Acoustic Isotherms for Argon, Nitrogen, Methane, Tetrafluoromethane, Dichlorodifluoromethane, and their Mixtures, Plus Derived Interaction Potential Force Constants

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Acoustic velocity data for various isotherms from 1 to 70 atm. are presented for argon (32°F.), nitrogen (32°F.), methane (32°, 70°F.) tetrafluoromethane (32°, 70°F), dichlorodifluoromethane (240°F., $p < 30$ atm.), and various mixtures (32°F.). Interaction potential force constants for the pure gases are derived from the acoustic data with values for tetrafluoromethane and dichlorodifluoromethane differing significantly from previous literature values. BWR constants are also reported for argon and tetrafluoromethane.

From $u(s, \rho)$, the functional dependence of the internal energy on entropy and density, it is possible to calculate the remaining thermostatic properties for simple compressible states of a substance. Often, however, this function is unknown. In place of this single complete function of state, one may display the same information by two incomplete equations of state: $f(p, T, \rho) = C$, the interrelationship between pressure, density, and temperature, and $c_{v\text{id}}(T)$, the ideal gas model specific heat. These two functions, each incomplete alone, complement one another to give a complete description of the thermostatic behavior of a gas; that is, all the thermostatic properties may be calculated therefrom. For pure liquid and solid states, the variation of pressure with temperature at phase equilibrium is also needed.

The function $c_{v\text{id}}(T)$ is commonly obtained from statistical mechanics with spectroscopically determined molecular constants. The former function, say in the form $p(T, \rho)$, could be found for specific gases by direct experimental measurements of p, ρ, and T over a wide range of states, a difficult and expensive procedure, indeed never ending for mixtures owing to their infinite number. Instead, parametric functional forms are usually assumed:

$$p = f(T, \rho, c_j) \tag{1}$$

where the various c_j's are parametric constants peculiar to specific substances. These constants are usually determined by a deviation-minimizing fit of a small amount of experimental $p\rho T$ data, or via certain specific thermostatic characteristics such as critical-point properties, slope of vapor-pressure curve, etc. To portray the behavior of mixtures in the form

$$p_{\text{mix}} = f(\rho_{\text{mix}}, T_{\text{mix}}, c_{\text{mix},j}) \tag{2}$$

it is necessary to relate the mixture constants to the composition and the pure-constituent values:

$$c_{\text{mix},j} = f(x_{ji}, c_{ji}) \tag{3}$$

Explicit forms of Equation (3) have been proposed for the various corresponding states $p\rho T$ relationships by many. For examples, Kay (*1*), Stewart-Burkhart-Voo (*2*), and Joffe (*3*), and for the Benedict-Webb-Rubin analytical equation by BWR (*4, 5*), among others. Recently, Leland and Chappelear compiled an extensive review of the corresponding states principle (*6*).

With the acoustic velocity data, three $p\rho T$ functions of state were tested in this work: the Gyorog-Obert (*7*) and Bird-Spotz (*8*) generalized virial equations, and the Benedict-Webb-Rubin (*4*) equation. Both the Gyorog-Obert and Bird-Spotz [Lennard-Jones (6-12) potential] are two parameter virial equations. The former is a generalization of experimental data, while the latter is a result of theoretical statistical mechanical calculations. Both contain the parameters ϵ and σ, which arise from simple intermolecular potential functions of the form $\phi = \epsilon F(r/\sigma)$. The BWR equation has eight parameters that fix the isometric curvature to agree with prescribed [though somewhat questionable (*9*)] criteria. All three of these equations, in general, establish the parameters for a specific gas from $p\rho T$ data.

The acoustic velocity, defined as $[\partial p/\partial \rho](\rho, s)$, may be expressed in terms of derivatives of the $p\rho T$ function of state and $c_{v\text{id}}(T)$. Apparently, virial coefficients cannot be established with confidence solely from acoustic velocity data (*10*), and in turn it would be expected that the form of a $p\rho T$ function could not be deduced from acoustic data. However, once the functional dependence of, say, p in terms of T and ρ is completely specified, it is desirable to test its ability to predict other properties, such as the acoustic velocity. Acoustic velocity data do indeed provide a critical check of a given $p\rho T$ function, and hence it will be seen that parameters for functions of state may be confidently determined from a relatively small amount of acoustic data.

