NEW GENERALIZED CORRELATION FOR VELOCITY OF SOUND

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ABSTRACT

A new method for the calculation of velocity of sound in compressed gases based on a three parameter theorem of corresponding states employing molar polarization at the critical temperature as the third parameter is proposed and tested. Comparisons are made with data for all classes of substances such as simple, quantum mechanical and polar fluids to establish the validity of the proposed method. The generalized charts presented in this paper give (on an overall basis) results in better agreement with experimental data on velocity of sound as well as isothermal variation of heat capacity and the isothermal and isobaric volume derivatives $(\partial V/\partial P)_T$ *and* $(\partial V/\partial T)_P$ *compared to all the methods available in literature for these properties.*

Key words: Velocity of sound in gases; Heat capacity; Derivative compressibility factors; Corresponding states.

1. INTRODUCTION

Velocity of sound is an important property needed in connection with the calculation of throat velocities and in the design of pulsation dampeners. Expressions for velocity of sound in compressed gases derived on the basis of considerations such as those of Buthod and Tien [1] can be written in terms of generalized properties as

$$C^2 = \frac{aTZ^2 (C_P^0 + \triangle C_P)}{Z_P (C_P^0 + \triangle C_P) - RZ_T^2} \tag{1}$$

While other forms of grouping the terms like those given by Sherwood [2] are possible the form represented by Equation (1) has the advantage that the generalized charts developed for $\triangle C_P$, Z_P and Z_T are useful: (i) in the calculation of isothermal variation of heat capacity and (ii) in the calculation of various thermo-dynamic properties involving $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$ employing Bridgman relations in terms of Z_P and Z_T given by Reid and Valbert [3]. Generalized charts and tables for all the properties can be developed on the basis of the new three parameter theorem of corresponding states proposed by the authors [4]. Some results of this work have been presented earlier [5] and details are given in this paper.

2. COMPRESSIBILITY FACTOR CORRELATION

A generalized compressibility factor correlation based on the use of molar polarization at the critical temperature as the third parameter proposed earlier [4] has the form:

$$Z = Z^{(0)} + P_{MC} Z^{(1)}. \tag{2}$$

The values of $Z^{(0)}$ and $Z^{(1)}$ are given in an earlier publication [6]. Molar polarization at the critical temperature can be calculated from the relation:

$$P_{MC} = R_M + \frac{4\pi N \mu^2}{9kT_C} \tag{3}$$

3. ISOTHERMAL VARIATION OF HEAT CAPACITY, $\triangle C_P$

Values of $\triangle C_P$ are obtained from $[(H^0 - H)/T_C)]^{(0)}$ and $[(H^0 - H)/T_C]^{(1)}$ of the correlation for isothermal variation of enthalpy $(H^0 - H)/T$ given earlier [4] making use of the equation

$$\triangle C_P = C_P - C_P^0 = - \frac{\partial}{\partial T_R}\left(\frac{H^0 - H}{T_C}\right) \tag{4}$$

The differentiations are carried out praphically and the values of the resulting functions denoted by $\triangle C_P^{(0)}$ and $\triangle C_P^{(1)}$ are presented in Tables I and II and Figs. 1 and 2. $\triangle C_P$ can be calculated from the $\triangle C_P^{(0)}$ and $\triangle C_P^{(1)}$ values given in these tables and charts through the relation:

$$\triangle C_P = \triangle C_P^{(0)} + P_{MC} \triangle C_P^{(1)} \tag{5}$$

A summary of comparison of the values of $\triangle C_P$ calculated using the present method as well as the other methods available in literature with experimental data is given in Table III. On an overall basis for 180 points the present method gives a per cent average absolute deviation of 17·3 compared to 22·4 for acentric factor method, 24·1 for Weiss and Joffe's method, 26·1 for Edmister's method, 26·1 for Lydersen's method and 27·1 for Sherwood's method.

4. DERIVATIVE COMPRESSIBILITY FACTORS

As already mentioned, derivative compressibility factors are useful in the calculation of various thermodynamic properties involving $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$. They are first suggested in terms of reduced properties by Edmister [7]. Later Reid and Valbert [3] gave values of $Z_P^{(0)}$, $Z_P^{(1)}$, $Z_T^{(0)}$ and $Z_T^{(1)}$ which can be employed along with Pitzer's acentric factor for the

TABLE I*

$\triangle C_P^{(0)}$ *of the relation for isothermal variation of heat capacity with pressure*

$$\triangle C_P = \triangle C_P^{(0)} + P_{MC} \triangle C_P^{(1)}$$

T_R \ P_R	0·75	1·25	1·50	3·00	5·00	7·00	8·00
1·10 ..	4·850	16·5000	27·500	16·000	12·400	10·200	9·450
1·30 ..	2·230	4·250	5·500	11 000	9·630	7·900	7·300
1·60 ..	1·000	1·820	2·250	5·100	5·150	4·800	4·550
1·80 ..	0·650	1·150	1·420	2·950	3·630	3·500	3·380
2·50 ..	0·335	0·540	0·650	1·230	1·850	2·250	2·350
3·00 ..	0·290	0·449	0·520	0·920	1·260	1·470	1·540

* Tables I, II, IV–VII are representative Tables. Full Tables can be had from the authors.

