on freezing. The gases are presumed to be sufficiently pure to exclude significant systematic errors due to contaminants.

The large difference between the volume change of argon during freezing found in these experiments and the volume change reported by Bridgman (*2*) (Figure 4) cannot be ignored. There are differences ranging from 35 to 100% between Bridgman's results and those of the authors. Any possible error in the piston-displacement method used in the present work would not seem large enough to account for this discrepancy. "Squaring-up" the experimental curve of displacement *vs.* pressure could lead to slightly too high a value, although no difficulty was found in reproducing the published data on the change in volume of water during freezing at comparable pressures. An undiscovered leak of gas prior to measuring the argon sample volume after the experiment, and an equivalent error in computing the sample size at the start of the experiment (from the vessel size and published *PVT* data on argon) would be an unlikely coincidence.

Bridgman pointed out that his bulb-filling method could be in error on the low side if the filling capillary became plugged with solid. This might possibly explain why Bridgman reported lower values than these.

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Velocity of Sound in Compressed Gases

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For estimating sound velocities, the tables in this article give greater accuracy than graphs. The tables are also practical for other purposes—for example, data on heat capacity function have been published by Edmister and by Lyderson, Greenkorn, and Hougen, based on earlier generalized equations of state. The present data, based on Pitzer's recent work, are calculated by numerical differentiation.

VALUES of the velocity of sound in compressed gases are required for various technical purposes, as for the design of pulsation dampeners and the calculation of throat velocities in supersonic nozzles. Few data are available and the sound velocity must usually be calculated from other properties of the gas. Simple formulas are available for ideal gases, which serve adequately for many purposes, but these are not useful if the gas properties differ appreciably from ideality.

Reliable values of the sound velocity may be obtained if the low-pressure heat capacity and an accurate equation of state for the gas in question are known. The present study explores the possibility that useful values of sound velocity might be calculated from a general reduced equation of state for all gases. The results are compared with limited experimental data on CH_4, C_2H_4, C_2H_6, C_3H_8, i-C_5H_{12}, *n*-C_5H_{12}, He, and CO_2.

Thermodynamics provides the following relations:

$$C^2 = -av^2\left(\frac{\partial P}{\partial v}\right)_s = \frac{a\,RT\,KZ^2}{Z - P_r\left(\frac{\partial Z}{\partial P_r}\right)_{T_r}} \qquad (1)$$

$$K = \frac{C_p}{C_v} = \frac{C_p^\circ + \Delta C_p}{(C_p^\circ + \Delta C_p) - (C_p - C_v)} \qquad (2)$$

$$\Delta C_p = \frac{\partial}{\partial T_r}\left(\frac{H - H^0}{T_c}\right)_{P_r} \qquad (3)$$

$$C_p - C_v = \frac{R\left[Z + T_r\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\right]^2}{Z - P_r\left(\frac{\partial Z}{\partial P_r}\right)_{T_r}} \qquad (4)$$

Here C is the sound velocity and Z is the compressibility factor, which is assumed to vary only with P_r and T_r, the reduced pressure and the reduced temperature, respectively. The above relations are the same as those used by Buthod and Tien (*1*) in a recent similar study.

Of the several reduced equations of state available, that of Pitzer and Curl (*12*) was selected, values of Z being taken from their tables for $Z_c = 0.27$ (this is equivalent to an "acentric factor," ω, of 0.2625, since $Z_c = 0.291 - 0.08\,\omega$). Values of $\partial Z/\partial P_r$ and $\partial Z/\partial T_r$ were obtained from large graphs of Z *vs.* P_r or T_r, using numerical or graphical methods, as seemed appropriate. Values of ΔC_p were obtained in the same manner, using Pitzer and Curl's values of $(H - H^0)/T_c$.

The result of these calculations is three functions:

$$C^2/aRTK = f_1(P_r, T_r) \qquad \text{(Table I)}$$

$$\Delta C_p = f_2(P_r, T_r) \qquad \text{(Table II)}$$

$$C_p - C_v = f_3(P_r, T_r) \qquad \text{(Table III)}$$

Values of C_p^0 needed in Equation 2 are available from API Research Project 44 (*2, 14*).

