THE BEATTIE–BRIDGEMAN EQUATION OF STATE AND BARTLETT'S P–V–T DATA ON A 3:1 HYDROGEN–NITROGEN MIXTURE

BY W. EDWARDS DEMING AND LOLA E. SHUPE

Direct Determination of the Constants

In previous papers[1] the constants for the Beattie–Bridgeman[2] equation of state have been published for the high pressure data obtained at this Laboratory with nitrogen and hydrogen. We now present constants determined by the same method for a 3:1 hydrogen–nitrogen mixture, the experimental data for which were published by Bartlett and his collaborators,[3] who record their own measurements from −70 to 300° up to 1000 atmospheres, and a few scattered ones taken from the work of Verschoyle. After comparing the observed pressures in the table with pressures calculated using the constants to be given in Equation 6, we shall study the schemes for combining the constants previously found for hydrogen and nitrogen to devise constants for the mixture.

To settle on a value for the ratio of PV at 0° and 0 pressure to PV at 0° and 1 atm., we took the weighted average of the best values[4] known to us for hydrogen and nitrogen, which are 0.99939 and 1.00046. The weighted average is $(3 \times 0.99939 + 1.00046)/4 = 0.99966$. Using Birge's value[5] 22414.1 cc. for the volume of a mole of an ideal gas at S. T. P. we have 22421.7 cc. for the volume of a mole of the 3:1 mixture at S. T. P. Bartlett expresses his PV with $PV = 1$ at S. T. P., so we multiply his specific volumes by 22421.7 to change them into cc. per mole. We use $R = 82.0489$ cc. atm. per mole per degree, and 273.18°K. for the ice point, as given by Birge.

As we mentioned in our paper on hydrogen, the three lowest temperatures in Bartlett's table should have been published as −69.90, −49.93, −24.99° instead of −70, −50, −25°. We have made these slight corrections and have interpolated to integral temperatures in our process of smoothing.[6] The pressures at integral temperatures and densities derived from Bartlett's publications are listed in the table later on. The extrap-

[1] Deming and Shupe, THIS JOURNAL, **52**, 1382 (1930); **53**, 843 (1931).

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

[3] Bartlett, Cupples and Tremearne, *ibid.*, **50**, 1275 (1928); Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.*, **52**, 1363 (1930).

[4] "International Critical Tables," Vol. III, p. 3.

[5] Birge, *Phys. Rev.* Supplement, 1, 1 (1929).

[6] Described in the preceding paper.

olations beyond 1000 atm. seemed to us reliable, judging from the perfect regularity of the ρ, Δ isotherms after the process of smoothing. The extrapolations were made by extending the ρ, Δ curves. The nearness of the experimental points to these curves, which are greatly magnified deviation curves, attests to the high precision of the experimental work.

Throughout this paper the notation will be the same as that in the papers on nitrogen and hydrogen, and the equations, tables, and figures will be numbered from the last ones in the paper on hydrogen.
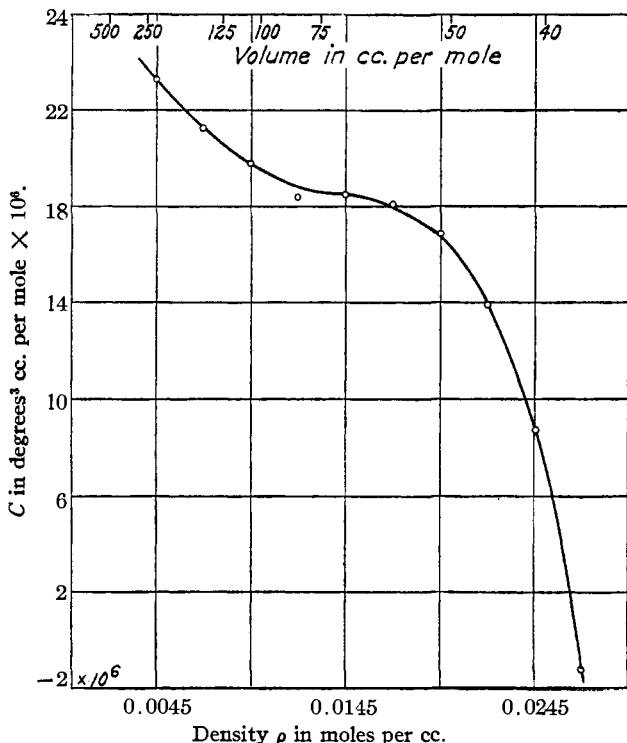

Fig. 2.—The values of c that render $\Sigma\left[(P_{obs.} - P_{calcd.})/P_{obs.}\right]^2$ an absolute minimum at each density of the 3:1 hydrogen–nitrogen mixture.