TABLE II

$-\triangle C_P^{(1)} \times 10^4$, *the correction term of the relation for isothermal variation of heat capacity with pressure*

$$\triangle C_P = \triangle C_P^{(0)} + P_{MC} \triangle C_P^{(1)}$$

T_R \ P_R	0·75	1·25	1·50	3·00	5·00	7·00	8·00
1·10 ..	60·00	85·50	94·50	136·50	158·00	165·00	170·00
1·30 ..	77·00	105·00	116·00	156·50	175·00	181·20	187·50
1·60 ..	94·00	121·00	133·00	190·00	230·00	254·00	263·00
1·80 ..	105·00	130·00	141·00	200·00	250·00	278·00	294·00
2·50 ..	142·50	186·00	205·00	280·50	332·00	365·00	378·00
3·00 ..	170·00	225·00	250·00	354·00	430·00	475·00	500·00

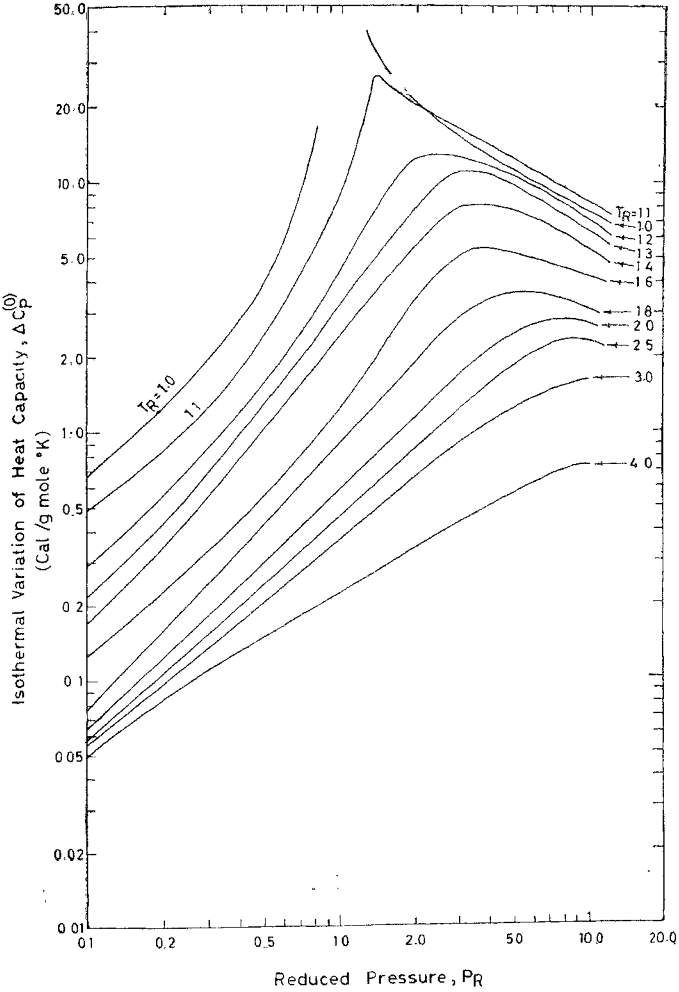

FIG. 1. $\Delta C_P^{(0)}$ as a function of P_R and T_R.