Using these tables, values of C are calculated as follows: P_r and T_r are obtained as ratios of the specified temperature and pressure to the known critical properties [if P_c and T_c are not known, they may be estimated closely by the methods described by Reid and Sherwood (*13*)]; ΔC_p and $C_p - C_v$ are found from Tables II and III and K is calculated from C_p^0 using Equation 2; $C^2/aRTK$ is obtained from Table I, and C calculated by substitution.

The procedure will be illustrated by estimating C for ethane at 90° F. and 116 atm. From the literature, $P_c = 48.3$ atm., $T_c = 550°$ R., and $C_p^0 = 12.8$; whence $P_r = 2.4$ and $T_r = 1.00$. From Tables II and III $\Delta C_p = 16.53$, $C_p - C_v = 15.93$,

Table I. Values of $C^2/aRTK$

T_R/P_R	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.90	0.82	0.50	0.01	1.96	3.00	3.70	4.40	5.20	5.87	6.50	7.20	7.83	7.97	7.06	6.26	5.99	7.15	8.62	10.49	13.12	18.72
0.95	0.84	0.54	0.34	0.02	1.16	1.69	2.36	2.8	3.22	3.58	3.80	4.10	4.27	4.30	4.59	5.00	5.58	6.45	8.56	10.90	13.65
1.00	0.87	0.70	0.47	0.29	0.04	0.07	0.62	1.12	1.42	1.80	2.12	2.32	2.49	2.61	2.70	3.56	4.26	5.19	6.49	8.31	10.04
1.05	0.89	0.76	0.62	0.48	0.32	0.17	0.11	0.21	0.52	0.68	0.87	1.10	1.30	1.46	1.65	2.60	3.43	4.23	5.32	6.46	9.39
1.10	0.91	0.80	0.69	0.58	0.46	0.36	0.27	0.20	0.26	0.35	0.49	0.71	0.92	1.12	1.24	1.97	2.73	3.51	4.24	4.71	5.33
1.15	0.92	0.83	0.73	0.65	0.56	0.49	0.41	0.36	0.32	0.34	0.40	0.48	0.58	0.71	0.85	1.52	2.09	2.68	3.26	4.02	4.97
1.20	0.93	0.85	0.78	0.71	0.64	0.58	0.52	0.47	0.44	0.44	0.45	0.48	0.51	0.56	0.62	1.17	1.84	2.39	2.95	3.61	4.27
1.25	0.94	0.88	0.82	0.76	0.70	0.65	0.60	0.57	0.53	0.52	0.52	0.52	0.54	0.56	0.58	0.87	1.35	1.92	2.45	3.01	3.52
1.30	0.95	0.90	0.84	0.79	0.75	0.70	0.67	0.64	0.61	0.59	0.58	0.59	0.61	0.62	0.64	0.81	1.19	1.68	2.16	2.65	3.16
1.40	0.96	0.92	0.89	0.86	0.82	0.79	0.77	0.74	0.72	0.70	0.69	0.68	0.68	0.70	0.72	0.86	1.11	1.41	1.77	2.12	2.50
1.50	0.97	0.95	0.92	0.90	0.87	0.85	0.83	0.82	0.80	0.79	0.79	0.78	0.78	0.78	0.79	0.91	1.11	1.37	1.67	1.96	2.31
1.60	0.98	0.96	0.94	0.93	0.91	0.89	0.88	0.87	0.87	0.86	0.85	0.85	0.85	0.85	0.86	0.93	1.07	1.28	1.51	1.81	2.13
1.70	0.99	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.91	0.90	0.90	0.90	0.90	0.91	0.91	1.00	1.12	1.29	1.49	1.72	1.99
1.80	0.99	0.98	0.98	0.97	0.97	0.96	0.95	0.95	0.95	0.95	0.95	0.95	0.96	0.96	0.98	1.05	1.16	1.32	1.50	1.69	1.90
1.90	1.00	0.99	0.99	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.99	1.00	1.00	1.09	1.21	1.36	1.52	1.71	1.90
2.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.01	1.01	1.01	1.02	1.03	1.04	1.04	1.12	1.23	1.38	1.53	1.71	1.89
2.50	1.01	1.01	1.02	1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.12	1.13	1.14	1.21	1.31	1.41	1.53	1.66	1.79
3.00	1.01	1.02	1.02	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.12	1.13	1.15	1.16	1.17	1.25	1.33	1.43	1.54	1.67	1.78
3.50	1.01	1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.11	1.13	1.14	1.16	1.17	1.24	1.30	1.37	1.47	1.56	1.68
4.00	1.01	1.02	1.03	1.04	1.05	1.06	1.07	1.07	1.09	1.10	1.11	1.12	1.13	1.14	1.15	1.21	1.27	1.34	1.41	1.52	1.61