Attempts to find the best value of c revealed immediately some peculiarities of this mixture. The best value of c for $\rho = 0.0270$ mole per cc. turned out to be negative; and the values found for the next three densities were so discordant that we finally computed c for every density. The graph of c vs. ρ (Fig. 2) shows these peculiarities. We chose $c = 16 \times 10^6$ as likely to give the best results over the whole range. The rather long extrapolations beyond 1000 atm. at the low densities and high temperatures are not responsible for the peculiar behavior depicted by the graph;

the calculations were repeated with the extrapolated pressures discarded and the resulting graph showed c to be a trifle more variable than before.

The tendency for c to decrease and finally to become negative as the density increases seems to be related to the similar tendency exhibited by ϕ with hydrogen and to a smaller extent, as will be seen, with this mixture. An explanation for this behavior is found in the existence of repulsive forces that come into play at high densities.[7]　The same might have been found true with nitrogen if that work had included higher densities.

The values of ψ and ϕ with $c = 16 \times 10^6$ that render the mean square per cent. deviations of the calculated pressures a minimum along each isochore were found and were then used to compute $B = (\psi V^2 - RV)/R$ and $A = \phi V^2$ at each density.　The graphs of A and B as functions of ρ are shown in Fig. 3.　There is little doubt that two lines for each are indicated; the locations finally selected are shown in the figure, and their slopes and intercepts determine A_0, a, B_0, b.

These pairs of lines intersect at 0.0137 and 0.0132 mole per cc.　Now this mixture probably has a critical density in this vicinity.　In general the critical curve for a binary mixture is fairly smooth between the two components.　The "International Critical Tables" give 0.0154 and 0.0111 mole per cc. for the critical densities of hydrogen and nitrogen; so the critical density of the mixture probably lies in the neighborhood of 0.014 mole per cc.　The intersections in Fig. 3 are close to this value.　We found the same with hydrogen in the preceding paper.　It appears that the equation of state has one set of constants below the critical density, and another set above it.　This behavior may be common to all gases; our work on nitrogen barely included the critical density, so we cannot predict its behavior.　Figure 2 shows a peculiar flattening of the c vs. ρ curve in the interval $0.0120 < \rho < 0.0145$, which may be related to the breaks in the A and B plots.　We are indebted to Professor Beattie for pointing out to us the possible connection between the breaks in the A and B plots and the critical density of the mixture.

From Fig. 3

Below the critical density

$$A_0 = 3000 \times 10^2 \qquad\qquad\qquad B_0 = 25.03$$
$$a = 21.36 \qquad b = -15.16 \qquad c = 16 \times 10^6$$

Above the critical density

$$A_0 = 3489 \times 10^2 \qquad\qquad\qquad B_0 = 21.42$$
$$a = 28.56 \qquad b = -30.58 \qquad c = 16 \times 10^6$$

$$(5)$$

in units of moles, atmospheres, and cubic centimeters.

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

Consideration of the deviations in Table III shows that the equation of

[7] Deming and Miss Shupe, an article to appear.

state with the constants of Equations 5 reproduces pressures almost within the experimental error up to 0.0270 mole per cc.; at this density the root mean square deviation is 1.8%.

The Constants Determined by Combination.—A scheme for computing analytically the $P–V–T$ relations of a mixture from those of the constituents would be valuable. In recent papers Beattie and others[8] have given histories of the different devices for making such calculations, and have investigated the result of combining the constants in the equations of state for the constituents to get constants to be used for the mixture.
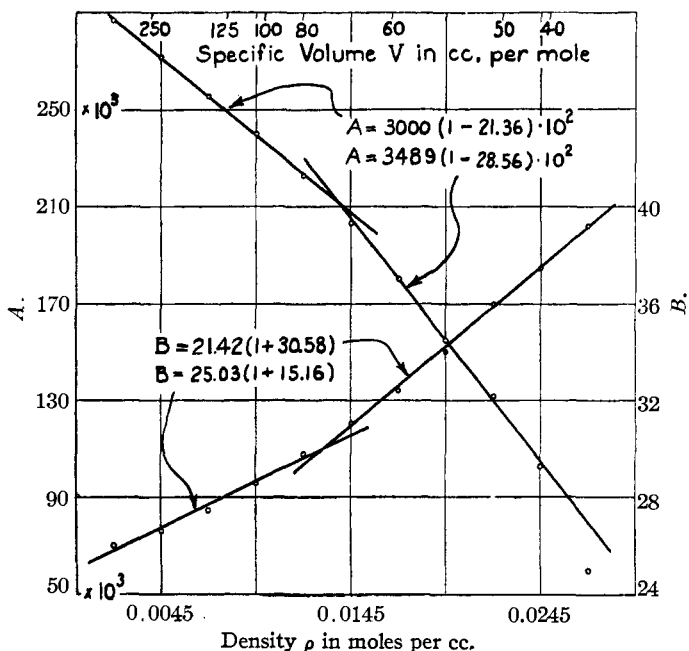

