Experimental Ideal Gas Reference State Heat Capacities of Gases and Vapors

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Measurement of resonant frequencies of acoustic standing waves in gases confined to a spherical cavity leads to accurate sonic speeds. These in turn are related thermodynamically to the ideal gas reference state heat capacities and the second acoustic virial coefficients of the sample gases. The experimental procedure is described and results are given for *n*-butane and isobutane. A technique that uses argon as a buffer gas allows the procedure to be extended to include studies on vapors of volatile liquids. Results on *n*-heptane are presented.

Introduction

Thermodynamics is in principle a powerful predictive tool for chemical processes. In actual practice, its use is limited by the availability of reliable imput data for pure substances and mixtures of interest. The experimental acquisition of such data is typically both tedious and difficult, especially the determination of thermochemical properties in the ideal gas reference state, which necessitates making measurements at low densities and extrapolating to zero pressure. The special difficulty in these cases results from the fact that the system under study at low pressures, a rarefied gas, is in reality little more than a polluted vacuum, and the magnitudes of its physical properties (density, specific heat, enthalpy, etc.) are dwarfed by those of the confining apparatus.

An alternative approach is to calculate the desired properties from theoretical models. In this case, the study of the ideal gas reference state is a distinct advantage because of the absence of intermolecular interactions, which invariably complicate the calculations and decrease the reliability of the final results. In practice, however, high-quality quantum mechanical calculations are limited to systems with few electrons. Although statistical mechanical methods can yield satisfactory theoretical results on hydrocarbon molecules as large as C_7, the required spectroscopic equipment and personnel needed for such efforts are limited at present, and there still exists the problem of making separate calculations for many distinct conformers of each molecule and combining them properly to reflect accurately on the properties of the equilibrium mixture. For these reasons, various predictive schemes for estimating ideal gas reference state properties based on empirical and semiempirical arguments have been developed (*1-7*). Experimental data on selected compounds are needed to evaluate the qualities of existing schemes and guide the development of new ones. The present report is on the initial activities of an ongoing research program undertaken to address part of this need. Ideal gas reference state heat capacities are determined experimentally. An added dividend of the experimental technique is some useful information about the departure from ideality at finite pressures. In particular, the method leads to measurements of the second virial coefficient and thereby provides some insight to the intermolecular potential.

Gas-phase heat capacities have been measured directly by the steady-state flow calorimetry technique (*8-10*) and indirectly by adiabatic expansion methods (*11-14*). Methods based on measurement of the speed of sound through gases are included in the latter category because the rarefactions and compressions accompanying a pressure wave occur nearly adiabatically. Common experience suggests that the speed of sound through air is the same for all frequencies, and this is nearly so, at least for audible sounds. There is, however, a small discrimination that becomes larger as either the frequency or the molecular complexity of the gas increases. Because the thermodynamic connection with sonic speed is strictly valid only in the limit of zero frequency (*15*), the best established speed of sound technique, ultrasonic interferometry (*16-18*), is not well suited for obtaining equilibrium thermodynamic properties of polyatomic gases. Low-frequency methods, which are better for the present purposes, are based on measuring the frequencies of the lowest resonant vibrations of a gas confined in a cavity. Depending on the shape and dimensions of the cavity, these frequencies are typically 1-2 orders of magnitude lower than those of practical ultrasonic interferometry. Early investigators used cylindrical resonators (*16-18*), and Colclough (*19*) analyzed the sources of error in their use. More recently, Moldover, Waxman, and Greenspan (*20*) pointed out the decided advantages of using spherical resonators, for which the systematic errors associated with gas-resonator-wall interactions can be significantly lower than in cylindrical resonators. These advantages are most pronounced for the spherically symmetric radial modes of gas vibration inside spherical cavities. These same investigators have developed the technique for obtaining accurate thermochemical properties of gases (*21-23*). We have adopted their procedure and extended its use to include vapors of volatile liquids as well as permanent gases. In the vapor studies, argon is used as a buffer gas to catalyze the flow of acoustic energy into and out of the internal degrees of freedom of the vapor molecules, thereby reducing the relaxation time that otherwise tends to render the acoustic compressions and rarefactions thermodynamically irreversible and complicates interpretation of the sonic measurements.