Table II. Values of ΔC_p

T_R/P_R	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.90	2.23	9.66	22.25	18.70	16.90	16.25	15.46	14.80	14.30	13.83	13.40	12.90	12.22	11.98	11.92	10.90	10.13	9.46	9.16	8.92	8.60
0.95	1.87	6.40	16.73	31.79	28.41	25.30	22.00	20.86	17.40	14.90	15.08	14.58	12.84	12.54	12.02	10.90	10.23	9.60	9.38	9.00	8.41
1.00	1.55	3.50	7.95	16.00		47.29	30.70	31.79	21.86	20.20	17.80	16.53	15.10	13.81	13.00	11.92	10.45	9.94	9.68	9.06	8.13
1.05	1.31	2.80	5.31	9.50	22.06	90.21	56.83	34.18	27.40	23.05	20.80	18.68	17.53	16.89	15.52	12.60	10.93	10.45	9.70	9.26	9.56
1.10	1.11	2.15	3.78	6.20	9.24	14.70	22.06	43.71	34.00	26.20	22.50	19.87	19.37	17.74	16.00	12.96	11.45	10.83	10.27	9.28	9.26
1.15	0.95	1.77	3.02	4.49	6.32	8.94	12.04	15.52	22.06	23.60	22.45	21.50	20.27	19.10	18.10	14.19	11.92	10.83	9.94	9.36	8.42
1.20	0.74	1.47	2.44	3.28	4.55	6.40	8.27	10.05	12.62	14.52	17.10	19.13	18.48	17.20	15.90	12.62	11.21	10.30	9.80	9.22	7.89
1.25	0.60	1.27	1.93	2.52	3.56	4.97	6.28	7.45	8.90	11.15	11.21	11.84	12.04	13.11	12.14	11.68	10.40	9.60	9.02	8.64	7.65
1.30	0.50	1.01	1.57	2.11	3.95	3.95	4.85	5.76	6.48	6.86	8.76	9.12	9.24	10.45	10.27	10.11	9.16	8.92	7.95	7.83	7.39
1.40	0.26	0.77	1.03	1.49	1.99	2.38	3.16	3.20	4.11	4.79	5.09	5.56	6.36	6.62	6.95	8.44	7.71	7.35	6.86	6.36	6.52
1.50	0.24	0.48	0.64	1.15	1.39	1.79	2.13	2.62	3.16	3.64	3.91	4.21	4.41	5.21	5.42	6.22	6.28	6.50	5.84	5.68	5.60
1.60	0.22	0.40	0.54	0.85	1.07	1.41	1.71	2.07	2.40	2.84	3.02	3.38	3.60	4.09	4.41	4.93	5.60	5.60	5.36	5.36	5.38
1.70	0.18	0.38	0.48	0.68	0.89	1.13	1.41	1.69	1.97	2.40	2.70	2.94	3.16	3.38	3.60	4.19	4.93	4.81	4.79	5.05	4.97
1.80	0.20	0.38	0.48	0.64	0.76	0.93	1.11	1.39	1.73	2.09	2.30	2.54	2.74	2.88	2.92	3.72	4.37	4.41	4.61	4.65	4.63
1.90	0.18	0.32	0.44	0.56	0.72	0.74	0.97	1.17	1.49	1.69	2.11	2.17	2.25	2.34	2.44	3.30	3.82	4.05	4.35	4.21	4.35
2.00	0.16	0.26	0.40	0.46	0.64	0.58	0.87	1.01	1.19	1.47	1.75	1.73	1.81	2.01	2.15	2.74	3.18	3.66	3.87	3.85	3.93
2.50	0.08	0.14	0.30	0.40	0.48	0.52	0.66	0.70	0.72	0.72	0.72	0.76	0.91	0.83	1.07	1.23	1.67	1.87	2.03	2.42	2.48
3.00	0.04	0.08	0.20	0.24	0.30	0.32	0.38	0.42	0.52	0.46	0.44	0.48	0.62	0.62	0.66	0.85	1.05	1.23	1.41	1.53	1.75
3.50	0.04	0.06	0.08	0.10	0.16	0.16	0.16	0.22	0.22	0.26	0.30	0.32	0.34	0.36	0.38	0.58	0.70	0.95	1.03	1.25	1.35
4.00	0.04	0.04	0.08	0.02	0.06	0.04	0.10	0.12	0.12	0.14	0.16	0.20	0.20	0.22	0.22	0.28	0.36	0.38	0.60	0.58	0.52