Fig. 3.—The A and B plots for the 3:1 hydrogen–nitrogen mixture.

Beattie and Ikehara have made an exhaustive study of this idea using the Beattie–Bridgeman equation of state. They combined a, b, c, $\sqrt{A_0}$ linearly by mole fraction, and compared three methods of combining B_0-linear, Lorentz, and linear square root. We propose here to extend this study to the high pressure data on the 3:1 hydrogen–nitrogen mixture.

Suppose B_{oh} and B_{on} are the B_0 constants for hydrogen and nitrogen, and that these two gases are present in a binary mixture to the extent of mole fractions x_h and x_n; then the B_0 constant for the mixture (B_{ox}) will be formed quadratically:

$$B_{ox} = B_{oh}x_h^2 + 2B_{hn}x_hx_n + B_{on}x_n^2 \qquad (6)$$

[8] Beattie, THIS JOURNAL, **51**, 19 (1929); Beattie and Ikehara, *Proc. Am. Acad. Arts Sci.*, **64**, 127 (1930); Keyes and Burks, THIS JOURNAL, **50**, 1100 (1928).

TABLE III

OBSERVED PRESSURES AS SMOOTHED FROM THE COMPILATION OF BARTLETT FOR 3:1 HYDROGEN–NITROGEN MIXTURE

Comparison with pressures calculated from the Beattie–Bridgeman equation of state, using the constants of Equation 5. Volumes are in cc. per mole, densities in moles per cc., pressures in normal atmospheres. R. M. S. denotes root mean square.

Density volume	T, °K. / T, °C.	203.18 −70	223.18 −50	248.18 −25	273.18 0	298.18 25	323.18 50	373.18 100	473.18 200	573.18 300	R. M. S. dev., %
0.0270	P obs.	840.34	938.41	1057.48	1176.10	1296.30	1420.35				
37.0370	% dev.	2.49	2.11	1.08	1.41	1.45	1.81				1.790
0.0245	P obs.	690.12	772.89	874.87	975.98	1076.01	1177.69	1376.34			
40.8163	% dev.	0.23	0.06	−0.04	−0.05	−0.06	0.13	0.19			0.129
0.0220	P obs.	566.21	634.84	720.10	803.70	886.61	970.95	1136.43	1461.07		
45.4545	% dev.	0.12	0.01	0.04	−0.01	−0.04	0.15	0.25	0.11		.120
0.0195	P obs.	461.75	518.10	587.71	657.22	725.28	792.84	929.77	1196.11	1462.84	
51.2821	% dev.	−0.24	−0.30	−0.30	−0.20	−0.23	−0.28	−0.06	−0.26	−0.29	.250
0.0170	P obs.	373.11	419.02	475.11	531.39	586.95	641.41	751.74	969.18	1185.21	
58.8235	% dev.	−0.26	−0.20	−0.25	−0.14	−0.10	−0.20	−0.09	−0.16	−0.25	.192
0.0145	P obs.	297.98	334.28	379.18	423.33	467.19	511.04	598.80	772.57	945.55	
68.9655	% dev.	0.19	0.22	0.27	0.23	0.20	0.20	0.28	0.27	0.02	.222
0.0120	P obs.	233.27	260.77	295.70	329.78	363.29	397.43	465.13	599.89	731.96	
83.3333	% dev.	0.23	0.11	0.30	0.27	0.14	0.21	0.27	0.32	0.02	.222
0.0095	P obs.	176.05	196.20	222.17	247.26	272.07	297.23	347.20	446.86	545.33	
105.263	% dev.	−0.09	−0.24	−0.06	0.00	−0.11	−0.06	−0.04	−0.01	−0.17	.114
0.0070	P obs.	124.74	138.58	156.28	173.70	190.88	208.13	242.46	311.15	379.61	
142.857	% dev.	−0.16	−0.29	−0.08	−0.04	−0.10	−0.10	−0.14	−0.14	−0.17	.152
0.0045	P obs.	77.78	86.11	96.61	107.14	117.55	127.92	148.52	189.91	231.36	
222.222	% dev.	−0.03	−0.13	−0.07	0.03	0.03	0.01	−0.09	−0.10	−0.06	.074
0.0020	P obs.	33.79	37.25	41.59	45.96	50.30	54.61	63.22	80.47	97.78	
500.000	% dev.	0.04	0.00	0.01	0.09	0.11	0.09	0.02	−0.01	0.04	.059
R. M. S. deviations %[a]		0.179	0.188	0.183	0.112	0.127	0.156	0.171	0.185	0.163	