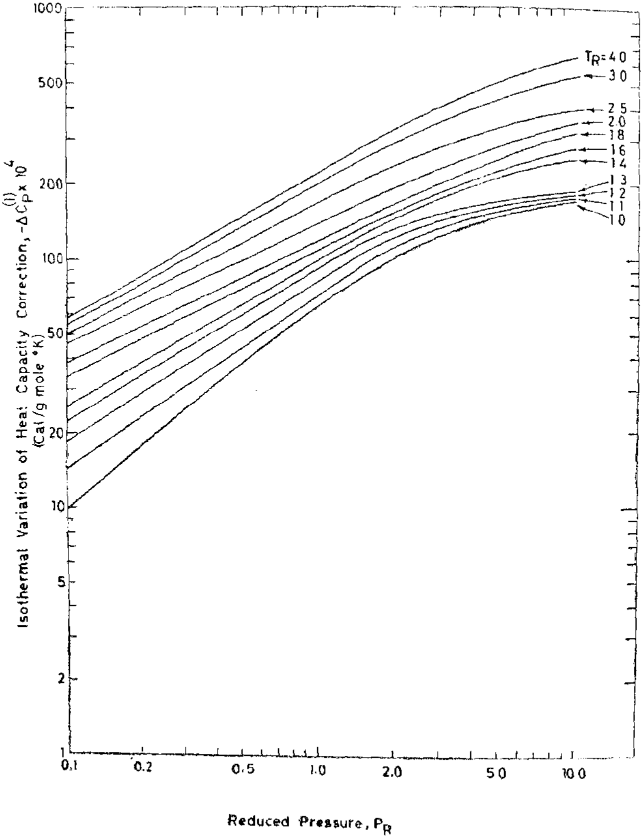

FIG. 2. $\Delta C_P^{(1)}$ as a function of P_R and T_R.

calculation of these derived properties. Derivative compressibility factors are defined by:

$$Z_P = Z - P_R \ (\partial Z/\partial P_R)\ T_R \tag{6}$$

$$Z_T = Z + T_R \ (\partial Z/\partial T_R)\ P_R \tag{7}$$

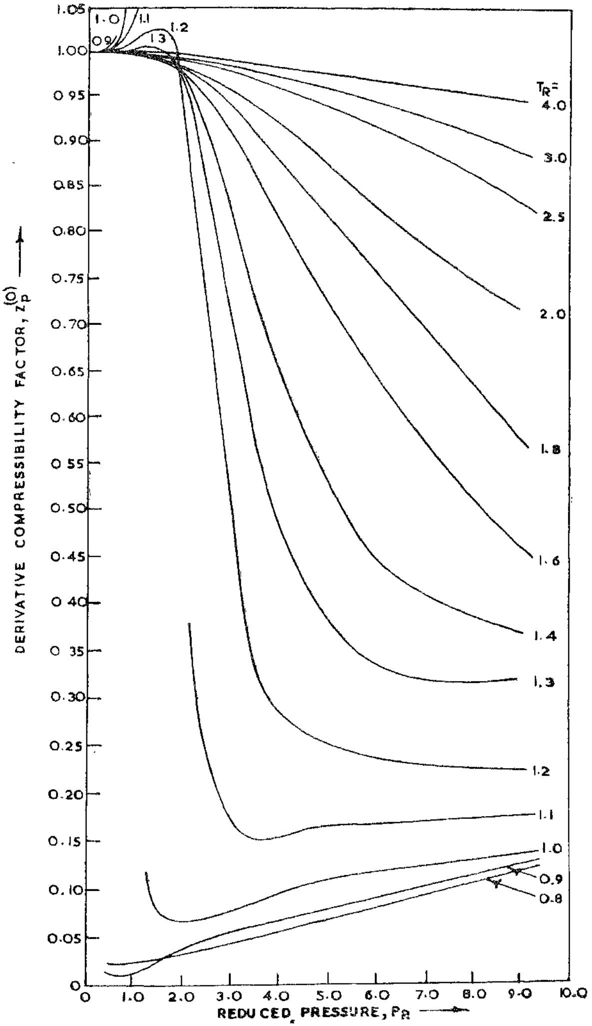

FIG. 3. $Z_P^{(0)}$ as a function of P_R and T_R.

TABLE III

Summary of comparison of calculated and experimental isothermal variations of heat capacity with pressure for each substance