Table III. Values of $C_p - C_v$

T_R/P_R	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
1.00						27.16	25.40	23.40	21.40	19.40	17.92	15.93	14.67	13.28	12.04	9.89	8.85	8.95	9.23	9.90	10.12
1.05	2.69	3.74	5.42	8.82	21.67		27.70	19.24	28.52	24.04	21.73	19.68	16.91	14.70	14.00	11.90	10.75	10.33	9.50	9.00	8.40
1.10	2.62	3.44	4.52	6.04	8.55	13.16	21.93	57.01	21.53	18.80	17.88	17.30	16.80	16.30	15.80	13.80	12.24	11.18	9.90	8.59	8.41
1.15	2.51	3.12	3.93	5.06	6.52	8.82	13.09	19.68	53.61	45.60	39.05	25.79	22.75	20.28	18.11	13.36	11.12	9.95	8.84	8.49	9.02
1.20	2.44	2.94	3.65	4.53	5.64	6.95	8.68	12.72	15.21	15.96	16.35	16.48	16.17	15.89	15.69	13.28	11.40	10.26	9.50	8.87	8.48
1.25	2.44	2.95	3.56	4.22	4.97	5.79	6.85	7.88	9.23	11.03	12.89	13.37	12.98	12.33	11.57	10.19	9.60	9.19	8.59	8.21	7.69
1.30	2.34	2.77	3.18	3.75	4.38	5.09	5.92	6.82	7.72	8.46	9.21	10.10	10.87	11.31	11.29	9.77	9.71	9.76	9.07	8.34	7.68
1.40	2.20	2.55	2.92	3.31	3.87	4.15	4.61	5.07	5.58	6.09	6.61	7.13	7.51	7.72	7.80	8.52	9.09	8.30	7.30	7.06	7.34
1.50	2.25	2.49	2.75	3.01	3.30	3.52	3.91	4.21	4.55	4.89	5.23	5.55	5.85	6.12	6.32	7.25	7.89	7.88	7.77	7.69	8.14
1.60	2.25	2.40	2.59	2.78	2.99	3.20	3.41	3.62	3.86	4.07	4.32	4.60	4.85	5.10	5.50	6.88	7.36	7.43	7.54	7.77	8.09
1.70	2.22	2.36	2.49	2.66	2.80	2.95	3.10	3.27	3.46	3.63	3.82	4.02	4.23	4.45	4.68	6.20	7.31	8.09	8.39	8.33	8.19
1.80	2.15	2.28	2.41	2.54	2.69	2.81	2.95	3.11	3.26	3.43	3.58	3.74	3.91	4.11	4.30	5.15	6.01	6.96	7.64	7.80	7.85
1.90	2.09	2.22	2.34	2.47	2.60	2.74	2.88	3.01	3.16	3.31	3.44	3.57	3.73	3.88	4.00	4.68	5.32	6.07	6.87	7.51	7.68
2.00	2.10	2.21	2.31	2.41	2.53	2.63	2.74	2.86	2.98	3.09	3.21	3.34	3.46	3.58	3.69	4.26	4.75	5.19	5.48	5.70	5.71
2.50	2.06	2.11	2.16	2.24	2.33	2.38	2.45	2.52	2.59	2.67	2.73	2.79	2.87	2.94	3.00	3.35	3.77	4.20	4.47	4.63	4.59
3.00	2.00	2.03	2.07	2.16	2.21	2.25	2.28	2.35	2.38	2.42	2.46	2.48	2.51	2.54	2.57	2.64	2.80	2.95	3.12	3.21	3.14
3.50	2.01	2.02	2.04	2.06	2.08	2.10	2.21	2.15	2.17	2.19	2.21	2.24	2.27	2.29	2.32	2.42	2.43	2.41	2.49	2.55	2.65
4.00	2.01	2.02	2.04	2.06	2.06	2.05	2.05	2.07	2.09	2.11	2.12	2.14	2.14	2.15	2.15	2.11	2.16	2.14	2.23	2.27	2.13

and from Equation 2 K is 2.23. From Table I, $C^2/aRTK$ is 2.316; whence:

$$C^2 = \frac{2.316 \times 4615 \times 550 \times 2.23}{30} = 437{,}000;\ C = 660 \text{ meters per second}$$

The experimental value is about 583 meters per second.