Sonic/Thermodynamic Connection

The speed of propagation c of an acoustic wave of frequency f through a fluid medium of density ρ is given by

$$c_f^2 = B_f/\rho \tag{1}$$

where B_f is the bulk modulus $-V(\partial P/\partial V)_f$, and the partial derivative is evaluated at the conditions that prevail during the wave passage. It is common to assume that the pressure changes occur reversibly and adiabatically, for which the partial derivative is readily calculable. These assumptions, however, are strictly valid only in the limit of zero frequency (*15*) for which eq 1 becomes

$$c_0^2 = \lim_{f\to 0} c_f^2 = -V(\partial P/\partial V)_s/\rho \tag{2}$$

The partial derivative of eq 2 may be evaluated for any fluid for which the equation of state is known. At the low to moderate pressures used in the present experiment, a reasonable choice is the truncated virial equation

$$P\tilde{V}/RT = 1 + B(T)/\tilde{V} \tag{3}$$

where P, $\tilde{V}$, T, and R have their usual meanings and $B(T)$ is

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the second virial coefficient. Substitution of this expression into eq 2 and taking $\rho = \tilde{M}/\tilde{V}$ gives

$$c_0^2 = \frac{\gamma^\circ RT}{\tilde{M}}\left[1 + \frac{A(T)}{\tilde{V}}\right] \tag{4}$$

where $\gamma^\circ = \tilde{C}_p{}^\circ/\tilde{C}_v{}^\circ$ for the ideal gas reference state at temperature T and $A(T)$ is the second acoustic virial coefficient equal to

$$A(T) = 2B + 2(\gamma^\circ - 1)T\frac{\mathrm{d}B}{\mathrm{d}T} + \frac{(\gamma^\circ - 1)^2}{\gamma^\circ}T^2\frac{\mathrm{d}^2B}{\mathrm{d}T^2} \tag{5}$$

The equations of this section provide a connection between the sonic speed c_0 and the thermodynamic properties γ° and $B(T)$. Their practical use requires measurement of c at different conditions of T and $\tilde{V}$. Experimental methods for measuring c include those based on time of flight, time domain reflectometry, and resonant frequency measurements. The latter method is used in this work; its principles are outlined briefly in the next section.

Spherical Acoustic Resonator

The pattern of normal-mode vibrations of any elastic system depends on its geometric features. A taut string of length L with fixed ends will support transverse vibrations with wavelengths equal to $2L/n$ where $n = 1, 2, 3, ...$ The corresponding frequencies of vibration depend as well on the elastic nature of the individual system that in turn determines the rate at which a stress suitable for initiating vibration is propagated through the system. Vibration patterns in bodies of gases are more complex than those of the one dimensional string, but the same principles apply. The pattern of longitudinal acoustic standing waves depends on the shape of the confining cavity, and the corresponding frequencies depend on the speed of sound through the gas. Measurement of normal-mode frequencies of a gas confined in a cavity for which the standing wave pattern is known can lead to determination of the gas-phase sonic speed.

The standing wave patterns in a lossless fluid confined to a spherical cavity with rigid walls was first worked out by Raleigh (*24*). Interesting geometric properties of these wave patterns are discussed by Ferris (*25*). The standing acoustic waves are characterized by a velocity potential $\Phi_{nlm}(r,\theta,\phi)$ that shows a remarkable similarity to the familiar hydrogenic atomic wave functions $\psi_{nlm}(r,\theta,\phi)$. Both are functions of r, the radial distance from the origin of spherical polar coordinates (r,θ,ϕ), times an angular function (a spherical harmonic). The numbers n, l, and m are restricted by mathematical and physical boundary conditions to specific sets of intergers. The solutions having $l = 0$ are spherically symmetric (s states in atoms and radial breathing modes in spherical resonators). These are of principal interest in this work because of the concomitant absence of tangential motion of the gas with respect to the wall.

