressures can be made more reliable than the original observations by carefully smoothing the curves used in the process of interpolation. Isochores at $v = 3, 4, 5, 7.5, 10, 12.5, 15, 20, 25, 30$ and 40 were chosen as being sufficiently representative of Bartlett's data, for our purpose.

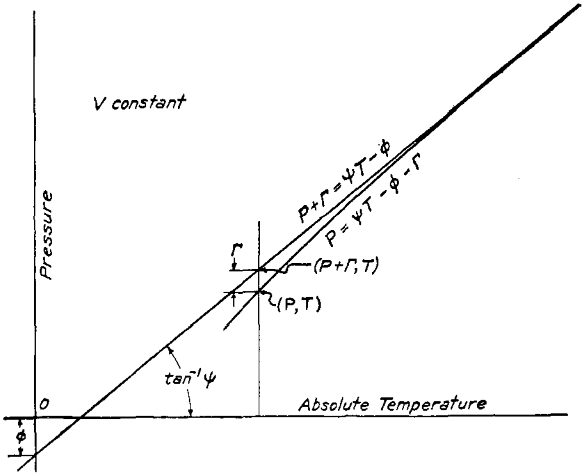

Fig. 1.—General shape of a nitrogen isochore.

The smaller the range of pressure, volume, and temperature that is used to determine the constants in any equation, the better will be the fit *over that range*. We have sought those values of the constants that will reproduce pressures with an accuracy of a few tenths of a per cent. from the lowest pressures to the highest pressures at which the formula will yield results of the desired accuracy. Accordingly we have favored the high-pressure, low-temperature data as far as is possible without destroying the fit at low pressures.

Following Beattie and Bridgeman's scheme, we write

$$P + \Gamma = \psi T - \phi \qquad (1)$$

ψ and ϕ are functions of v; Γ is a function of v and of T. The isochores for high volumes are almost straight lines, but with lower volumes curvature sets in at the low temperature end, as shown in Fig. 1. Γ may be looked upon as a correction term, one that when added to P straightens the isochore. (1) Is the equation of this straight line in the variables $P + \Gamma$ and T, ψ being the slope and ϕ the negative intercept on the P axis. Beattie and Bridgeman put

$$\left.\begin{array}{lll} \Gamma T^2 = \psi c/v & \psi = R(v + B)v^{-2} & \phi = Av^{-2} \\ B = B_0(1 - b/v) & A = A_0(1 - a/v) & \end{array}\right\} \qquad (2)$$

with A_0, B_0, a, b, c constants, mentioning the possibility of extending the expressions for A and B to include higher powers of $1/v$.

The problem is to find the best values of ψ, ϕ, c and hence of B, A, c, for each isochore, and then to express B and A by series in $1/v$ with as few terms as practicable; c is supposed to be constant and hence independent of v. By *best* values, we shall mean those that render $(1/n)\Sigma(P_{\text{obs.}} - P_{\text{calcd.}})^2/P^2_{\text{obs.}}$ or $(1/n)\Sigma(\%\ \text{dev.})^2$ a minimum along any isochore. For any isochore, $\Sigma(\%\ \text{dev.})^2$ is a function of ψ, ϕ, c. (Dev. = deviation = $P_{\text{obs.}} - P_{\text{calcd.}}$. n is the number of temperatures at which pressure is measured along any isochore, ten in Bartlett's data.) The process of finding the best values of ψ, ϕ, c for any isochore is formally the same as Least Squares with the observations on v and T considered infallible compared with those on P. Dr. Bartlett considers his measurements on v to be less reliable than those on P and T. Accordingly, if only one of the three variables P, v, T is to be adjusted, it should be v. However, this is impracticable because the equation of state cannot be solved explicitly for v. Our method, therefore, must not be called Least Squares.