EXPERIMENTAL METHOD

The acoustic velocity of a number of single constituent gases and various mixtures was measured, for several isotherms, from 1 to 70 atm. The experimental apparatus employed in this work was developed by El-Hakeem (*11*);

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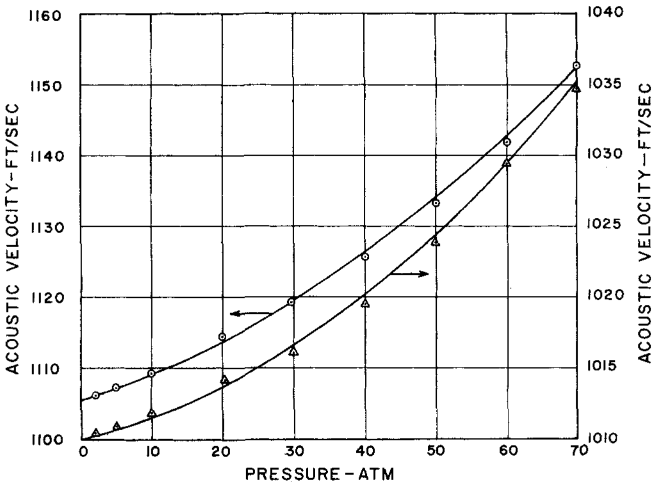

Fig. 1. Nitrogen and argon acoustic velocity at 32°F. (⊙: nitrogen data of this work), △: argon data of this work), (—: Gyorog-Obert virial equation).

however, the measurement technique was the totally reflecting, constant geometry, minimum amplitude detection scheme advocated by Romer, Gaggioli, and El-Hakeem (*12*). Further details regarding the intricacies of operation are presented elsewhere (*13*). Essentially, the half wavelength of an acoustic wave propagating in a confined gas was measured between successive sound-amplitude minima and at a number of different frequencies. From these data, obtained at various pressures, the acoustic velocity dependence on pressure was found.

The objective of the acoustic method is to find the isentropic velocity of sound from tests wherein the gas is confined in a tube and displays real (nonideal) behavior. Irreversibilities arise, principally, from the viscous interactions of the gas with the tube walls and the resultant energy transports by heat. This behavior requires the correction of the measured velocities to their isentropic counterparts. According to Romer (*14*), who generalized the Helmholtz-Kirchhoff ideal-gas correction

$$V \equiv \left[\frac{\partial p}{\partial \rho} \right] (s, \rho) = \lambda f \left(1 + \frac{A}{\sqrt{4\pi r^2 f}} \right) \qquad (4)$$

where

$$A = \left(1 + \frac{\gamma - 1}{\sqrt{N_{Pr}}} \right) \left(\frac{\mu}{\rho} \right)^{1/2} \qquad (5)$$

and λf is the measured velocity of sound in the tube. Values for the transport properties in Equation (5) were selected from the literature [such as (*15* to *18*)], and those for mixtures were calculated from empirical mixture rules (*19*). The tube correction amounted to no more than about 0.25% of the measured velocity value.

The composition of the binary mixtures was determined by a novel method based upon the zero pressure intercept of a given experimental isotherm. Since this intercept is in fact the ideal gas velocity for the mixture, the composition of the binary mixture follows from the simultaneous solution of

$$V^2_{id} = \left(1 + \frac{R}{c_{v_{id}}} \right) \left(\frac{R}{M} \right) T \qquad (6)$$

$$c_{v_{id}} = c_{v_{2,id}} + (c_{v_{1,id}} - c_{v_{2,id}}) x_1 \qquad (7)$$

$$M = M_2 + (M_1 - M_2) x_1 \qquad (8)$$

which requires an overall iterative method involving Equations (4) through (8).

DATA AND COMPARISON WITH THEORY

The isentropic acoustic velocity is defined by

$$V^2 \equiv \frac{\partial p}{\partial \rho} (\rho, s) \qquad (9)$$

From this definition and a number of well-known thermodynamic relations, it can be shown (*20*) that, with the reduced virial equation of state and $c_{v_{id}}(T)$

$$V^2 = \frac{R}{M} T \left[\Phi + \frac{\Psi}{\chi} \frac{R}{c_{v_{id}}} \right] \qquad (10)$$