[a] Density 0.0270 is excluded from these R. M. S. deviations.

The three methods mentioned above apply to the interaction factor B_{hn}, thus

$$\text{By the linear method, } B_{hn} = {}^1/_2(B_{oh} + B_{on}) \tag{7}$$
$$\text{By the Lorentz method, } B_{hn}^{1/3} = {}^1/_2(B_{oh}^{1/3} + B_{on}^{1/3}) \tag{8}$$
$$\text{By the linear square root method, } B_{hn}^2 = B_{oh}B_{on} \tag{9}$$

We shall use subscripts h and n for hydrogen and nitrogen; then $x_h = {}^3/_4$ and $x_n = {}^1/_4$, since our specific volumes are in cc. per mole.

If we combine the constants for hydrogen and nitrogen that were found to hold for densities below critical, the synthetic constants cannot be expected to hold above the critical density of the mixture. For nitrogen we found

$$\left. \begin{array}{ll} A_{on} = 1254 \times 10^3 & B_{on} = 46.045 \\ a_n = 18.68 \qquad b_n = -25.88 & c_n = 61.64 \times 10^6 \end{array} \right\} \tag{10}$$

These have been changed to units of moles, atmospheres, and cubic centimeters. From Equation 3

$$\left. \begin{array}{ll} A_{oh} = 1240 \times 10^2 & B_{oh} = 19.90 \\ a_h = 56.18 \qquad b_h = -10.72 & c_h = 20 \times 10^6 \end{array} \right\} \tag{11}$$

Combination of 10 and 11 gives

$$\left. \begin{array}{ll} A_{om} = 2889 \times 10^2 & a_m = 46.80 \\ b_m = -14.51 & c_m = 30.41 \times 10^6 \end{array} \right\} \tag{12}$$
$$\text{By the linear method, } B_{om} = 26.43 \tag{13}$$
$$\text{By the Lorentz method, } B_{om} = 25.76 \tag{14}$$
$$\text{By the linear square root method, } B_{om} = 25.42 \tag{15}$$

Pressures were calculated with these constants and compared with the observed pressures listed in Table III.   The root mean squares of the deviations were taken with respect to temperature, and with respect to density for the five densities below critical.   The most comprehensive presentation of these deviations seemed to be the graphical one in Figs. 4 and 5.   Root mean square deviations for the pure gases using Equations 3 and 10, and for the 3:1 mixture using Equations 5 are shown for comparison.

The graphs fail to give information in two respects: they do not tell whether the deviations at a particular density are predominantly positive or negative, and they do not tell the extent of variation among the deviations at a particular density or temperature.   Two general statements cover these points.   At any one density the deviations for any one gas are roughly of the same magnitude, so unless they are nearly zero it is possible to state that they are either predominantly positive or predominantly negative.   The deviations at all the densities within the range shown might be expected to be predominantly of the same sign.   This is the case; they all turned out to be predominantly negative for all three methods of combination.

