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## DETERMINATION OF COMPRESSIBILITY FACTORS USING SONIC VELOCITY MEASUREMENTS

Equations of state for gases would be more reliable representations of experimental data if measurements of specific volumes could be avoided. This may be accomplished by introduction of the sonic velocity, which is relatively easy to measure experimentally, into the thermodynamic network. The specific volume may be replaced by an integral, evaluated along an isotherm, involving the sonic velocity, the specific heat ratio, and the pressure. Compressibility factors evaluated with this modified equation of state agree almost exactly with those obtained from the standard form.

DETERMINATION of  $z$  through direct application of the equation  $p\bar{v} = zRT$  is complicated by difficulties in obtaining accurate experimental values for  $\bar{v}$ . This may be circumvented by employing sonic velocity measurements at constant temperature and a series of pressures. A closed resonance tube with fixed ends, described elsewhere (2) for a different experimental purpose, is a suitable device. A low-amplitude, variable-frequency signal, emitted at one end of the tube and detected at the other, defines a sequence of standing waves which permits calculation of the sonic velocity in the contained gas at a given temperature and pressure. The pressure is altered by addition or deletion of gas, maintaining constant temperature  $T_1$ , and the sonic measurement is repeated. Hence a set of sonic velocities  $a = a(p, T_1)$  is rapidly obtained.

The sonic velocity is related to the state variables by

$$a^2 = (\partial p / \partial \rho)_s = \gamma (\partial p / \partial \rho)_T \quad (1)$$

where  $s$  is the entropy and  $\gamma$  the specific heat ratio,  $C_p/C_v$ . Differentiation of the equation of state,  $p = \rho zRT$ , gives

$$(\partial p / \partial \rho)_T = \frac{zRT}{1 - (p/z)(\partial z / \partial p)_T} \quad (2)$$

and combining Equations 1 and 2 yields

$$(\partial z / \partial p)_T - z/p = -(\gamma RT/a^2)(z^2/p) \quad (3)$$

This expression may be linearized by the change of variable  $u = z^{-1}$  and the resulting standard, first-order differential equation integrated to give

$$z(p, T_1) = \frac{p}{RT_1 \int_0^p (\gamma/a^2) dP} \quad (4)$$

This solution satisfies Equation 3 and also the required condition that  $\lim_{p \rightarrow 0} z = 1$  [making use of the property

$\lim_{p \rightarrow 0} (\gamma RT/a^2) = 1$ ].  $\int_0^p \gamma/a^2 dP$  has the units of density  $\rho$ . In

fact, Equation 4 may be regarded as a modified equation of state wherein  $\rho(p, T_1) = \int_0^p \gamma/a^2 dP$ , provided that the integration is performed along the isotherm  $T_1$  (as indicated).

The integral may be evaluated graphically for any  $p$ , using the experimentally determined set  $a(p, T_1)$  plus appropriate values for  $\gamma$ , thus determining the set  $z(p, T_1)$ . Another run of sonic measurements at a new temperature,  $T_2$ , permits calculation of another set  $z(p, T_2)$ , etc.

It would be desirable and pertinent at this point to determine the applicability of Equation 4 using existing sonic measurements on a variety of gases. Unfortunately, suitable data are severely limited. The literature records many investigations of the sonic properties of gases, but only a few data sets show a pressure variation sufficient for computing the integral in Equation 4. Typically (7) previous workers have been interested in fine molecular structure, a type of measurement favored by conditions which minimize intermolecular forces. Usually operation through a narrow pressure range (ambient

or below) has been featured, rather than the sequence of higher pressures which would make Equation 4 meaningful.

An exception is the data set of Herget (4) on ethylene at 23° C., plotted in Figure 1. As shown, the sonic measurements plus the ideal gas point at zero pressure (computed from  $a = \sqrt{\gamma RT}$ ) define a smooth curve. This can be used to evaluate graphically the integral in Equation 4 when combined with suitable values for  $\gamma$ , the latter being available from a compilation by Din (3).

Table I summarizes the pertinent calculations for a comparison of  $z$ , determined from Equation 4 and from the equation of state  $z = pv/RT$  (where values for  $v$  are also obtained from Din's compendium). The figures in the last two rows of Table I show virtually perfect agreement, thus amply supporting the validity of Equation 4.

For many cases the variation of  $\gamma$  with pressure will be negligible, so that the graphical integrations may be performed

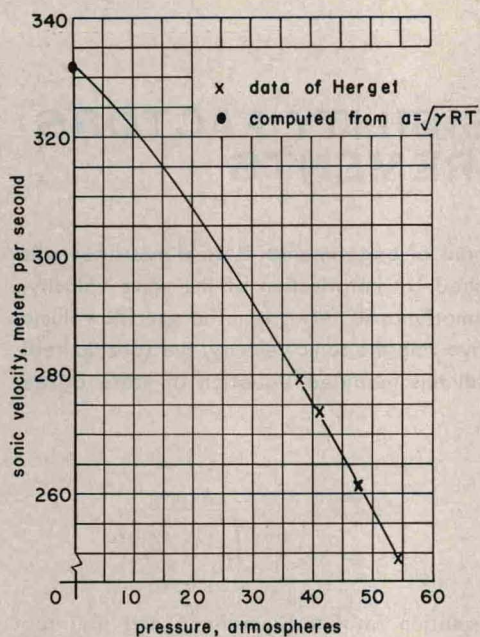


Figure 1. Sonic velocities in ethylene gas at 23° C.

Table I. Comparison of Compressibility Factors Derived from Sonic Velocity and Specific Volume Data

(Ethylene at 23° C.)					
Pressure, atm.	0	10	20	30	40
$\gamma (=C_p/C_v)$ [from (3)]	1.24	1.30	1.40	1.54	1.82
$a$ , meters/sec. (from Figure 1)	332	321	308	292	275
$\int_0^p \gamma/a^2 dP$ , atm. (sec./meter) <sup>2</sup> × 10 <sup>4</sup> (performed graphically)	0	1.17	2.54	4.22	6.31
$v$ , cc./g. [from (3)]	$\infty$	82.2	38.1	23.1	15.8
$z = \frac{p}{RT \int_0^p \gamma/a^2 dP}$	1.00	0.96	0.89	0.80	0.72
$z = pv/RT$	1.00	0.95	0.88	0.80	0.73

using a constant  $\gamma$  to determine  $z$  values. In other instances, if an equation of state is already available [either as  $z = z(p, T)$  or in another form], it may be used to evaluate the coefficient  $(\partial p/\partial \rho)_T$ . Then Equation 1 together with the  $a(p, T)$  measurements will determine  $\gamma$  as a function of pressure.

The method should not be used for two-phase systems, or for single phases close to the critical point. Under these conditions Equation 1 is not applicable, since the density,  $\rho$ , is subject to large fluctuations and is not uniquely defined. [A modification of Equation 1 for this situation has been discussed by Nozdrev (5).]

#### Literature Cited

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