Figure 1 compares values calculated in this way with data obtained from various sources. Although the result is fair, it is evident that the method of calculation may lead to serious error. There are several possible reasons for the discrepancies:

1. Equation 1 is for sound at "low" frequencies in a gas under equilibrium conditions of molecular excitation. This should not be important, since the data quoted were obtained at frequencies from 3 mc. to 900 kc. per second (*11*).
2. The generalized reduced equation of state is not sufficiently accurate, and the use of values based on a single Z_c introduces additional errors when applied to various gases. Values of Z are probably correct to within a few per cent, but the derivatives $\partial Z/\partial T_r$ and $\partial Z/\partial P_r$ are subject to large error in the vicinity of the critical. This is particularly true for ΔC_p, which is obtained by two differentiations of P-V-T data.
3. Accurate measurement of slopes of curves is difficult. This seems to have introduced no great error, except in the immediate vicinity of the critical.
4. There are experimental errors in the values of C. There is no reason to believe that this was important; it was necessary, however, to obtain most of the data by reading values from small graphs given in place of tables in the published reports.

At the critical temperature, C decreases steadily as pressure is increased above atmospheric, passing through a sharply pointed minimum at the critical pressure. The method of calculation described is evidently incapable of defining this sharp dip with reasonable accuracy. Above the critical pressure C rises sharply and at high values of P_r reaches values which are large relative to C at 1 atm. The sharp dip at $P_r = 1$ becomes less and less pronounced as T_r is increased from unity.

In reviewing the calculations, it appears that discrepancies of more than 10% between calculated and observed values of C were encountered in the following regions: for CH_4 ($Z_c = 0.289$), at P_r greater than 6 (about 4000 p.s.i.g.); for C_2H_4 (near the critical temperature) at P_r between 1.0 and 2.0; for C_2H_6 (at $T_r = 1.00$) from P_r 1.8 to 2.2; for C_3H_8, from P_r 0.8 to 3 at $T_r = 0.95$, 0.8 to 2 at $T_r = 1.00$, $P_r = 1.6$ to 2.2 at $T_r = 1.15$, P_r 1.6 to 1.8 at $T_r = 1.20$, and P_r 4 to 5 at $T_r = 1.3$; for C_5H_{12} from P_r 0.8 to 1.4 at the critical temperature; for helium (well above the critical temperature) at pressures higher than P_r of 6.0 (4200 p.s.i.g.). The calculated values for CO_2 do not agree well with the data of Herget (*3*) for T_r close to unity in the range of P_r from about 0.5 to 1.5.

Many of the data were obtained in the critical region, and comparison of data with calculated values presents a severe test of the calculation procedure. Even more refined calculation procedures fail in the critical region. For example, the values of C calculated by Hilsenrath and others (*4*) for CO_2, using an equation of state designed especially for this gas, are less than 5% of the experimental value at 38° C. ($T_r = 1.024$) and 100 atm. The calculated values based on the generalized reduced equation of state check Herget's data at 38° C. within 10% except in the range of P_r from about 0.7 to 1.4.

Evidently the method presented is sufficiently good for engineering purposes for most common gases at temperatures greater than T_r = about 1.3. The pressure region of greatest discrepancy moves from near the critical at the critical temperature to values of P_r of 6 or more as T_r is increased to 3.