where

$$\Phi \equiv 1 + 2B^* \rho^* + 3C^* \rho^{*2} + 4D^* \rho^{*3}$$

$$\Psi \equiv \left[1 + \rho^* \frac{d}{dT^*} (T^* B^*) + \rho^{*2} \frac{d}{dT^*} (T^* C^*) + \rho^{*3} \frac{d}{dT^*} (T^* D^*) \right]^2$$

$$\chi \equiv 1 - \frac{R}{c_{v_{id}}} \left[\rho^* \frac{d^2}{dT^{*2}} (T^* B^*) + \frac{1}{2} \rho^{*2} \frac{d^2}{dT^{*2}} (T^* C^*) + \frac{1}{3} \rho^{*3} \frac{d^2}{dT^{*2}} (T^* D^*) \right] T^*$$

Values for the generalized virial coefficients and their derivatives were taken from both the experimental correlations of Gyorog-Obert (*7*) and from the theoretical calculations of Bird-Spotz (*8*). The acoustic velocities for nitrogen, argon, methane, tetrafluoromethane, and dichlorodifluoromethane were then calculated by Equation (10). The calculated values are compared with experimental values in Figures 1 through 4. Calculations for both sets of virial coefficients were found to differ by no more than 0.5 ft./sec.; because of this close agreement, only the Gyorog-Obert results are presented. These figures reveal that the acoustic behavior of nitrogen and argon (Figure 1) at 32°F., and methane (Figure 2) at 32° and 70°F., are portrayed very well by the virial equation of state, with the commonly accepted molecular parameters from the literature.

In addition, for these gases and tetrafluoromethane, dichlorodifluoromethane it was possible to infer (via a least-squares fit) the molecular parameters, ϵ/κ and b_0, from the

Table 1. Force Constants

	Gyorog-Obert				Bird-Spotz			
	ϵ/κ (°K)		b_0 (cc./g.-mole)		ϵ/κ (°K.)		b_0 (cc./g.-mole)	
Gas	This work	Literature	This work	Literature	This work	Literature	This work	Literature
N_2	95.70	96.30	62.48	63.64	96.94	96.30	62.39	63.64
A	118.67	119.40	48.39	50.30	119.99	119.40	49.85	50.30
CH_4	149.93	148.20	68.14	70.16	149.49	148.20	69.86	70.16
CF_4	167.47	152.50	104.35	131.00	168.86	152.50	102.48	131.00
CCl_2F_2	264.98	268.00	234.63	173.31	264.98	268.00	234.63	173.31

TABLE 2.

$C(T)$ for CF_4 (cc./g.-mole)^2

Temperature, °C.	Douslin Experiment	Gyorog-Obert This work	Gyorog-Obert Literature	Bird-Spotz This work	Bird-Spotz Literature
0	7,100	7,600	9,730	5,444	10,004
50	5,380	5,869	8,302	4,783	8,305
100	4,490	5,085	7,441	4,344	7,447
150	3,980	4,584	6,581	4,002	6,589
200	3,660	4,094	5,914	3,820	5,834
250	3,440	3,746	5,671	3,667	5,663
300	3,250	3,604	5,430	3,568	5,423
350	3,100	3,386	5,232	3,494	5,234

acoustic data. The iterative procedure for establishing these parameters converged well with data from only a single isotherm (but requiring data at several pressures). Furthermore, the values determined separately from different isotherms were in excellent agreement. Table 1 shows a comparison of the inferred values in this work with those reported in the literature (*7*, *8*), wherein the parameters were determined from compressibility data (but requiring data at several temperatures). It is seen that there was only a slight adjustment of the constants in all cases except dichlorodifluoromethane (Figure 3) and tetrafluoromethane (Figure 4). In both of these cases the disparity was large. From the results shown in Table 2, one may conclude that the new inferred values for tetrafluoromethane are preferable; the third virial coefficient, $C(T)$, for tetrafluoromethane is shown from Douslin's experimental compressibility measurements (*21*) and for the two virial equations with both new (this work) and old (literature) parameters. The agreement between compressibility (Douslin) and acoustic (this work) values is quite good. [And this agreement has impact upon contentions (*21*) that the Lennard-Jones (6-12) potential is not appropriate for tetrafluoromethane; this impact will be discussed in a future article.] Upon reexamination of the original source of the tetrafluoromethane parameters taken from the literature, it is suggested that the temperature range of the second virial data was insufficient to reflect the best values of the molecular parameters. The accuracy with which the tetrafluoromethane acoustic data is portrayed at two different temperatures in Figure 4 is further evidence of the credibility of the new inferred parameters [and of the applicability of the Lennard-Jones (6-12) potential to tetrafluoromethane].

