

# Vapor Phase Helmholtz Equation for HFC–227ea from Speed of Sound Measurements <sup>1</sup>

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## ABSTRACT

The work presents measurements of speed of sound in the vapor phase of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea). The measurements were obtained in a stainless-steel spherical resonator of  $\sim 900 \text{ cm}^3$  at temperatures between 260 K and 380 K and at pressures up to 500 kPa. Ideal-gas heat capacities and acoustic virial coefficients are directly produced from the data. A Helmholtz equation of state  $a^R(\tau, \delta)$  of high accuracy is proposed, whose parameters are directly obtained from speed of sound data fitting. From the ideal-gas heat capacity equation formerly developed the Helmholtz equation  $a(\tau, \delta)$  for the vapor phase is finally produced. From this equation of state, representing the  $P\rho T$  vapor surface, any other thermodynamic state function can be derived. Due to the high accuracy of the equation only very precise experimental data are suitable for the model validation and only density measurements have these requirements. A very high accuracy is reached in density prediction, showing the obtained Helmholtz equation to be very reliable. The deduced vapor densities are furthermore compared with those obtained from acoustic virial coefficients having the temperature dependencies calculated from hard-core square-well potentials.

KEY WORDS: Acoustic virial coefficient, Helmholtz energy equation of state, Ideal gas heat capacity, Speed of sound, Vapor density, 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea).

## **1 INTRODUCTION**

As a consequence of the high accuracy level of experimental techniques reached in the last few years in speed of sound measurements, there is a renewed interest in using acoustic data to obtain thermodynamic equations to enable the calculation of any other thermodynamic properties. This work presents new speed of sound measurements obtained in the vapor phase of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) and a simple and original method for converting these data into a Helmholtz energy  $a^R$  equation. Contrarily to the conventional methods adopted to reduce these kind of measurements, the coefficients of the proposed equation have been fitted directly on speed of sound data, avoiding the use of either potential models or complex integration procedure generally utilized in the conventional methods. The proposed equation has been validated on vapor phase density data and the high accuracy reached shows that this kind of procedure is capable of yielding reliable results well beyond the range of temperature and pressure in which the equation has been fitted.

## **2 APPARATUS, MATERIALS AND PROCEDURES**

The experimental apparatus consisted of a spherical resonator, placed in a temperature controlled stirred fluid bath. A detailed description of the apparatus and the resonator has been given in a previous publication [1]. Temperatures were measured on ITS-90 using two capsule type platinum resistance thermometers embedded in cylindrical extensions of the resonator's poles. Pressures were measured with an estimated accuracy of 100 Pa using a capacitive absolute transducer calibrated against standard pressure balances in the range 0-500 kPa. The HFC-227ea sample was supplied by Solvay Fluor (D) with a stated minimum purity of 99.99 moles per cent. Before use it was degassed

by vacuum sublimation. No analysis or further purification was attempted. Each isotherm included measurements of the speed of sound at several pressures. At each state point the speed of sound was deduced from the measured resonance frequencies and calculated half-widths of the lowest three or four purely radial modes of the cavity. Experimental frequencies were corrected according to the model developed by Moldover [2] to account for thermal boundary layer losses, effects of coupling with shell motion and the presence of the gas-inlet port. For the present measurements, the thermal boundary layer correction is the most important. This was calculated using thermal conductivity data measured by Liu [3]. All the remaining corrections were very small and they were included for the sake of completeness. The thermodynamic and transport properties of HFC-227ea required for these corrections were obtained from the REFPROP database [4]. The speeds of sound determined from the individual modes were averaged together, then weighted by the statistical variance between the resonance fits and the data. The resonance frequency measurements for HFC-227ea were taken along eight isotherms between 270 and 370 K and spanned pressures ranging from 12 to 500 kPa. Below 330 K the maximum pressure was 0.7 times the vapor pressure to avoid pre-condensation effects. The speed of sound values were obtained from the corrected resonance frequencies, together with the value of the resonator's radius determined from a calibration with argon. In Table I we list mean values of the speed of sound for each of the 78 states investigated, together with fractional standard deviations and the number of resonant modes from which they were determined.