In the language of mathematics, it would be customary to call the values of ψ, ϕ, c that minimize $(1/n)\Sigma(\%\ \text{dev.})^2$ the *critical* values, and the minimum an *absolute* minimum. *Critical* and *best* are here synonymous. With a particular value of ψ, ϕ, or c, not its critical value, the minimum will be *constrained* or *relative*, and will be larger in value than the absolute minimum. Closeness of fit at isolated points is not the only thing required in fitting an equation; the trends or derivatives must also be reproduced. When $\Sigma(\%\ \text{dev.})^2$ is small, the trend as well as the actual pressures is accurately represented. This is in contrast with $\Sigma(\%\ \text{dev.})$, which might be zero for an isochore while the trends are inaccurately represented. Thus with deviations -4, $+4$, -3, $+3$, 0, 5, -5, $\Sigma(\%\ \text{dev.}) = 0$, $\Sigma\ (\%\ \text{dev.})^2 = 100$, and derivatives obtained from such a fit would be entirely misleading.

The critical values of ψ, ϕ, c for v = 5, 7.5, 10, 12.5 are listed in Table I.

TABLE I

CRITICAL VALUES OF ψ, ϕ, c AND THE ABSOLUTE MINIMUM OF $(1/10)\Sigma(\%\ \text{DEV.})^2$ FOR FOUR LOW VOLUMES

v	ψ	ϕ	c	$(1/10)\Sigma(\%\ \text{dev.})^2$
5	0.8162825	57.167	1.848×10^6	0.1191
7.5	.4869524	26.042	2.077	.0431
10	.3451921	14.6366	2.313	.0185
12.5	.2670248	9.3459	2.477	.0086

c has an upward trend with increasing v, so it is necessary to give it an average value. Pressures calculated at the higher volumes are not very sensitive to changes in c, so an average of the critical values of c for the four low volumes of Table I was taken. $c = 2.2 \times 10^6$ was used in the subsequent work.

The next task is to determine what values of ψ and ϕ with $c = 2.2 \times 10^6$ render $(1/10)\Sigma(\%\ \text{dev.})^2$ a (relative) minimum for each isochore. The values found are used to compute $B = (\psi v^2 - rv)/r$ and $A = \phi v^2$ for each volume. These, together with the absolute and relative minimum values of $(1/10)\Sigma(\%\ \text{dev.})^2$, are shown in Table II.

TABLE II

VALUES OF ψ AND ϕ THAT RENDER $(1/10)\Sigma(\%\ \text{DEV.})^2$ A (RELATIVE) MINIMUM WITH $c = 2.2 \times 10^6$, FOR EACH ISOCHORE, AND THE VALUES OF B AND A COMPUTED THEREFROM. RELATIVE AND ABSOLUTE MINIMUM VALUES OF $(1/10)\Sigma(\%\ \text{DEV.})^2$

			Minimum of $(1/10)\Sigma(\%\ \text{dev.})^2$			
v	ψ	ϕ	Relative	Absolute	B	A
3	1.683837	137.911	0.38710	....	2.1747	1241.2
4	1.100409	82.863	.23570	....	2.0119	1325.8
5	0.8126459	55.263	.12896	0.11911	1.9371	1381.6
7.5	.4866500	25.8571	.04448	.04313	1.8471	1454.5
10	.3454291	14.7938	.01984	.01851	1.7950	1479.4
12.5	.2673827	9.5385	.00936	.00862	1.7657	1490.4
15	.2179586	6.6577	.00582	....	1.7454	1498.0
20	.1590196	3.7642	.00314	....	1.7195	1505.7
25	.1251262	2.4145	.00209	....	1.7034	1509.1
30	.1031291	1.6794	.00155	....	1.6929	1511.5
40	.0762905	0.9464	.00106	....	1.6801	1514.2

The values of A and B from this table are plotted as functions of $1/v$ in Fig. 2. If every A and B point within a given range lay on a straight line, it would be a simple matter to finish fitting the equation *over that range.* The problem of placing the straight lines in Fig. 2 is not one in