The frequencies at which resonance occurs in a spherical cavity of radius a are given by

$$f_{nl} = c_f\nu_{nl}/2\pi a \tag{6}$$

where ν_{nl} is an eigenvalue of the boundry value problem. The values of the first 84 eigenvalues including the first 7 radial modes are given by Ferris (*25*). Moldover et al. (*20–23*) have refined the analysis to include the effects of the thermal boundary layer at the resonator wall, the elastic compliance of the resonator, sound absorption by the gas, perturbations due to attachment of transducers, and departures from perfectly spherical geometry. Corrections for these effects are necessary for the most accurate measurements of sonic speed but are small enough to be neglected in the present work, especially in view of the experimental procedure in which resonances are measured relative to those in argon.

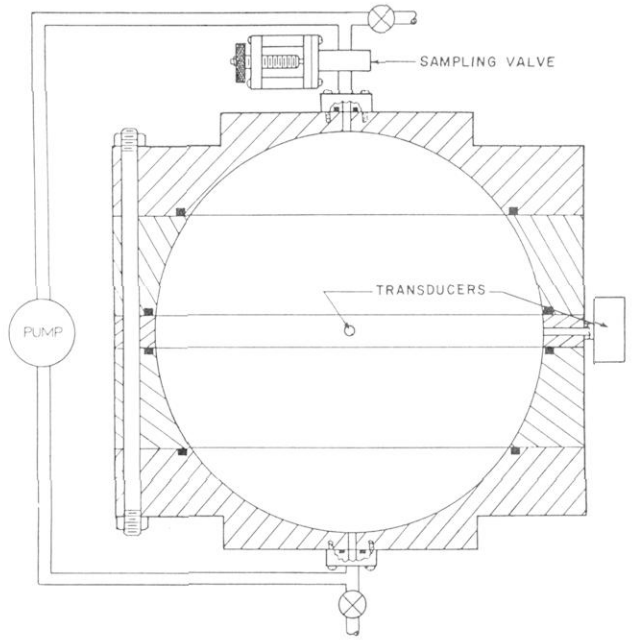

Figure 1. Spherical acoustic resonance apparatus.

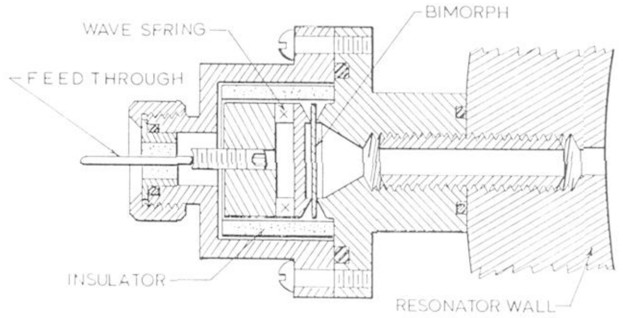

Figure 2. Bimorph transducer assembly and mounting means.

Experimental Technique

Apparatus. The heart of the experimental apparatus is the resonator cavity, Figure 1, which was machined from five separate pieces of 2024 aluminum alloy. When properly assembled with alignment pins, these create a smooth-walled spherical cavity having a diameter of 0.3048 m (12 in.). The joints between the sections are sealed by viton o-rings. Four reamed holes pass through the resonator wall into the cavity. The top and bottom sections each has a central 0.318-cm-diameter hole for emptying and filling the cavity. The center ringlike section has two 0.56-cm-diameter holes leading to the exciting and receiving transducers. The bimorph transducer and the electrical feed-through assembly are shown in Figure 2.

The resonator is prepared for filling by evacuating through the charging valve. With a diffusion pump, the pressure is reduced below 10^{-4} Pa (10^{-6} Torr). The evacuated system is back-filled with permanent sample gas. The pressure is measured with a sensitive capacitance manometer calibrated against a precision McLeod gauge. The resonator temperature is monitored by two precision four-wire Pt resistance thermometers located in holes drilled on opposite sides of the aluminum shell.