### **3. EXPERIMENTAL RESULTS**

The speed of sound results have been analysed in terms of the series expansion:

$$u^2(p,T) = (RT\gamma^o/M) \left[ 1 + (\beta_a/RT)p + (\gamma_a/RT)p^2 + (\delta_a/RT)p^3 + \dots \right] \quad (1)$$

where  $\beta_a$ ,  $\gamma_a$  and  $\delta_a$  are the second, third and fourth acoustic virial coefficients, which are functions of temperature alone. In this equation,  $R = 8.314471 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  is the universal gas constant [5], and  $\gamma^o = c_p^o/c_v^o$  is the ratio of the isobaric to the isochoric ideal-gas heat capacity. Equation (1) was fitted to acoustic data on each isotherm by adjusting the first three or four acoustic virial coefficients (up to  $\gamma_a$  or  $\delta_a$ ), depending on the statistical significance of the fit. Table II shows the results of these isotherm fits. The heat capacity values in Table II can be represented by:

$$c_p^o/R = 8.7303 - 1.250 \times 10^{-3} (T/\text{K}) + 1.547 \times 10^{-4} (T/\text{K})^2 - 2.19 \times 10^{-7} (T/\text{K})^3 \quad (2)$$

with a standard deviation  $\delta = 0.016 \cdot R$ . The ideal-gas heat capacity  $c_p^o$  is shown in Fig. 1a and as deviations from eq. (2), calculated as  $\Delta c_p^o/c_p^o = (c_{p \text{ exp}}^o - c_{p \text{ calc}}^o)/c_{p \text{ calc}}^o$ , in Fig. 1b. To our knowledge there is only one previous determination of  $c_p^o$  for HFC-227ea [6]. The deviation from our results, which are shown in the same Fig. 1b lie between  $0.025 \cdot R$  and  $-0.25 \cdot R$  in the overlapping temperature range and diverge further at higher temperatures. All the isotherms were then combined together to define a surface  $u(p,T)$ , whose deviations from a fitted correlation were a measure of the internal consistency between the isotherms. The correlation yielded estimates of the first three density virial coefficients,  $B$ ,  $C$  and  $D$ , from the analysis of the acoustic data and suitable parameterized expressions for the acoustic virial coefficients defined by a hard-core square-well (HCSW) approximation of the intermolecular potential [7]. Figure 2 displays measurements and the “square-well” fit to the second acoustic virial coefficient  $\beta_a$  as a function of temperature. The surface  $u(p,T)$  was fitted with 8

adjustable parameters, while eq. (2) was used to represent the experimental  $\gamma^o(T)$  values required to calculate the temperature dependence of the acoustic virial coefficients. The regression led to the parameters:  $b_{0B} = 184.527 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $\varepsilon/k_B = 499.55 \text{ K}$ ,  $r_B = 1.318$ ,  $b_{0C} = 383.717 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $\varepsilon/k_C = 780.09 \text{ K}$ ,  $r_C = 1.070$ ,  $b_{0D} = 264.17 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $\varepsilon/k_D = 175.704 \text{ K}$  with  $r_D = 2$ . Here,  $b_{0i}$ ,  $\varepsilon/k_i$  and  $r_i$  are the co-volume, the scaled well depth and the ratio of the width of the well to that of the hard core for the second  $B$ , third  $C$  and fourth  $D$  virial coefficient respectively. Figure 3 displays a comparison of estimated temperature dependence  $B(T)$  from this work with that obtained from  $p$ - $\rho$ - $T$  measurements [8-10].

#### 4. GAS DENSITY DETERMINATION FROM SPEED OF SOUND

##### 4.1 Reduction procedure

The problem of deriving accurate and easy procedures to yield thermodynamic models from speed of sound data has become very expected in these last years as consistent and precise amount of experimental speed of sound data have been obtained, in particular for the new refrigerant fluid generation. Referring to the gas phase, the conventional method estimates the gas density from a virial-type equation of state in which the temperature dependencies of the first three density virial coefficients are calculated using the HCSW potentials model [11,12]. Among the presently available reduction methods, an original procedure has been recently proposed [13] consisting in the solution of the analytical relations between the density and the speed of sound and using a numerical integration procedure based on the predictor-corrector method. This method does not assume a specific type form of equation of state, but it requires initial conditions usually referred to a particular isotherm close to the critical temperature.

In this work, a new and original approach of reducing speed of sound data is presented. The proposed procedure differs from the previous ones in these fundamentals. At first a Helmholtz energy type equation is assumed instead of the conventional virial equation. The structure of the selected equation comes from the optimization method proposed by Wagner and coworkers [14,15], through which all the modern high precision dedicated EoS are nowadays obtained. This optimization procedure allows to select from a so-called bank of  $F_i(T, \rho)$  terms the combination which yields the smallest weighted least squares deviation after fitting the proposed terms to the experimental  $(P, \rho, T)$  values. The final form obtained consists of an eight terms Helmholtz equation which conforms to the best result that can be yielded with the cited optimization method. Then, the parameters of the optimised equation are fitted directly on speed of sound data following a standard non linear fitting procedure. The values of the coefficients are estimated minimising the weighted sum of squares of the calculated speed of sound data and the measured ones. In this way, contrary to the cited integration procedure, no initial conditions have to be specified and complex numerical computation methods can be avoided.