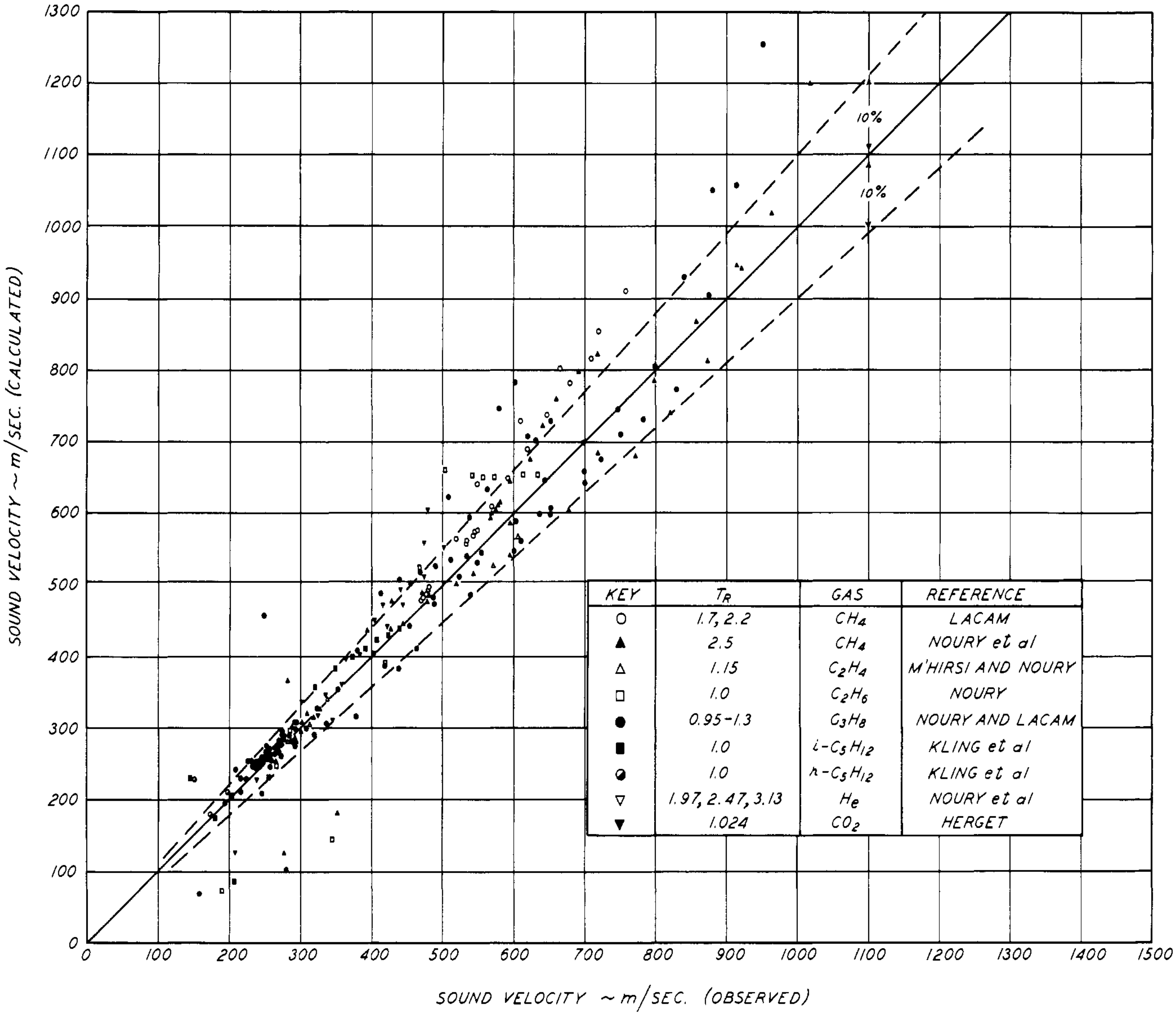

Figure 1. Velocity of sound in compressed gases

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NOMENCLATURE

a = dimensional constant; $aR = (4615/M)$ sq. m./(sec.)(° R.)
C = velocity of sound, meters per sec.
C_p = heat capacity at constant pressure, B.t.u./(lb. mole)(° F.)
C_p^0 = C_p at "low pressure" (in ideal gas range)
C_v = heat capacity at constant volume, B.t.u./(lb. mole)(° F.)
H = enthalpy, B.t.u./lb. mole
H^0 = enthalpy at low pressure (ideal gas range), B.t.u./lb. mole
K = ratio of heat capacities, C_p/C_v
M = molecular weight
P = pressure, atm.
P_c = critical pressure, atm.
P_r = reduced pressure, $= P/P_c$
R = gas constant, B.t.u./(lb. mole)(° R.)
T = temperature, ° R.
T_c = critical temperature, ° R.
T_r = reduced temperature, $= T/T_c$
v = specific volume, cu. ft./lb.
V = molal volume, cu. ft./lb. mole
Z = PV/RT
Z_c = value of Z at T_c and P_c
ΔC_p = $C_p - C_p^0$
$(\partial P/\partial v)_s$ = rate of change of pressure with volume at constant entropy

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