Substance	Reduced temperature range	Reducedp pressure range	Per cent average absolute deviation*						Source of experimental data
			Present method	Acentric factor method	Weiss and Joffe method	Edmister's method	Lydersen's method	Sherwood's method	
Ammonia	1·00– 1·40	0·25– 9·00	14·12 (56)	17·32 (56)	14·70 (26)	34·01 (42)	15·87 (32)	15·95 (56)	*a*
Hydrogen	1·60– 4·00	0·25– 7·00	17·67 (59)	32·30 (59)	35·89 (57)	25·90 (55)	41·42 (28)	37·69 (59)	*b*
Methane ..	1·34– 1·57	1·56– 2·12	15·98 (9)	19·96 (9)	14·61 (9)	20·62 (9)	21·33 (9)	9·98 (9)	*c*
Nitrogen ..	2·37– 2·64	0·29– 3·75	15·39 (14)	10·69 (14)	11·47 (14)	19·48 (14)	32·05 (12)	33·10 (14)	*d*
Oxygen ..	1·93– 2·15	0·19– 2·51	4·39 (14)	7·49 (14)	15·22 (14)	10·68 (14)	16·09 (12)	28·42 (14)	*d*
Propane ..	1·07– 1·44	0·16– 3·24	20·41 (24)	27·96 (24)	22·03 (24)	28·10 (24)	27·74 (24)	31·58 (24)	*e*
Steam ..	1·00– 1·30	0·25	34·88 (4)	12·61 (4)	27·56 (4)	23·75 (4)	10·41 (4)	35·47 (4)	*b*
Overall ..			16·39 (180)	22·39 (180)	24·08 (148)	26·07 (162)	26·12 (122)	27·08 (180)	
For the same points (using the present method)			..	16.39	17.26	17.18	17·95	16·39	
For 116 common points			17.98	16.52	19.05	21.89	26·92	25·23	

* Numbers in the parenthesis of these columns refer to the number of points compared.

Footnotes for Table III

Present method Generalized charts and tables given in this paper.

Acentric factor method: Edmister, W. C., *Hydrocarbon Processing*, 1967, **46** (5), 187–190.

Weiss and Joffe method: Weiss, A. H. and Joffe, J., *Industrial and Engineering Chemistry*, 1957, **49**, 120–124.

Edmister's method: Edmister, W. C., *Petroleum Refiner*, 1948, **27** (11), 609–615.

Lydersen's method: Lydersen, A. L., Greenkorn, R. A., and Hougen, O. A., *Generalized Thermodynamic Properties of Pure Fluids*, College of Engineering, University of Wisconsin, Engineering Experimental Station, Report No 4, Madison, Wis., October 1955.

Sherwood's method: Sherwood, T. K., *Journal of Chemical and Engineering Data*, 1962, **7**, 47–60.

(*a*) Din, F., *Thermodynamic Functions of Gases*, Butterworths, London, 1956, **1**, 96.

(*b*) Hilsenrath, J. and Others, *Tables of Thermodynamic and Transport Properties of Air, Carbon dioxide, Hyderogen, Nitrogen, Oxygen and Steam*, 1960, pp. 277, 454, 455, Pergamon, Oxford.

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(*d*) Workman, E. J., *Physical Review* (Second Series), 1931, **37**, 1345–1355

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TABLE IV

$Z_P{}^{(0)}$ *of the relation for derivative compressibility factor*

$$Z_P = Z_P{}^{(0)} + P_{MC}\, Z_P{}^{(1)}$$

T_R \ P_R	0·75	1·25	1·50	3·00	5·00	7·00	8·00
0·80 ..	0·0217	0·0268	0·0295	0·0440	0·0685	0·0951	0·1060
0·90 ..	0·0114	0·0130	0·0185	0·0554	0·0820	0·1045	0·1124
1·10 ..	1·0500	1·1360	0·9862	0·1600	0·1650	0·1679	0·1710
1·30 ..	1·0050	1·0050	0·9983	0·6570	0·3830	0·3191	0·3182
1·60 ..	0·9982	0·9960	0·9850	0·8931	0·7122	0·5778	0·5245
1·80 ..	0·9990	0·9934	0·9885	0·9330	0·8163	0·7013	0·6480
2·50 ..	0·9990	0·9979	0·9950	0·9790	0·9940	0·9020	0·8767
3·00 ..	1·0000	0·9992	0·9993	0·9881	0·9710	0·9386	0·9220

The relations are applied individually to $Z^{(0)}$ and $Z^{(1)}$ of the present compressibility factor correlation and the resulting functions $Z_P^{(0)}$, $Z_P^{(1)}$, $Z_T^{(0)}$ and $Z_T^{(1)}$ are given as functions of P_R and T_R in Tables IV, V, VI and VII and Figs. 3, 4, 5 and 6.

TABLE V

$Z_P^{(1)} \times 10^4$, *the correction term of the relation for derivative compressibility factor*

$$Z_P = Z_P^{(0)} \times P_{MC} Z_P^{(0)}$$

$T_R \backslash P_R$	0·75	1·25	1·50	3·00	5·00	7·00	8·00
0·80 ..	6·635	—2·100	—2·888	— 7·466	—9·120	—10·798	— 9·936
0·90 ..	7·700	—0·950	—1·730	— 6·450	—8·240	— 9·798	— 8·936
1·10 ..	10 215	1·350	0·520	— 4·500	— 6·476	— 7·798	— 6·936
1·30 ..	12·825	3·660	2·890	— 2·550	— 4·712	— 5·798	— 4·936
1·60 ..	16·250	7·100	6·355	0·458	— 2·066	— 2·797	— 1·936
1·80 ..	18·700	9·415	8·665	2·514	— 0·302	— 0·797	0·064
2·50 ..	27·167	17·474	16·750	9·710	5·873	6·213	7·064
3·00 ..	33·200	23·231	22·525	14·850	10·283	11·213	12·064