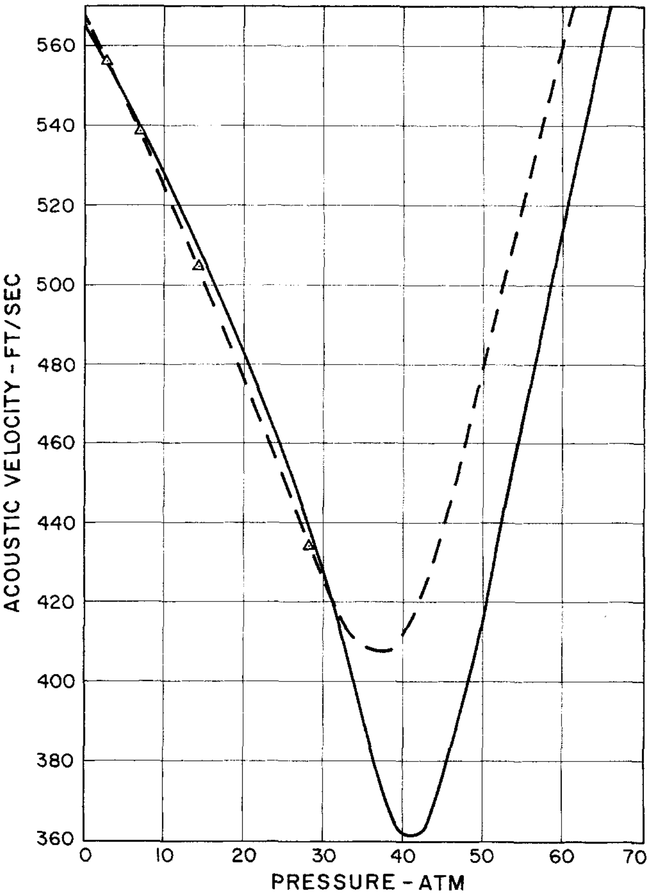

Fig. 3. Dichlorodifluoromethane acoustic velocity at 240°F. (△: data of this work), (—: Gyorog-Obert virial equation with literature parameters), (- - -: Gyorog-Obert virial equation with inferred parameters).

To apply any parametric function of state to mixtures, a means must be available to evaluate the mixture parame-

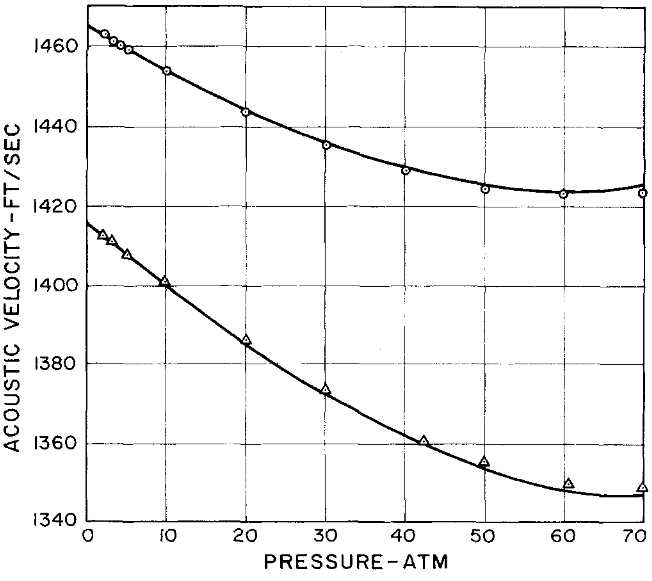

Fig. 2. Methane acoustic velocity at 32°, 70°F. (△: 32°F. data of this work), (○: 70°F. data of this work), (—: Gyorog-Obert).