For measurements on vapors of volatile liquids, the samples are injected by syringe through a specially designed sampling valve, Figure 3. A rubber septum seal is mounted on the valve body prior to opening. The liquid sample is injected through the

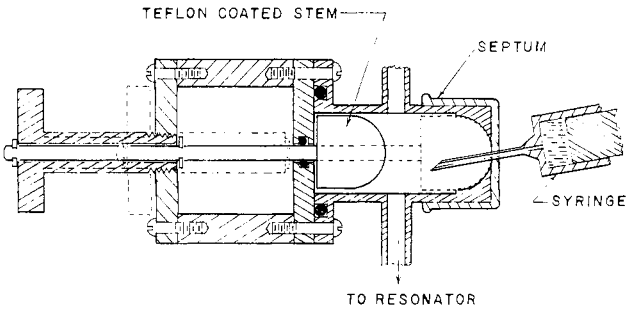

Figure 3. Liquid sample injection valve. Dashed lines show valve in closed position.

septum into the opened valve, and the valve is reclosed before the septum is removed. This arrangement avoids introduction of air into the resonator. Mixing of the injected sample and the buffer gas was ensured by a circulation pump, Figure 1, operating at a throughput of 4 L/min.

In operation the exciting transducer is driven by the output of a voltage-controlled oscillator (VCO) that in turn is driven by a variable dc input. The VCO input may be controlled manually with a precision voltage divider or automatically with a DAC port on the dedicated minicomputer (PC-AT compatible) used in data acquisition and analysis. The output of the receiving transducer is displayed on an oscilloscope and simultaneously analyzed by an integrating power level circuit that gives a digital readout of signal intensity.

Measurements. The chemicals employed were argon (Matheson Gas products; 99.9995 mol %), normal butane and isobutane (Phillips Chemicals Co.; >99.9 mol%), and *n*-heptane (Aldrich Chemical Company, Inc.; >99 mol%, Gold Label). The principal impurity in the butanes was the minor isomer. Heptane was purified by a zone crystallization technique, degassed, dried through molecular sieves, and then used for the experiments. Since mass spectrometric and gas chromatographic analysis of argon showed no detectable impurities, it was used without further treatment.

Studies were made on the gases *n*-butane, isobutane, and argon and on *n*-heptane–argon mixtures. The pure gases were studied at three temperatures (298.15, 323.15, and 348.15 K) and the mixtures at 298.15 K only. For each sample, the frequencies of the first six radial modes were measured. Figure 4 shows a typical signal.

Calculations. Butanes. Although the present technique is suitable for making absolute sonic speed measurements, it is less trouble to make relative measurements. Little accuracy is lost in doing so if the thermodynamics of the reference system are well documented. Argon satisfies these conditions and was chosen as the comparison standard. Using eq 6 to compare the frequency $f_n(\tilde{V},T)$ of the nth radial mode of sample gas at $\tilde{V}$ and T to the corresponding frequency $f_{n,\mathrm{Ar}}(\tilde{V}_{\mathrm{Ar},T})$ in pure argon at the same temperature, one obtains

$$c_n^{\,2}(f,\tilde{V},T) = c_{n,\mathrm{Ar}}^{\,2}(\tilde{V}_{\mathrm{Ar},T})\left(\frac{f_n}{f_{n,\mathrm{Ar}}}\right)^2 \qquad (7)$$

Since argon has no internal modes to influence the sonic speed and since the dissipative effects due to transport phenomona are very small, we may equate $c_{n,\mathrm{Ar}} = c_{0,\mathrm{Ar}}$ and substitute eq 4 into eq 7 to obtain

$$c_n^{\,2}(f,\tilde{V},T) = c_{0,\mathrm{Ar}}^{\,2}\left(\frac{f_n}{f_{n,\mathrm{Ar}}}\right)^2 = \left(\frac{f_n}{f_{n,\mathrm{Ar}}}\right)^2 \frac{\gamma_{\mathrm{Ar}}{}^{\circ}RT}{\tilde{M}_{\mathrm{Ar}}}\left[1 + \frac{A(T)_{\mathrm{Ar}}}{\tilde{V}_{\mathrm{Ar}}}\right] \qquad (8)$$