TABLE VI

$Z_T^{(0)}$ *of the relation for derivative compressibility factor*

$$Z_T = Z_T^{(0)} + P_{MC} Z_T^{(1)}$$

$T_R \backslash P_R$	0·75	1·25	1·50	3·00	5·00	7·00	8·00
0·80 ..	0·1140	0·1390	0·1720	0·2200	0·3100	0·4140	0·4640
0·90 ..	0·5550	0·3955	0·3700	0·3630	0·3990	0·4940	0·5810
1·10 ..	1·5377	2·9054	3·5415	1·1888	0·7740	0·7240	0·7640
1·30 ..	1·2700	1·5620	1·6465	1·6503	1·1653	0·9920	0·9719
1·60 ..	1·1412	1·2680	1·3295	1·7391	1·4067	1·2040	1·1920
1·80 ..	1·1130	1·1870	1·2460	1·5778	1·4353	1·3666	1·2742
2·50 ..	1·0307	1·0700	1·0870	1·2951	1·2085	1·2510	1·2459
3·00 ..	1·0102	1·0525	1·0640	1·0795	1·1281	1·1442	1·1675

TABLE VII

$Z_T^{(1)} \times 10^4$, *the correction term of the relation for derivative compressibility factor*

$$Z_T = Z_T^{(0)} + P_{MC} Z_T^{(1)}$$

T_R \ P_R	0·75	1·25	1·50	3 00	5·00	7·00	8·00
0·80 ..	8·25	9·20	8·95	6·50	3·40	1·95	1·40
0·90 ..	10·25	11·20	10·95	8·70	5·75	3·95	3·40
1·10 ..	14·25	15·20	15·25	13·10	9·40	7·95	7·40
1·30 ..	18·25	19·20	20·50	17·60	15·75	11·95	11·40
1·60 ..	24·25	25·20	25·75	24·10	19·40	17·95	17·40
1·80 ..	28·25	29·30	29·95	28·50	23·40	21·95	21·40
2·50 ..	42·25	43·20	44·65	43·90	37·40	35·96	35·40
3·00 ..	52·25	53·20	55·20	54·90	47·40	45·95	45·40

Values of Z_P and Z_T calculated for different conditions for each of the substances mentioned in Tables VIII and IX are used to calculate $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$ from the equations:

$$(\partial V/\partial P)_T = -\, RTZ_P/P^2 \qquad (8)$$

$$(\partial V/\partial T)_P = R\ Z_T/P \qquad (9)$$

In the calculation of $(\partial V/\partial P)_T$ for 126 points the present methods gives a per cent average absolute deviation of 1·2 as against 3·7 for Reid and Valbert method employing acentric factor as the third parameter. The per cent average absolute deviation in the calculations of $(\partial V/\partial T)_P$ for a total of 128 points using the presnet method is 5·5 compared to 9·1 in using Reid and Valbert's method.

5. VELOCITY OF SOUND

Equation (1) along with all the tables and charts presented is employed for the calculation of velocity of sound in 9 compressed gases. On an overall basis for 107 points the present method gives a per cent average absolute deviation of 6·4 compared to 8·5 in using Sherwood's method. A summary of this comparison is given in Table X and Figs. 7 and 8.