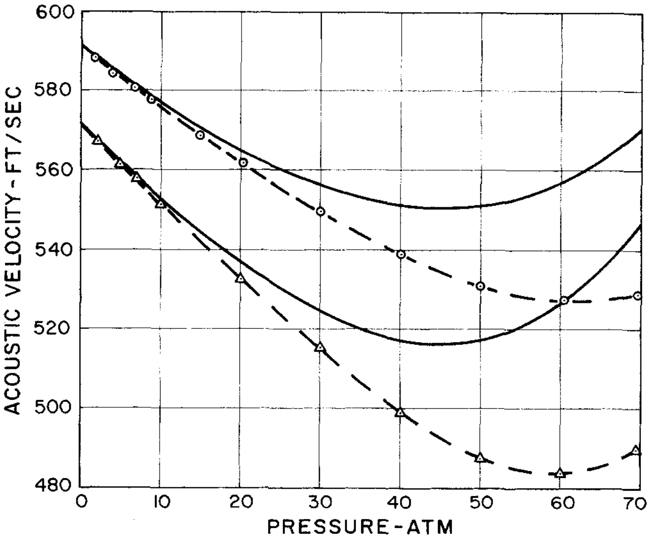

Fig. 4. Tetrafluoromethane acoustic velocity at 32°, 70°F. (△: 32°F. data of this work), (○: 70°F. data of this work), (—: Gyorog-Obert virial equation with literature parameters), (- - -: Gyorog-Obert virial equation with inferred parameters.)

TABLE 3. BENEDICT-WEBB-RUBIN-EQUATION CONSTANTS
[Units: atm. liters/(g.-mole) (°K.)

Gas	A_0	B_0	C_0	a	b	c	α	γ
CF_4	4.3313	0.1134	58,441	0.14326	0.005903	12,283	0.00033	0.01329
A	1.2830	0.0354	14,981	0.02390	0.001158	3040.6	1×10^{-10}	0.02060

ters in terms of the corresponding pure-component values and the composition. The application of Equation (10) to mixtures requires a mixture rule for ϵ/κ and b_0. One possible way to obtain these mixture parameters would be to extend the method of Nelson and Obert (22). They showed, for pure components, that by comparing a corresponding states principle with the virial density expansion

$$\epsilon = k_1 T_c \qquad (11)$$

$$b_0 = k_2 \frac{T_c}{p_c} \quad k_1, k_2 \text{ constants} \qquad (12)$$

The accuracy of these equations is, essentially, equivalent to the accuracy of the Onnes principle of corresponding states: $z = z(T/T_c, p/p_c)$. If Equations (11) and (12) are assumed to hold not only for pure components but also for homogeneous mixtures, then these equations may be combined with the various critical parameter mixture rules to yield molecular parameter mixture rules. As examples, Kay's rule would become

$$\epsilon_{\text{mix}} = \sum_i x_i \epsilon_i \qquad (13a)$$

$$\frac{\epsilon_{\text{mix}}}{b_{0_{\text{mix}}}} = \sum_i x_i \frac{\epsilon_i}{b_{0_i}} \qquad (13b)$$

while for the Stewart-Burkhardt-Voo rule

$$b_{0_{\text{mix}}} = \frac{1}{3} \sum_i x_i b_{0_i} + \frac{2}{3} \left[\sum_i x_i \sqrt{b_{0_i}} \right]^2 \qquad (14a)$$

$$\epsilon_{\text{mix}}\, b_{0_{\text{mix}}} = \left[\sum_i x_i \sqrt{\epsilon_i b_{0_i}} \right]^2 \qquad (14b)$$

and, finally, for Joffe's rule

$$b_{0_{\text{mix}}} = \frac{1}{8} \sum_{i,j} x_i x_j \left(b_{0_i}^{1/3} + b_{0_j}^{1/3}\right)^3 \qquad (15a)$$

$$\epsilon_{\text{mix}}\, b_{0_{\text{mix}}} = \left[\sum_i x_i \sqrt{\epsilon_i b_{0_i}} \right]^2 \qquad (15b)$$

Other mixture rules can be similarly treated. It is also necessary to know the ideal-gas specific heat for the mixture which is obtained from the exact expression

$$(c_{v_{\text{id}}})_{\text{mix}} = \sum_i x_i c_{v,i,\text{id}} \qquad (16)$$

From this point, with the mixture molecular parameters, the use of Equation (10) is the same as for pure components.