Here the linear square root method seems to be a little better than the

other two, but none of them are satisfactory except at the lowest densities. The representation of data by the linear square root method of combination for B_0 is almost within the experimental error to densities as high as 0.0070 mole per cc., where, as can be seen in Fig. 4, the R. M. S. deviation is 1.17%.
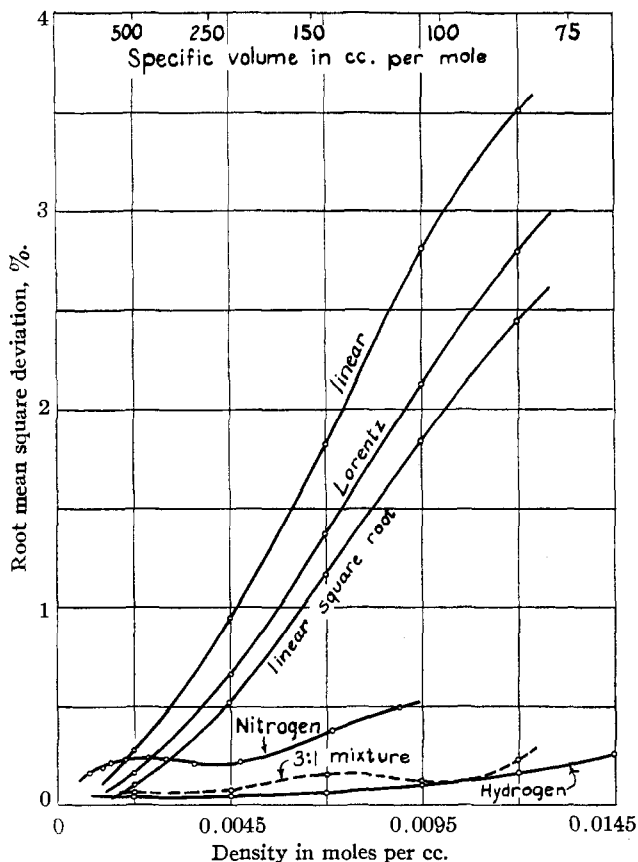

Fig. 4.—Root mean square deviations of pressures calculated by three methods of combining the B_0 constant, taken over the nine temperatures.

This is a different conclusion from that reached by Beattie and Ikehara, who say: "On the whole, linear combination for B_0 was slightly favored over the Lorentz method, while the linear square root relation gave the least satisfactory results. . . . Linear combination for each of the constants R, $\sqrt{A_0}$, a, B_0, b, and c of the Beattie–Bridgeman equation of state gives a satisfactory over-all correlation of the compressibility data on gas mixtures, although in some cases the representation of the data may not be within the experimental error."

A 3:1 hydrogen–nitrogen mixture was only one of many studied by

Beattie and Ikehara; their Fig. 15 shows percentage deviation *vs.* pressure at 0° up to 200 atmospheres for linear and Lorentz combination, using Verschoyle's data.   Comparing their results as read from their Fig. 15 with our calculations, we find that our deviations by the linear and Lorentz methods are a little larger than theirs, but our results by the linear square root method are better than either their linear or Lorentz combinations.
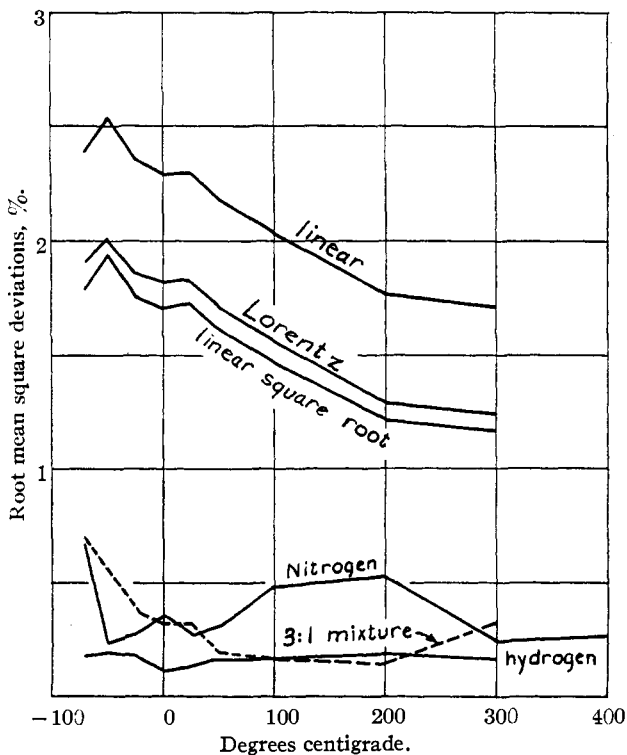

Fig. 5.—Root mean square deviations of pressures calculated by three methods of combining the B_o constant, taken over the five densities below critical.

One might expect our deviations to be larger since our constants were determined for each constituent up to the critical density at each temperature.   The constants that Beattie and Ikehara combined were determined for comparatively low densities, and their combination might be expected to fit the 3:1 mixture quite well at not too high pressures.

It should be noted that the data that we have used for the constituents and their mixture should be consistent, since Bartlett's work was all done with the same apparatus, and his measurements naturally received the most weight in the smoothing and averaging because he covered such a wide range of temperature and pressure.