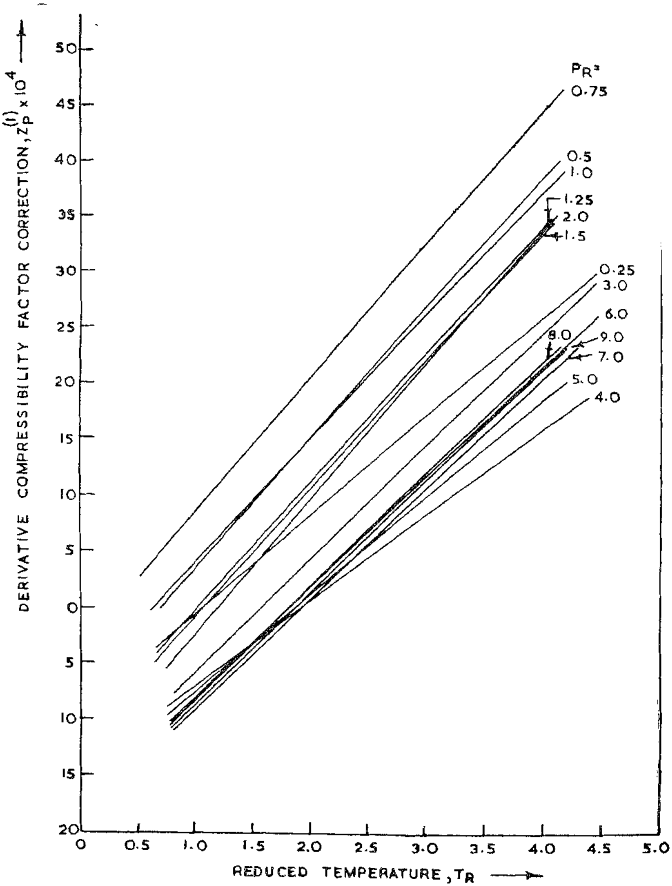

FIG. 4. $Z_P^{(1)}$ as a function of T_R and P_R.

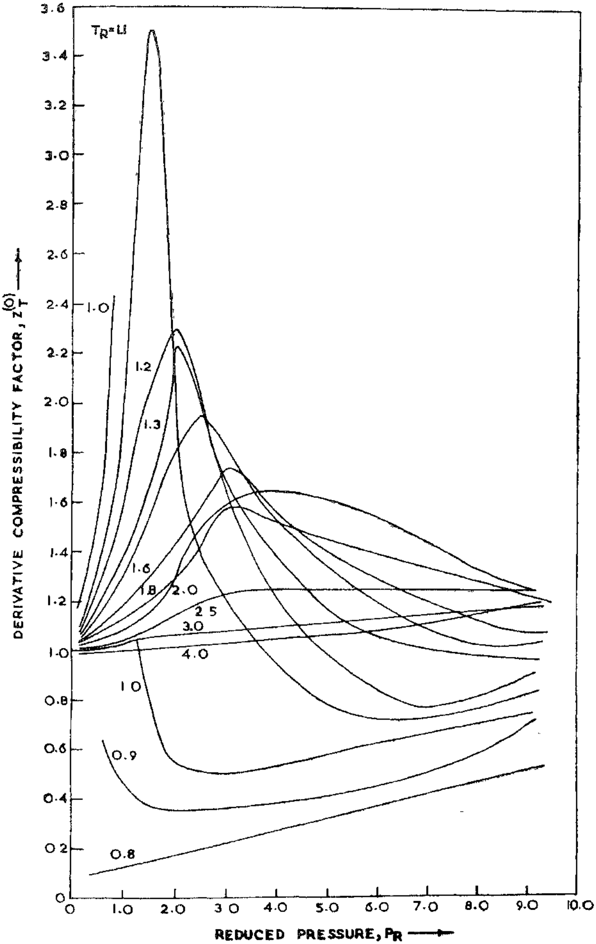

FIG. 5. $Z_T^{(0)}$ as a function of P_R and T_R.

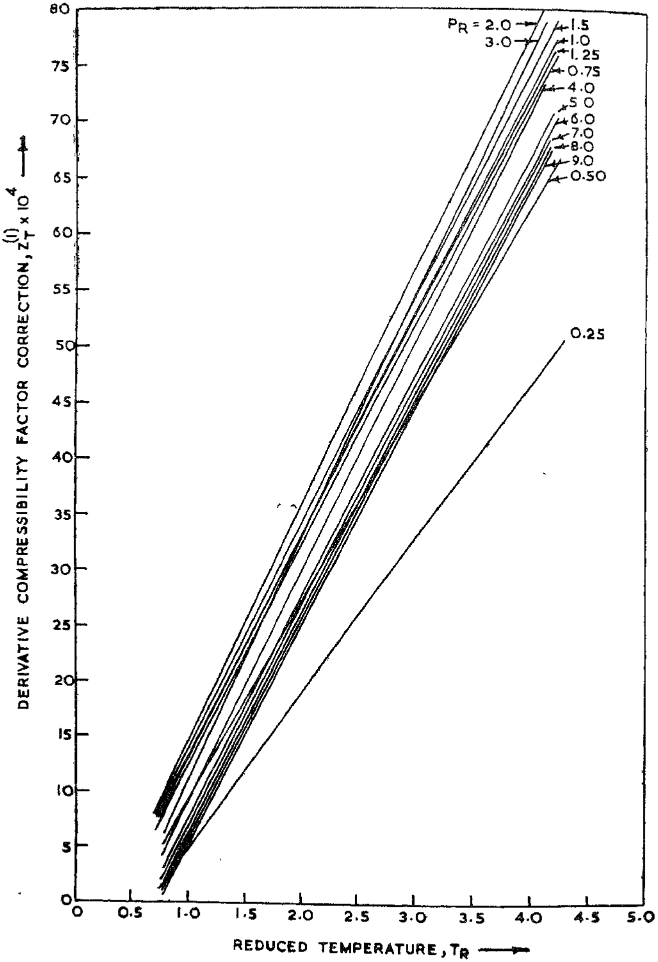

FIG. 6. $Z_T^{(1)}$ as a function of T_R and P_R.