Another equation of state often applied to mixtures is the Benedict, Webb, and Rubin equation (4):

$$z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \right) \rho + \left(b - \frac{a}{RT} \right) \rho^2 + \frac{a\alpha\rho^5}{RT} + \frac{c\rho^2}{RT^3} (1 + \gamma\rho^2) e^{-\gamma\rho^2} \qquad (17)$$

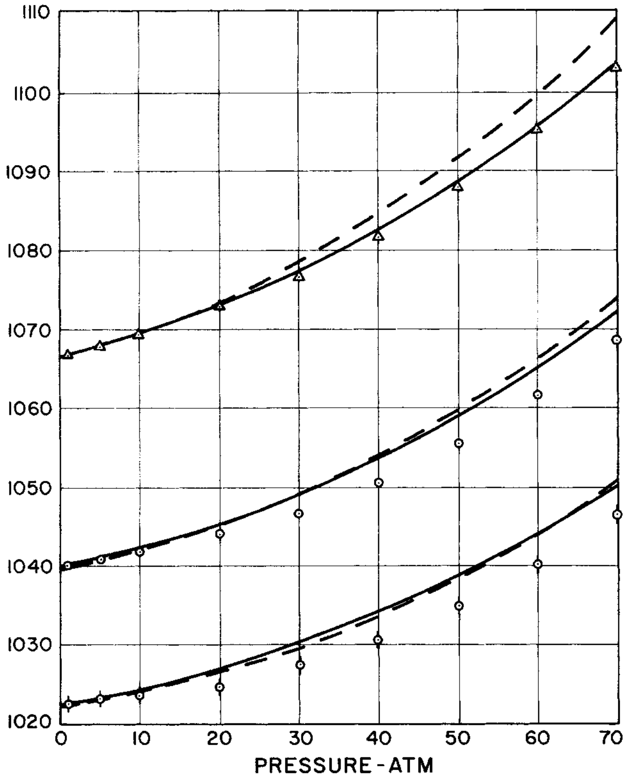

Fig. 5. Nitrogen-argon mixture acoustic velocity at 32°F. (△: data of this work, x_{N_2} = 0.7461), (⊙: data of this work, x_{N_2} 0.5130), (⊙: data of this work, x_{N_2} = 0.2978), (—: corresponding states), (- - -: BWR equation).

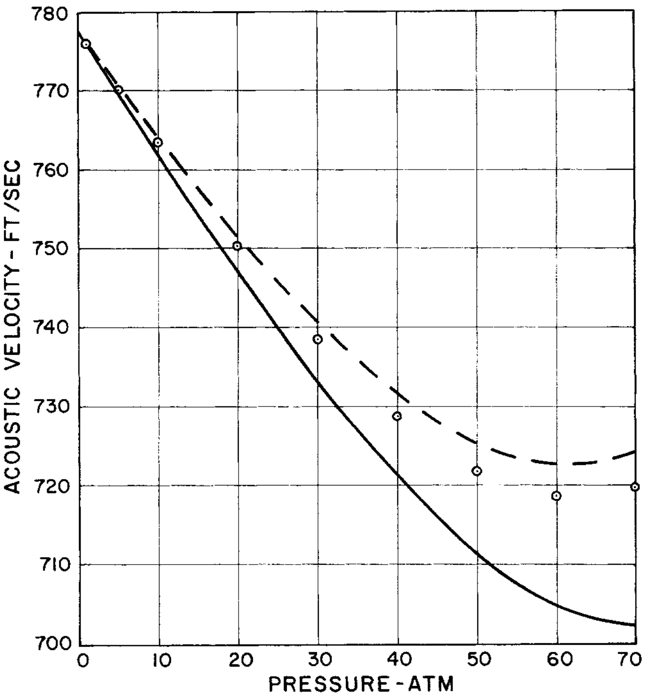

Fig. 6. Methane-tetrafluoromethane mixture acoustic velocity at 32°F. (⊙: data of this work, x_{CH_4} = 0.5355), (—: corresponding states), (- - -: BWR equation).

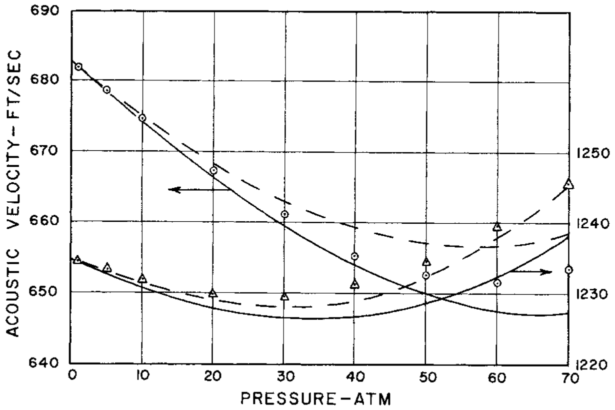

Fig. 7. Tetrafluoromethane-argon and nitrogen-methane mixture acoustic velocity at 32°F. (⊙: tetrafluoromethane argon data of this work, $x_{CF_4} = 0.5390$), (△: nitrogen-methane data of this work, $x_{N_2} = 0.4647$), (—: corresponding states), (- - -: BWR equation).