The Helmholtz energy equation assumed is expressed in the following dimensionless form:

$$\phi(\tau, \delta) = \frac{A_m}{RT} = \phi^o(\tau, \delta) + \phi^R(\tau, \delta) \quad (6)$$

where  $A_m$  is the molar free energy,  $R$  the universal gas constant,  $\tau = T_c / T$  the inverse reduced temperature and  $\delta = \rho / \rho_c$  the reduced density.  $T_c = 375.95\text{K}$  and  $\rho_c = 580.0 \text{ kg/m}^3$  are the critical parameters of HFC-227ea [16]. The dimensionless form  $\phi$  of eq.

(6) is split into an ideal part  $\phi^o$ , which approximates the ideal behaviour of the fluid, and a residual part  $\phi^R$  which takes into account the real behaviour of the fluid.

From the ideal gas heat capacity  $c_p^o$ , eq. (5), the dimensionless ideal part  $\phi^o$  can be expressed as:

$$\phi^o = \frac{A^o}{RT} = \frac{I}{RT} \left\{ \int_{T_0}^T c_p^o dT + h_0^o - RT - T \int_{T_0}^T \frac{c_p^o - R}{T} dT - RT [\ln(\rho/\rho_0)] - T s_0^o \right\} \quad (6a)$$

where  $h_0^o$  and  $s_0^o$  are the enthalpy and the entropy values of the ideal gas in a reference state. From the molar free energy equation expressed by eq. (6), the speed of sound  $u$  is deduced from the following relation:

$$\frac{u^2(\tau, \delta)}{RT} = I + 2\delta\phi_{\delta}^R + \delta^2\phi_{\delta\delta}^R + \frac{(I + \delta\phi_{\delta}^R - \delta\tau\phi_{\delta\tau}^R)^2}{c_v / R} \quad (7)$$

where  $\phi_{\delta}^R$  and  $\phi_{\delta\delta}^R$  are the first and second derivatives of the residual part  $\phi^R$  with respect to  $\delta$ , while  $\phi_{\delta\tau}^R$  is the cross-derivative of the residual part  $\phi^R$  with respect to  $\delta$  and  $\tau$ .  $c_v$  is the isochoric heat capacity, which is related to the fundamental eq. (6) by the relation:

$$\frac{c_v(\tau, \delta)}{R} = -\tau^2 (\phi_{\tau\tau}^o + \phi_{\tau\tau}^R) \quad (8)$$

where  $\phi_{\tau\tau}^o$  and  $\phi_{\tau\tau}^R$  are the second derivatives, with respect to  $\tau$ , of the ideal part  $\phi^o$  and of the residual part  $\phi^R$ , respectively.

In this work, the  $c_p^o$  function is obtained from the same speed of sound measurements, as shown in the preceding, and enables the derivative  $\phi_{\tau\tau}^o$ , required to calculate the  $c_v$  value, eq. (8), to be determined directly from the known ideal gas relation:

$$c_p^o - c_v^o = R \quad (9)$$

All the derivatives are easily calculated from the following assumed form of the residual part  $\phi^R$ :

$$\phi^R(\tau, \delta) = \sum_{i=1}^8 a_i \tau^{t_i} \delta^{d_i} \quad (10)$$

The main difference of the assumed equation form with respect to a classical virial equation is the independence of the coefficients  $a_i$ ,  $t_i$  and  $d_i$  from temperature; besides, these coefficients are directly obtained fitting the speed of sound data without considering any potential energy model. The proposed procedure does not require the solution of a strict algorithm, avoiding the specific initial conditions proposed by Trusler [17]. Using a classical non linear regression procedure, the coefficients for the residual part  $\phi^R$  are reported in Table III.

#### 4.2. Model validation

The obtained Helmholtz free energy equation has been validated on vapour phase density comparing the calculated values with the available experimental density data [18]. The results are expressed in terms of AAD % as shown in Figs. 4 to 7. The available density data cover the ranges  $0.81 \leq T_r \leq 1.0$  and  $0.033 \leq P_r \leq 0.74$ , which differ significantly from the speed of sound measurements range, i.e.  $0.72 \leq T_r \leq 0.98$  and  $0.004 \leq P_r \leq 0.167$ , on which the parameters have been fitted.

The accuracy of the proposed model in density prediction reaches an AAD % value of 0.00426, while the corresponding value of the HCSW model is 0.00428. The selected pressure range, out of the fitting range, in which the density data have been assumed was  $0.226 \leq P_r \leq 0.542$ . In this range the AAD % of the present model is 0.148 and that

of the HCSW model is 0.182. A number of 65 points were inside the fitting range and 55 were out.