This equation gives the sonic speed in the sample gas in terms of experimental frequencies and well-known properties of the reference gas [$\gamma_{\mathrm{Ar}}{}^{\circ} = {}^5/_3$, and $A(T)$ may be calculated by eq 5 with data given in ref 15; values of $A(T)$ for Ar at 273.15 and 298.15 K are given in ref 21]. Values of $c_0(\tilde{V},T)$ can, in principle, be obtained from eq 8 by plotting experimental values of $c_n(f,\tilde{V},T)$ determined for a number of radial modes vs resonance frequency, f, and extrapolating the plot to zero frequency. For the present systems, however, the plots have very nearly zero slope, which indicates that irreversibility due to vibrational relaxation effects has a negligible influence on the sonic speeds. For these systems, c_0 is taken as an average of the measured c_n values. The standard deviation of these averages are typically about 0.001 ms^{-1} and have little influence on the overall precision of the sonic speed measurements, which is about ± 0.01 ms^{-1}. For more complex molecular species or studies in smaller spheres with concomitant higher frequencies, an extrapolation procedure would be called for.

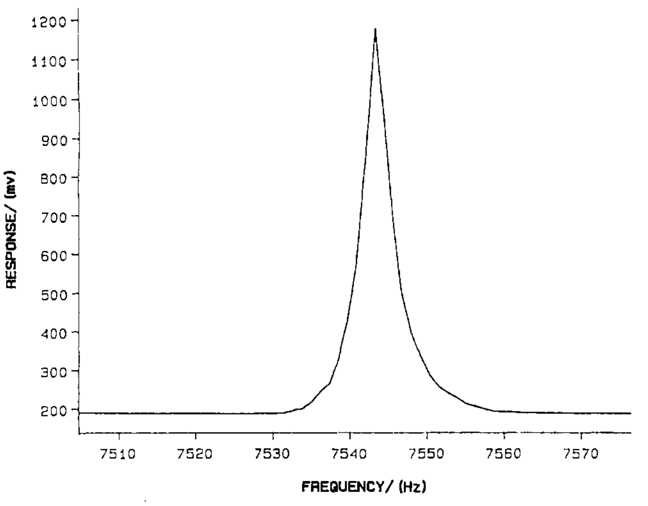

Figure 4. Typical radial-mode resonance signal shown as intensity (mV) vs frequency (Hz).

Finally at each temperature, the best fit intercept $a(T)$ and slope $b(T)$ of the linear relationship $c_0^{\,2}(\tilde{V},T) = a(T) + b(T)/\tilde{V}$ gives, according to eq 4

$$\gamma^{\circ}(T) = \frac{a(T)\tilde{M}}{RT} \qquad (9)$$

and

$$A(T) = b(T)/a(T) \qquad (10)$$

The ideal gas reference state heat capacity $\tilde{C}_p{}^{\circ}$ may be computed from eq 9 and the independent thermodynamic relationship $\tilde{C}_p{}^{\circ} - \tilde{C}_v{}^{\circ} = R$. Its value is

$$\tilde{C}_p{}^{\circ} = \left[\frac{\gamma^{\circ}}{\gamma^{\circ} - 1}\right]R \qquad (11)$$

n-Heptane. The use of sonic methods for the determination of thermodynamic properties of polyatomic vapors like heptane faces special problems. These result from the low vapor densities that often are below the range of sensitivity of practical receiving transducers and from the dissipative effects of relaxation phenomona involving irreversible flow of acoustic energy into and out of internal molecular modes. We deal with both problems by the expedient of measuring sonic speeds in mixtures of sample vapor in an inert buffer gas. The buffer provides a strong acoustic signal and catalyzes the equilibration of internal modes by collisional activation and deactivation. In this experiment, argon is used as a buffer, but well-characterized molecular species may be used in cases where unbuffered relaxation times are particularly long. The experiment measures shifts in radial-mode resonance frequencies of pure argon caused by injecting small amounts of sample vapor. A method for obtaining the ideal gas reference state heat capacity of the sample vapor by means of linear extrapolation of functions of experimental parameters is outlined below.