TABLE VIII

Comparison of calculated and experimental isothermal volume derivative with pressure $(\partial V/\partial P)_T$ *for each substance*

Substance	No. of points compared	Reduced temperature range	Reduced pressure range	Per cent average absolute deviation		Source of experimental data
				Present method	Reid and Valbert method	
Ethane	42	1·00–1·60	0.25–6.00	1.33	4.95	*a*
Hydrogen	72	1·00–4·00	0.25–6.00	1.11	2.81	*b*
Steam	12	1·00–1·20	0.25–1.25	1.12	3.92	*a*
Overall	126			1.18	3.65	

TABLE IX

Summary of comparison of the calculated and experimental isobaric volume derivative with temperature $(\partial V/\partial T)_P$ *for each substance*

Substance	No. of points compared	Reduced temperature range	Reduced pressure range	Per cent average absolute deviation		Source of experimental data
				Present method	Reid and Valbert method	
Ethane ..	43	1.10–1.60	0.25–6.00	7.41	9·84	*a*
Hydrogen ..	73	1.00–3.00	0.25–6.00	5.30	7·68	*b*
Steam ..	12	1.00–1.20	0.25–1.25	1.09	6·32	*a*
Overall ..	128			5.48	9·07	

(*a*) Viswanth, D. S., Ph.D. Thesis, University of Rochester, Rochester, New York, 1962.
(*b*) Johnston, H. L. and White, D., *Transactions of the ASME.* 1950, **72**, 785–87.

TABLE X

Summary of comparison of calculated and experimental velocities of sound in each compressed gas

Gas	No. of points compared	Reduced temperature range	Reduced pressure range	Per cent average absolute deviation		Source of experimental data
				Present method	Sherwood's method	
Argon	30	1·20–1·80	0·25–1·50	4·72	4·07	*a*
Carbon dioxide	4	1.00	0·25–1·25	12·87	33·52	*b*
Ethane	6	1·00	0·25–2·00	10·88	24·17	*c*
Ethylene	11	1·00–1·10	0·75–8·00	10·87	10·51	*d*
Nitrogen	6	2·00	0·25–1·50	2·86	2·24	*e*
Oxygen	6	1·60–1.80	0·25–0·75	2·75	5·86	*f*
n-Pentane	7	1·00	0·25–3·00	3.69	10·63	*g*
i-Pentane	7	1·00	0·25–3·00	5·65	12·32	*g*
Propane	30	1·10–13·0	1·25–9·00	6·83	5·95	*h*
Overall	107			6·39	8·45	

(*a*) Van Itterbeek, A , Van Dael, W and Grevandunk, W. G., *Physica*, 1959, **25**, 640–44.
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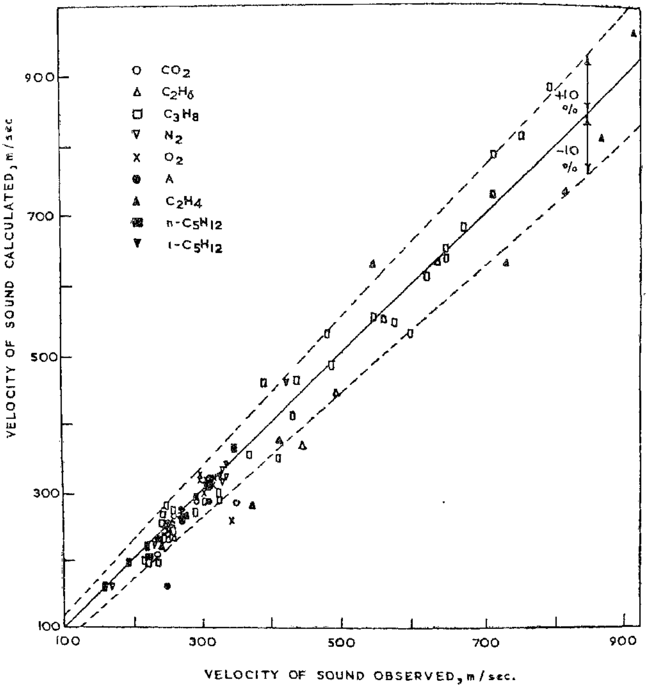

FIG. 7. Comparison of velocities of sound calculated using the present method with Experimental Data.