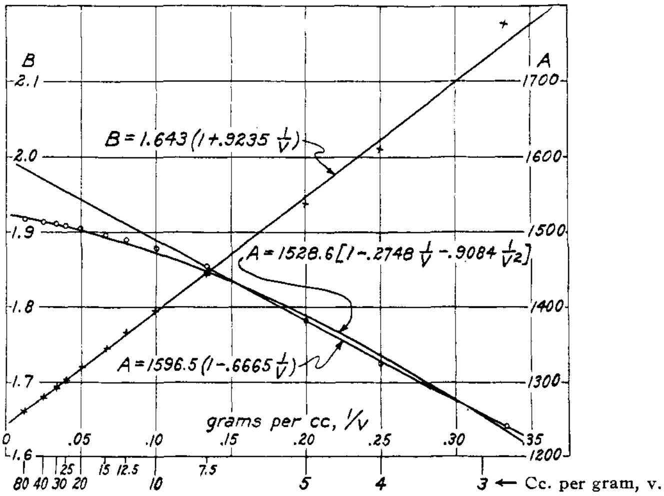

Fig. 2.—The B and A plots.

TABLE III

OBSERVED PRESSURES AS INTERPOLATED FROM BARTLETT'S DATA BY ANDREWS' METHOD, AND THE COMPARISON WITH PRESSURES CALCULATED FROM THE BEATTIE–BRIDGEMAN EQUATION OF STATE

Deviations (i) are computed with ϕ determined by the straight line; (ii), by the parabola. Pressures are in atmospheres; volumes are in cc. per g. R. M. S. denotes root mean square. All calculations are rounded off finally to the number of figures shown.

Vol.	T°K. T°C.	203.13 −70	223.13 −50	248.13 −25	273.13 0	293.13 20	323.13 50	373.13 100	473.13 200	573.13 300	673.13 400	R. M. S. deviation, %
3	P obs.	175.89	212.01	258.78	303.07	339.30	394.51	485.07	659.06	824.84	987.86	
	(i) % dev.	1.89	0.39	0.38	−0.03	0.14	0.73	1.39	1.49	0.77	0.08	0.957
	(ii) % dev.	1.41	.00	.06	− .30	− .11	.52	1.22	1.37	.67	− .01	.785
4	P obs.	126.88	150.15	179.76	208.17	231.57	267.28	324.92	438.20	547.08	653.37	
	(i) % dev.	0.65	−0.31	−0.42	−0.78	−0.58	0.02	0.35	0.58	0.06	−0.63	.498
	(ii) % dev.	.95	− .05	− .20	− .59	− .41	.17	.47	.67	.13	− .57	.500
5	P obs.	101.63	118.64	140.22	161.11	178.22	204.37	246.43	329.09	409.88	488.93	
	(i) % dev.	0.36	−0.33	−0.38	−0.62	−0.45	0.10	0.29	0.31	−0.01	−0.55	.381
	(ii) % dev.	.56	− .15	− .23	− .49	− .33	.20	.38	.38	.04	− .51	.364
7.5	P obs.	69.77	79.72	92.47	104.97	115.02	130.26	155.10	204.23	252.70	300.48	
	(i) % dev.	0.37	−0.15	−0.09	−0.14	−0.07	0.20	0.28	0.26	0.05	−0.29	.215
	(ii) % dev.	.20	− .30	− .21	− .25	− .18	.11	.21	.20	.00	− .32	.216
10	P obs.	53.64	60.67	69.67	78.51	85.57	96.24	113.76	148.57	182.99	217.11	
	(i) % dev.	0.41	0.03	0.13	0.11	0.12	0.26	0.28	0.26	0.08	−0.15	.214
	(ii) % dev.	.09	− .25	− .12	− .11	− .09	.08	.13	.14	− .01	− .23	.143
12.5	P obs.	43.666	49.107	56.022	62.850	68.284	76.487	89.982	116.897	143.557	170.039	
	(i) % dev.	0.39	0.14	0.21	0.21	0.20	0.29	0.26	0.24	0.10	−0.09	.229
	(ii) % dev.	.02	− .19	− .07	− .05	− .04	.07	.08	.10	− .01	− .18	.102
15	P obs.	36.854	41.284	46.898	52.450	56.861	63.521	74.487	96.411	118.157	139.780	
	(i) % dev.	0.37	0.19	0.25	0.25	0.22	0.29	0.24	0.23	0.11	−0.05	.235
	(ii) % dev.	.00	− .15	− .04	− .01	− .02	.07	.05	.08	− .01	− .15	.079
20	P obs.	28.111	31.340	35.411	39.447	42.651	47.487	55.465	71.439	87.312	103.123	
	(i) % dev.	0.33	0.22	0.27	0.27	0.23	0.27	0.21	0.20	0.10	−0.02	.230
	(ii) % dev.	− .02	− .09	.00	.03	.01	.07	.03	.06	− .01	− .11	.056