Equations 4 and 6 combine to give the following relationship for the sample vapor/argon mixtures

$$c_n^2(P,T,X) = 4\pi^2 a^2\left(\frac{f_n}{\nu_{n0}}\right)^2 = \frac{\gamma^\circ(P,T,X)RT}{\bar{M}}\left[1 + \frac{A(T,X)}{\tilde{V}}\right] \qquad (12)$$

where X is the mole fraction of sample vapor in the buffered mixture, $\bar{M}$ is the average molecular weight, $\gamma^\circ(P,T,X)$ is the ratio of reference state heat capacities, and $A(T,X)$ is the acoustic virial of the mixture. For constituents of an ideal gas mixture, the partial molal heat capacities are equal to the corresponding molar heat capacities, $\tilde{C}_p{}^\circ$ and $\tilde{C}_v{}^\circ$ for the sample vapor, and to $5R/2$ and $3R/2$ for argon. With $\tilde{C}_p{}^\circ - \tilde{C}_v{}^\circ = R$ and with a reduced constant-volume heat capacity defined as $C^* = \tilde{C}_v/R$, $\gamma^\circ(P,T,X)$ becomes

$$\gamma^\circ(P,T,X) = \frac{C_p(P,T,X)}{C_v(P,T,X)} = 1 + \frac{1}{(C^* - 1.5)X + 1.5} \qquad (13)$$

The experimental value of $\gamma^\circ(P,T,X)$ could be obtained from eq 12 if the value of $A(T,X)$ were known. Instead, we consider the shift in resonance frequency produced by adding small amounts of sample vapor to the system charged initially with pure argon. Prior to the addition of any sample vapor, $X = 0$ and eq 12 becomes

$$(C_n{}^\circ)^2(P^\circ,T) = 4\pi^2 a^2\left(\frac{f_n{}^\circ}{\nu_{n0}}\right)^2 = \frac{(5/3)RT}{\bar{M}^\circ}\left[1 + \frac{A^\circ(T)}{\tilde{V}}\right] \qquad (14)$$

where $f_n{}^\circ$, $^5/_3$, $\bar{M}^\circ$, and $A^\circ(T)$ are the nth radial mode resonance frequency, heat capacity ratio, molecular mass, and acoustic virial of pure argon. Combining eq 12 and 14 and solving for $\gamma^\circ(P,T,X)$ gives

$$\gamma^\circ(P,T,X) = \frac{5}{3}\frac{\bar{M}}{\bar{M}}\left(\frac{f_n}{f_n{}^\circ}\right)^2 \frac{[1 + A^\circ(T)/\tilde{V}]}{[1 + A(T,X)/\tilde{V}]} \qquad (15)$$

Calculation of the right-hand side of this equation requires a knowledge of $A(T,X)$ which contains the acoustic virial coefficients for the mixture. Since, however, the solutions are dilute and the subsequent analysis involves extrapolation to zero sample vapor mole fraction, it is sufficient to consider the bracketted nonideality terms in the numerator and denominator of eq 15 to be equal, resulting in the simpler relationship

$$\gamma^\circ(P,T,X) = \frac{5}{3}\frac{\bar{M}}{\bar{M}^\circ}\left(\frac{f_n}{f_n{}^\circ}\right)^2 \qquad (16)$$

To the extent that his approximation is justified, a plot of $1/[\gamma^\circ(P,T,X) - 1]$ vs X should be a straight line with intercept 1.5 and slope $C^* - 1.5$. The ideal gas reference state heat capacity of the sample vapor is then $\tilde{C}_v{}^\circ = C^*R$. This procedure may be performed for each radial mode observed and the heat capacities extrapolated to zero frequency, but for n-C_7H_{16} in argon, we see no systematic change with frequency over the first six radial modes. This is taken as evidence that the catalytic action of the buffer gas is effective.