Nomenclature

a	.. Dimensional constant = (8307/M), m^2/sec^2. °K.
C	.. Velocity of sound, m/sec.
C_p	.. Heat capacity, cal/g.mole. °K or BTU/lb.mole. °R.
C_p°	.. Ideal gas heat capacity, cal/g.mole. °K or BTU/lb. mole. °R.
Δc_p	.. Isothermal variation of heat capacity, cal./g.mole. °K or BTU/lb.mole.°R.

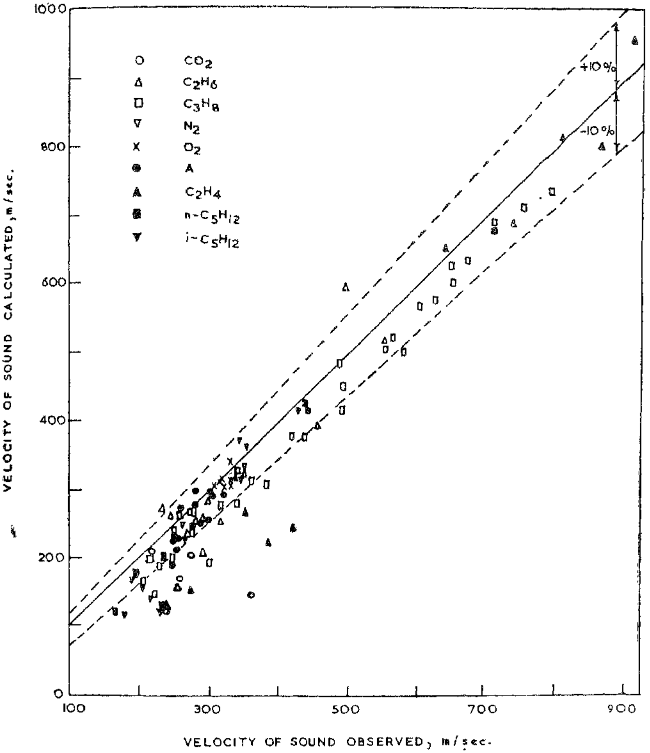

FIG. 8. Comparison of velocities of sound calculated using Pitzer's method with Experimental Data.

$\Delta C_p^{(0)}$	.. Main part of the correlation for isothermal variation of heat capacity, Equation (5).
$\Delta C_p^{(1)}$	.. Correction term of the correlation for isothermal variation of heat capacity, Equation (5).
H	.. Enthalpy, cal./g.mole or BTU/lb.mole.
H°	.. Ideal gas enthalpy, cal./g.mole or BTU/lb.mole.

$(H^\circ - H)/T_C$	Isothermal variation of enthalpy with pressure; cal./g.mole. °K or BTU$_1$lb.mole. °R.
$[(H^\circ - H)/T_C]^{(0)}$	Main part of the correlation for isothermal variation of enthalpy with pressure.
$[(H^\circ - H)/T_C]^{(1)}$	Correction term of the correlation of isothermal variation of enthalpy with pressure.
M	Molecular weight.
B	Pressure, atm.
P_{MC}	Molar polarization at the critical temperature, cc/g.mole.
R	Universal gas constant.
T	Temperature, °K.
T_C	Critical temperature, °K.
T_R	Reduced temperature $= T/T_C$.
V	Volume, cc./g. mole.
$(\partial V/\partial P)_T$	Isothermal pressure derivative of volume, cc./atm.
$(\partial V/\partial T)_P$	Isobaric temperature derivative of volume, cc./°K.
Z	Compressibility factor.
$Z^{(0)}$	Main part of the correlation for compressibility factor, Equation (2).
$Z^{(1)}$	Correction term of the correlation for compressibility factor, Equation (2).
Z_P	Derivative compressibility factor.
$Z_P^{(0)}$	Main part of the correlation for derivative compressibility factor (Z_P), Equation (6).
$Z_P^{(1)}$	Correction term of the correlation for derivative compressibility factor (Z_P), Equation (6).
Z_T	Derivative compressibility factor.
$Z_T^{(0)}$	Main part of the correlation for derivative compressibility factor (Z_T), Equation (7).
$Z_T^{(1)}$	Correction term of the correlation for derivative compressibility factor (Z_T), Equation (7).
μ	Dipole moment, debye units.

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