Summary

Bartlett and his collaborators have recently extended their P–V–T measurements on a 3:1 hydrogen–nitrogen mixture to include nine temperatures in the interval -70 to $300°$, up to 1000 atmospheres. A few observations from the work of Verschoyle were used with Bartlett's in a process of smoothing and averaging, in which interpolations and extrapolations were made to even densities from 0.0020 to 0.0270 mole per cc. and at even temperatures from -70 to $300°$.

The writers have calculated the constants in the Beattie–Bridgeman equation of state

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

by two methods: (1) direct determination, and (2) combination of constants previously found for the constituents of the mixture. As with hydrogen, they find breaks in the plots of A and B vs. ρ in the region where one would expect the critical density to lie, namely, about 0.0135 mole per cc. By direct determination

Below the critical density
$$A_0 = 3000 \times 10^2 \qquad\qquad B_0 = 25.03$$
$$a = 21.36 \qquad b = -15.16 \qquad c = 16 \times 10^6$$
Above the critical density
$$A_0 = 3489 \times 10^2 \qquad B_0 = 21.42$$
$$a = 28.56 \qquad b = -30.58 \qquad c = 16 \times 10^6$$

$$\tag{5}$$

in units of moles, atmospheres, and cubic centimeters. Pressures calculated with these constants agree with the observed pressures within a few tenths of a per cent. up to 0.0270 mole per cc.; at this point the calculated pressures are all too low with a root mean square deviation of 1.8%. At any density, the fit is about as good at one temperature as at another.

For studying the combination of the constants of the constituents to derive constants for the mixture, a, b, c, $\sqrt{A_0}$ for hydrogen and nitrogen at densities below critical were combined linearly. The B_0 for each were combined in three different ways, namely, by the linear, Lorentz and linear square root methods. The deviations of pressures calculated with these synthetic constants increase rapidly as the density increases. Of the three, the linear square root method comes the nearest to being satisfactory; it reproduces pressures with a root mean square error of 1.17% at 0.0070 mole per cc., so it can be trusted to reproduce the P–V–T relations almost within the experimental error up to this density.

This conclusion disagrees with that recently published by Beattie and Ikehara, who state that the linear square root method is not as good as the other two. It is pointed out that the conclusions differ because of the different ranges of pressure and temperature that were used for determining the constants of the pure gases.

The peculiarity in the *c* *vs.* ρ graph (Fig. 2) exhibiting the tendency for *c* to decrease and finally become negative as the density increases is believed to be related to the similar tendency of ϕ with hydrogen, and both are evidence for the predominance of repulsive forces between molecules at high densities.

WASHINGTON, D. C.

FLAME TEMPERATURES OF HYDROCARBON GASES[1]

BY G. W. JONES,[2] BERNARD LEWIS,[3] J. B. FRIAUF[4] AND G. ST. J. PERROTT[5]

In a previous report by Loomis and Perrott[6] methods were described and results given for the flame temperatures of methane, propane, carbon monoxide and natural gas. They tried several methods for measuring the temperatures of stationary flames, details of which are given in the report mentioned. The spectral-line reversal method was finally adopted for the measurement of the flame temperatures of combustible gases, because after the apparatus has been properly calibrated and standardized, a large number of determinations may be made easily, accurately and quickly. This method was first used by Kurlbaum,[7] subsequently modified by Kurlbaum and Schulze,[8] and later by Fery.[9] More recently, Henning and Tingwaldt[10] used the method to measure the maximum temperature of the acetylene–oxygen flame, 3100°. Griffiths and Awbery[11] have also described this method and investigated its limitations and factors affecting the accuracy of the results obtained. Tests made by them to determine the influence of flame thickness on the observed flame temperatures showed that within the limits of $1/2$ inch to 2 inches, thickness is immaterial to the result, but to ensure sensitivity it is advisable to employ a thick flame. They also investigated the distribution of temperature from base to tip of the flame. The results showed a relatively uniform temperature

[6] A. G. Loomis and G. St. J. Perrott, *Ind. Eng. Chem.*, 20, 1004 (1928).

[7] Kurlbaum, *Physik. Z.*, 3, 332 (1902).

[8] Kurlbaum and Schulze, *Ber. deut. phys. Ges.*, 5, 428 (1903).

[9] Fery, *Compt. rend.*, 137, 909 (1903).

[10] Henning and Tingwaldt, *Z. Physik*, 48, 805 (1928).

[11] E. Griffiths and J. H. Awbery, *Proc. Roy. Soc.* (London), A123, 401 (1929)