Results

Butanes. Research-grade normal butaine and isobutane was provided by the Phillips Chemical Co. Sample purities exceeded 99.9% with the principal impurity in each case being the minor isomer. Experiments are planned over the full range of operating temperatures of the resonator seals and transducers. Problems with the temperature control necessitated limiting the temperature in this study to about 350 K. The temperature range will be extended upward in future experiments after the new isothermal enclosure is installed. Measurements were made at pressures that at room temperature ranged from atmospheric down to about 0.007 MPa (50 Torr). The thermodynamic results are given in Tables I–III along with other values where available. The acoustic virials were calculated with data from the NBS compilations of thermophysical properties of the butanes, ref 28 and 29.

Table I. Ideal Gas Reference State Heat Capacities of Isobutane

	$\tilde{C}_p{}^\circ$, J mol^{-1} K^{-1}					
T, K	this work	Chen[a]	Scott[b]	Spencer[c]	Rihani[d]	Wacker[e]
298.15	96.69	96.65	96.78	101.71	97.07	96.78
323.15	102.30	103.51		108.45	104.22	103.56
348.15	107.15	110.41		115.06	111.17	110.36

[a] Statistical mechanical calculation using a combination of experimental and theoretical parameters, see ref 26. [b] Semiempirical theory, see ref 3. [c] Empirical model, see ref 27. [d] Group contribution method, see ref 1. [e] Flow calorimetric method, see ref 8.

Table II. Ideal Gas Reference State Heat Capacities of Normal Butane

	$\tilde{C}_p{}^\circ$, J mol^{-1} K^{-1}				
T, K	this work	Chen[a]	Scott[b]	Spencer[c]	Rihani[d]
298.15	98.84	98.58	97.49	99.91	100.70
323.15	105.06	104.93		107.40	107.24
348.15	114.02	113.34		113.89	113.60

[a] See footnote a of Table I. [b] See footnote b of Table I. [c] See footnote c of Table I. [d] See footnote d of Table I.

Table III. Second Acoustic Virial Coefficients of Butanes

		acoustic virial A_1, cm^3/mol	
T, K	gas	this work	Hyanes and Goodwin (*28*, *29*)
298.15	n-C_4H_{10}	-1141	-1214
323.15	n-C_4H_{10}	-997	-1014
348.15	n-C_4H_{10}	-815	-860
298.15	i-C_4H_{10}	-1132	-1131
323.15	i-C_4H_{10}	-1001	-945
348.15	i-C_4H_{10}	-916	-800

The only other experimental data available for comparison with the present results are the flow calorimetric measurements of Wacker et al. (*8*) for isobutane. Our results are in good agreement with them especially considering the fact that the aforementioned problem with temperature control makes our elevated temperature data less reliable than that near the ambient laboratory temperature (ca. 300 K).

n-Heptane. The principal reason for undertaking this research was to develop a method for obtaining reliable ideal gas heat capacities of vapors at constant volume, especially those typical of the C_7-plus fraction of petroleum. The limited data on n-heptane represent the first fruits of these labors and are offered here as indicative of the method's potential. Samples of liquid n-C_7H_{16} (Aldrich spectrophotometric grade) injected by syringe into the resonator previously filled with argon at 0.1 MPa and maintained at 298 K. The amount of substance n-heptane added was determined from the measured mass difference of the injection syringe before and after sample injection. The results are given in Table IV. Figure 5 is a plot of $1/[\gamma^\circ(P,T,X) - 1]$ vs X. From its slope, the experimental ideal gas heat capacity at constant volume is determined and is shown in Table V along with other reported values. The excellent agreement of the present result with the only other