By proceeding in a manner analogous to the derivation of Equation (10), the same relation is obtained for V, but with

$$\Phi = 1 + 2\left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right)\rho + 3\left(b - \frac{a}{RT}\right)\rho^2 + \frac{6a\alpha\rho^5}{RT} + \frac{c\rho^2 e^{-\gamma\rho^2}}{RT^3}(3 + 3\gamma\rho^2 - 2\gamma^2\rho^4) \quad (18a)$$

$$\Psi = \left[1 + \left(B_0 + \frac{2C_0}{RT^3}\right)\rho + b\rho^2 - \frac{2c\rho^2(1+\gamma\rho^2)e^{-\gamma\rho^2}}{RT^3}\right]^2 \quad (18b)$$

$$\chi = 1 + \frac{6}{c_{v\mathrm{id}}T^3}\left[\left(C_0 + \frac{c}{2}e^{-\gamma\rho}\right)\rho + \frac{c}{\gamma}(e^{-\gamma\rho} - 1)\right] \quad (18c)$$

The standard BWR empirical equations (5) were the means for evaluating the eight constants of Equations (17) and (18) for mixtures. The results of calculations with Equation (10), by using the virials and Kay's rule [Equation (13)], and by using the BWR equation, are compared with the experimental data in Figures 5 through 7. Isotherms calculated with other mixture rules are presented in (*13*); the same trends are displayed. It must be noted that the specific BWR constants for tetrafluoromethane and *A* were not available in the literature and were inferred from the acoustic data of the pure constituents. The values appear in Table 3.

CONCLUSIONS

1. The generalized virial equations of state of both Gyorog-Obert and Bird-Spotz with the commonly accepted molecular parameters, closely portrayed the acoustic behavior of nitrogen, argon, and methane.
2. Molecular parameters can be inferred from acoustic measurements. This technique is superior to inference from second virial or viscosity data in that a more limited range of experimental data suffices. For example, the parameters for nitrogen were obtained from only one acoustic isotherm (1 to 70 atm. pressure), whereas the nitrogen parameters obtained from second virial data required data over an extensive temperature range.
3. The compressibility of tetrafluoromethane can be closely described by the Gyorog-Obert, or Bird-Spotz, virial equation if the molecular parameters are inferred either from acoustic data or from a sufficiently large temperature range of second virial data. The same confidence is placed in the dichlorodifluoromethane acoustic inferred parameters.
4. The mixture behavior can be adequately portrayed by both the Benedict-Webb-Rubin equation (with its mixture rule) and the virial equations (with Kay's mixture rule). The agreement is, however, not as close as that found for the pure species. Preliminary evidence does indicate that a small additional amount of acoustic data will enable the inference of a better mixture rule.

NOTATION

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = Benedict-Webb-Rubin equation parameters
B^*, C^*, D^* = generalized virial coefficients [$B^* \equiv B/b_0$, $C^* \equiv C/b_0^2$, etc., where B, C, etc., are the temperature coefficients in the Maclaurin density expansion of the function $z(T, \rho)$]
b_0 = molecular potential parameter ($b_0 \equiv 2/3\ \pi N_0\sigma^3$)
$c_{v\mathrm{id}}$ = ideal gas model specific heat
f = sound-field frequency
M = molecular weight
N_0 = Avagadro's number
N_{Pr} = Prandtl number
p = pressure
p_c = critical pressure
r = radius of cylindrical sound tube
R = universal gas constant
T = absolute temperature
T_c = critical temperature
T^* = reduced temperature, $T^* \equiv [T/(\epsilon/\kappa)]$
V = acoustic velocity, [$V^2 \equiv \partial p/\partial\rho\ (s, \rho)$]
x = mole fraction
z = compressibility factor, ($z \equiv p/\rho RT$)