TABLE III (*Concluded*)

Vol.	T°K. T°C.	203.13 −70	223.13 −50	248.13 −25	273.13 0	293.13 20	323.13 50	373.13 100	473.13 200	573.13 300	673.13 400	R. M. S. deviation, %
25	*P* obs.	22.730	25.267	28.457	31.626	34.140	37.935	44.203	56.763	69.258	81.714	
	(i) % dev.	0.29	0.22	0.26	0.26	0.22	0.25	0.18	0.17	0.09	0.00	.212
	(ii) % dev.	− .02	− .06	.01	.04	.02	.06	.02	.05	− .01	− .09	.046
30	*P* obs.	19.080	21.169	23.790	26.397	28.467	31.589	36.751	47.097	57.398	67.672	
	(i) % dev.	0.26	0.21	0.24	0.25	0.21	0.23	0.16	0.15	0.08	0.00	.194
	(ii) % dev.	− .02	−0.05	.02	.04	.02	.06	.01	.04	− .01	− .07	.040
40	*P* obs.	14.444	15.986	17.918	19.842	21.371	23.675	27.491	35.139	42.761	50.368	
	(i) % dev.	0.20	0.18	0.21	0.21	0.18	0.19	0.13	0.12	0.07	0.01	.162
	(ii) % dev.	− .02	− .03	.02	.05	.02	.05	.01	.03	− .01	− .06	.033
(i) R. M. S. dev. %		0.674	0.234	0.277	0.353	0.274	0.307	0.480	0.523	0.243	0.274	
(ii) R. M. S. dev. %		.546	.151	.122	.263	.173	.186	.417	.480	.205	.275	
V		1.6432	1.7535	1.8903	2.0273	2.1451	2.3283	2.6194	3.1929	3.7367	4.2611	
P obs.		600	600	600	600	600	600	600	600	600	600	
(i) % dev.		28.7	19.7	12.4	7.76	5.77	4.30	2.47	1.12	0.10	−0.73	
(ii) % dev.		16.9	11.5	7.04	4.19	3.26	2.84	1.88	1.08	.16	− .66	
V		1.4218	1.4850	1.5671	1.6503	1.7175	1.8249	1.9947	2.3356	2.6547	2.9762	
P obs.		1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	
(i) % dev.		42.8	33.3	25.1	19.3	15.9	12.6	8.48	4.40	1.51	0.12	
(ii) % dev.		27.9	21.4	16.0	12.4	10.3	8.67	6.12	3.54	1.19	.02	

curve-fitting; they should be drawn with a view to giving a good fit over a limited range rather than a barely passable fit over a long range. The lines drawn in Fig. 2 give

$$\left.\begin{array}{ll} A_0 = 1596.5 & a = 0.6665 \\ B_0 = 1.643 & b = -0.9235 \\ \text{which with } c = 2.2 \times 10^6 & \end{array}\right\} \qquad (3)$$

are the values that we have determined for the five constants. The values that Beattie and Bridgeman[1] gave for nitrogen, when changed into our units, are $A_0 = 1711.9$, $a = 0.9338$, $B_0 = 1.801$, $b = -0.2466$, $c = 1.5 \times 10.^6$ Their calculations were based on data from several sources, with the temperature range from -148.58 to 400° and with most of the pressures lying below 100 atmospheres, so their constants could hardly be expected to hold at high pressures.