Table IV. Resonant Frequencies in *n*-Heptane + Argon Mixture, with ρ_{argon} = 0.040 94 mol/L and T = 298.15 K

		resonant frequency, Hz					
X_{C_7}	ρ_{C_7}, mol/L	f_{10}	f_{20}	f_{40}	f_{50}	$\gamma°(T,X)$	C, m·s^{-1}
0.003 100	0.000 1273	1494.32	2569.39	4678.10	5727.48	1.6439	318.596
0.006 153	0.000 2535	1481.33	2547.17	4637.40	5677.63	1.6228	315.828
0.009 085	0.000 3753	1469.44	2526.68	4600.17	5632.02	1.6038	313.291
0.015 563	0.000 6472	1444.95	2484.55	4523.40	5537.80	1.5657	308.060
0.024 900	0.001 0454	1413.36	2430.12	4424.10	5417.31	1.5185	301.323
0.031 228	0.001 3200	1394.00	2396.80	4364.13	5343.10	1.4909	297.204

Table V. Ideal Gas Reference State Heat Capacity of Normal Heptane at 298.15 K

C, (J/mol)/K	method	% dev[a]	ref
139.38	thermal accommodation coeff correlation	−15.20	Beeck (*30*)
155.56	statistical	−5.38	Pitzer (*4*)
175.39	empirical correlation	+6.68	Spencer and Flannagan (*27*)
170.53	empirical correlation	+3.73	Spencer (*31*)
147.21	Einstein function correlation	−10.50	Stull et al. (*32*)
163.79	flow calorimetry[b]	−0.04	Waddington (*10*)
165.98	statistical	+0.96	Person and Pimentel (*5*)
170.40	vapor-pressure correlation	+3.65	Barrow (*33*)
173.70	group additive correlation	+5.41	Rihani and Doraiswamy (*1*)
166.06	group additive correlation	+1.02	Benzon et al. (*2*)
165.92	group additive correlation	+0.92	Thinh et al. (*34*)
165.18	group additive correlation	+0.47	Scott (*3*)
164.40	spherical acoustic resonator[b]		this work

[a] Percent deviation from present result. [b] Experimental measurement.

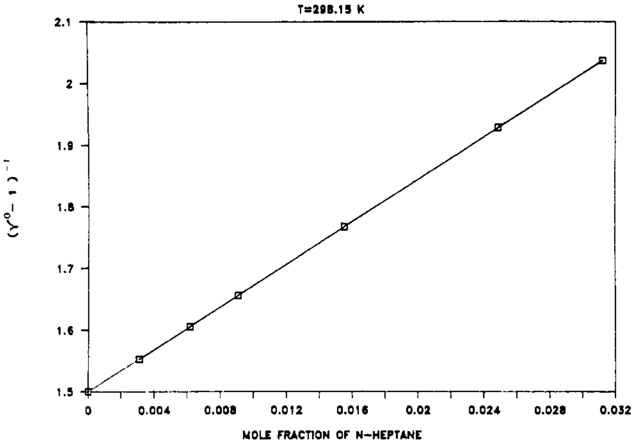

Figure 5. Variation of $1/[\gamma°(P,T,X) - 1]$ with mole fraction of *n*-heptane in argon. The squares mark actual data points, and the line is the linear regression best fit.

reported experimental measurement (Waddington) and the good agreement with the result of the most advanced group additive correlation (Scott) points to the adequacy of the present resonance method for determining ideal gas reference state heat capacities of volatile liquids.

The precision of pressure, temperature, and speed of sound measurements in the present technique are +10 Pa, ±0.001 K, and ±0.01 ms^{-1}, respectively. The standards for the measurements were traceable to the National Institute of Science and Technology (NIST, formerly NBS), USA. The uncertainty in the frequency measurement of the counter was ±0.01 Hz. The amount of substance of *n*-heptane added was determined from the measured difference of the injection syringe before and after sample injection. The resultant composition was considered known to within ±0.03 mol % of *n*-heptane.

Conclusions

Spherical acoustic resonators can be used to obtain ideal gas reference state heat capacities of gases and vapors. For systems with vapor pressures higher than about 0.007 MPa, the second acoustic virial coefficient may also be determined. When the procedure is applied to a system over a reasonably wide temperature range, the ordinary second virial coefficient may be extracted from the variation of $A(T)$, and doing this will be a goal of future experiments.

Acknowledgment

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Registry No. *n*-Butane, 106-97-8; isobutane, 75-28-5; argon, 7440-37-1; *n*-heptane, 142-82-5.

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