Greek Letters

γ = ratio of specific heats, ($\gamma \equiv c_p/c_v$)
ϵ, σ = intermolecular potential energy parameters
κ = Boltzmann constant
ϵ/κ = molecular potential parameter
λ = sound-field wavelength
μ = viscosity
ρ = density
ρ^* = reduced density, ($\rho^* \equiv b_0\rho$)

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A Statistical Model of a Porous Medium with Nonuniform Pores

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A random network model of a porous medium with nonuniform pores has been constructed. Nonuniformity is achieved by assigning two-parameter distributions to pore radius and pore length. Statistical derivations result in expressions for bulk model properties which are consistent with known empirical behavior of porous media such as capillary pressure, hydraulic permeability, and longitudinal and transverse dispersion. A series of experiments is suggested whereby the parameters of porous media structure may be determined from observed macroscopic behavior by using the expressions developed in this paper.

This study describes a simple model of the structure of a porous medium with nonuniform pores. There are models, statistical in nature, which describe the microstructure of porous catalysts (*4, 6, 9, 15, 18, 21*). (Darcy's law may not be valid for flow in the microstructures.) These models are generally capillary unit cell models. The appropriate mass transfer equation is integrated to find effectiveness factors for these porous catalysts. The model described herein is for bulk phenomena associated with a pressure gradient (Darcy's law is valid) rather than diffusion due to a concentration gradient. Previous statistical models for describing bulk phenomena did not include nonuniformity (*5, 10, 17*). Real porous media even though seemingly homogeneous* and isotropic are most often nonuniform, and this nonuniformity may affect the observable bulk phenomena. A parametric statistical model is used to calculate macroscopic properties of the medium such as capillary pressure, permeability, and dispersion in order to relate these properties to the structure of the model. A pore can be described in terms of its radius, length, and orientation in a flow field. The model is constructed of two-parameter distribution functions. The parameters of these distribution functions may be related to the physical properties of the prototype structure. Orientation is random with all directions allowed. Various properties of a porous medium are found by integrating over the joint distributions resulting from the model so constructed. Random walk of particles of fluid is used to describe macroscopic dispersion during laminar flow through the model. Finally, the results are discussed in view of experimental data and continuum theories to examine the effect of nonuniformity on the observable phenomena. These studies, more experimental data, and extensions to heterogeneous anisotropic models are necessary to understand and develop a more general theory of dispersion in real porous media.

THE MODEL

The model pore space is approximated by a large number of randomly oriented, straight, cylindrical pores. The elemental pore in this network is presented in Figure 1 as a straight cylinder of length l and radius r. The pore is oriented in space by an angle θ from the z axis (the direction of flow) and by an angle ψ which is the angle between the y axis and the projection of the center line of the pore in the x-y plane. We assume for this study that all directions of an elemental pore are equally likely and $0 \leq \theta \leq \frac{\pi}{2}$, $0 \leq \psi \leq 2\pi$. The model can be constructed in terms of dimensionless quantities by defining

$$l^* = \frac{l}{L}; \quad 0 \leq l \leq L \quad \text{and} \quad 0 \leq l^* \leq 1 \qquad (1)$$

and

$$r^* = \frac{r}{R}; \quad 0 \leq r \leq R \quad \text{and} \quad 0 \leq r^* \leq 1 \qquad (2)$$

Both L and R must be finite in a real porous medium.

To make the model nonuniform, the dimensionless length l^* and dimensionless radius r^* are each assumed to be distributed according to the beta function (*11*).

$$f(x; p_1, p_2) = \frac{(p_1 + p_2 + 1)!}{p_1!\, p_2!} (x)^{p_1} (1 - x)^{p_2} \qquad (3)$$

where p_1 and p_2 are arbitrary parameters. The beta function was selected as the probability distribution function for both radius and length, since the random variables have a range of zero to one and the distribution has a spectrum of skew and symmetric shapes depending on the choice of the parameters. Familiar two-parameter distributions (for example, normal, chi squared, etc.) lack flexibility to simulate natural petrographic phenomena and particularly suffer from the shortcomings of infinite range which are contrary to Equations (1) and (2).

If we assume the radius, length, and orientation of the elemental pores to be independent,† then the probability

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* In a flow sense homogeneous means no distortion of bulk streamlines from flow in a homogeneous potential field.

† In a uniform, isotropic medium of constant porosity, length and radius are dependent (through pore volume). In general, radius and length are not dependent.