It was not possible to fit satisfactorily all the A points in Fig. 2 with a straight line. However, they lie close to the parabola

$$A = 1528.6(1 - 0.2748/v - 0.9084/v^2) \qquad (4)$$

Introducing this parabola amounts to introducing a sixth parameter, a'; and

$$\left.\begin{array}{lll} A_0 = 1528.6 & a = 0.2748 & a' = 0.9084 \\ B_0 = 1.643 & b = -0.9235 & \\ c = 2.2 \times 10^6 & & \end{array}\right\} \qquad (5)$$

are the values that we have determined for the six constants. With ϕ, ψ and ΓT^2 from Equation 2, the equation

$$P_{\text{calcd.}} = \psi T - \Gamma - \phi \qquad (6)$$

gives the calculated pressure at a chosen temperature and volume. Table III lists the observed pressures and shows how the calculated pressures compare with them. A few of Bartlett's measurements for $v < 3$ are appended.

The agreement between observed pressures and those calculated both with the straight line and the parabola for A is remarkably good down to $v = 3$ cc. per g. over the entire temperature range. A study of the root mean square deviations shows that the parabola gives better agreement when the entire range of volume is considered—enough better to recommend the use of the six constants of Equation 5 rather than the five constants of Equation 3.

One of the chief uses of an equation of state comes in thermodynamic calculations. There it is necessary that the equation represent trends accurately in order that the derivatives be reliable. From Fig. 2 it can be seen that the parabola follows the trend of the A points over the entire range of volume, whereas no straight line could do so. Further, the agreement between calculated and observed pressures for $v < 3$ (Table III) is also much better with the parabola; this shows that it still approximates the trend beyond the range of Fig. 2. So the behavior of nitrogen seems to be well represented by the six constants of Equation 5, for volumes down to 3 cc. per g. and from −70 to 400°. Calculations made with these constants should be fairly trustworthy over this range.

An examination of Table III shows that, while the equation of state seems satisfactory down to about $v = 3$ cc. per g., there is clearly something wrong when $v < 3$ at the low temperatures. There is no doubt that the addition of terms in $1/v^2$ for B and $1/v^3$ for A would effect an improvement, but this would bring in two more constants that are not needed when $v \geq 3$. The equation seems to have a definite limitation in the neighborhood of 3 cc. per g. at medium and low temperatures.

The data on hydrogen and its 3:1 mixture with nitrogen obtained by Bartlett and his collaborators is being similarly treated, and the results will appear shortly.

It is a pleasure to acknowledge our indebtedness to Dr. Oscar C. Bridgeman and Professor James A. Beattie, the authors of the equation of state, for many helpful suggestions. We have had the willing coöperation of Dr. Bartlett throughout the course of this work.

Summary

Bartlett has recently extended his P–V–T measurements on nitrogen to include ten temperatures in the interval −70 to 400°, up to 1000 atmospheres. His measurements and compilations cover a much greater range than has hitherto been embraced. It is now possible to subject an equation of state to a severe test and to ascertain its limitations. The writers find for nitrogen the values

$$A_0 = 1528.6 \qquad a = 0.2748 \qquad a' = 0.9084$$
$$B_0 = 1.643 \qquad b = -0.9235 \qquad c = 2.2 \times 10^6$$

in the units of grams, atmospheres, and cubic centimeters, for the constants in the Beattie–Bridgeman equation of state,

$$Pv^2 = rT\,[v + B_0\,(1 - b/v)]\,(1 - c/vT^3) - A_0\,(1 - a/v - a'/v^2)$$

r correspondingly expressed in cc. atm. per g. per degree. In this investigation a method of curve-fitting has been used that accurately reproduces trends as well as actual pressures in the P–V–T relations. With the constants given above, over the temperature range −70 to 400° the equation reproduces pressures with a root mean square deviation of 0.50% at 4 cc. per g., the maximum being 0.95%; and with a root mean square deviation of 0.78% at 3 cc. per g., the maximum deviation being 1.41%. Thus the equation with the above constants reproduces trends and pressures satisfactorily from −70 to 400° down to 3 cc. per g. Below 3 cc. per g. the calculated pressures are invariably too low, and the discrepancy becomes very large at low temperatures and low volumes.

WASHINGTON, D. C.