## 5. CONCLUSIONS

In this work new speed of sound measurements were performed for 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) in the vapor phase. The measurements span the temperature ranges from 270 to 370 K and pressures up to 500 kPa. Ideal-gas heat capacities and acoustic virial coefficients are deduced directly from the results.

A new procedure is proposed which determines the coefficients of an optimized Helmholtz energy equation form directly fitting the experimental speed of sound values. This method compares favourably with the other conventional methods and allows to obtain a high accurate equation specific for the vapour phase. The density values calculated from this equation are compared with existing experimental data in similar  $T_r$  and  $P_r$  ranges and also outside the fitting ranges. Inside the fitting range the error deviation is within  $\pm 0.015$  %, while outside it reaches  $\pm 0.7$  %. Due to the low pressure range considered, the proposed structure of the equation is likely to fit directly speed of sound data in similar pressure ranges with similar precision for all the fluids belonging to the HCFC and HFC families. This leads to the conclusion that the obtained Helmholtz equation can represent a valid alternative to other approaches based on the use of classical virial and potential energy model equations.

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Table I - Mean speed of sound values  $\langle u \rangle$  determined from  $N$  radial modes with fractional standard deviations  $\delta = 10^5 \left[ \frac{\langle u_{\text{exp}} \rangle - u_{\text{fit}}}{u_{\text{fit}}} \right]$  from eq. (1) at temperatures  $T$  and pressures  $p$  in HFC-227ea .

$T$ (K)	$p$ (kPa)	$\langle u \rangle$ (m/s)	$N$	$10^5 \cdot \delta$	$T$ (K)	$p$ (kPa)	$\langle u \rangle$ (m/s)	$N$	$10^5 \cdot \delta$
270.022	118.8	114.0606	4	3.3	280.022	174.2	114.5341	4	-8.6
	107.6	114.5427	4	-0.9		157.7	115.1879	4	-4.2
	96.14	115.0289	4	0.7		140.5	115.8699	4	0.1
	84.12	115.5300	4	2.1		122.7	116.5416	4	2.0
	72.13	116.0214	4	3.8		105.1	117.2028	4	1.7
	60.09	116.5073	4	5.4		87.19	117.8689	3	0.7
	48.08	116.9860	4	5.4		69.85	118.4977	3	0.9
	36.06	117.4602	4	3.9		52.31	119.1221	3	1.5
	23.96	117.9312	4	1.7		34.88	119.7346	3	0.1
12.03	118.3890	4	-0.3	17.58	120.3333	3	-1.9		
290.047	249.1	114.5902	4	-10.1	299.928	349.1	114.0709	4	-3.3
	225.4	115.4722	4	-4.9		315.5	115.2566	4	-0.1
	200.3	116.3819	4	-0.9		280.5	116.4607	4	1.6
	175.3	117.2686	4	2.5		245.5	117.6269	4	2.6
	150.3	118.1362	4	4.5		210.4	118.7624	4	3.4
	125.2	118.9878	4	4.5		175.4	119.8622	4	5.2
	98.65	119.8735	3	2.2		140.3	120.9363	4	5.5
	74.76	120.6505	3	1.2		105.2	121.9858	4	3.2
	49.81	121.4446	3	1.7		69.83	123.0182	3	1.9
25.02	122.2205	3	0.3	35.00	124.0092	3	2.2		
309.967	449.5	114.0298	4	5.5	329.948	500.2	119.2327	4	-2.2
	400.7	115.6454	4	2.8		450.6	120.5186	4	-5.3
	350.6	117.2359	4	3.1		400.5	121.7799	4	-6.2
	300.5	118.7679	4	3.0		350.5	123.0091	4	-6.0
	250.5	120.2462	4	2.8		300.3	124.2087	4	-5.6
	200.4	121.6744	4	3.1		249.5	125.3980	4	-5.7
	150.3	123.0559	4	4.1		198.7	126.5563	4	-4.5
	100.2	124.4024	4	1.6		149.7	127.6487	4	-2.5
	49.9	125.7113	3	2.3		100.1	128.7329	4	-2.9
				49.9	129.8064	3	-0.5		
349.951	458.8	126.0383	4	-3.8	369.993	497.3	130.5475	4	9.7
	399.8	127.2190	4	-3.8		449.6	131.3376	4	5.2
	349.5	128.2068	4	-3.2		400.3	132.1396	4	4.9
	299.5	129.1707	4	-2.0		350.3	132.9494	4	0.8
	249.3	130.1283	4	-4.9		298.8	133.7663	4	1.6
	199.0	131.0663	4	-3.7		249.3	134.5422	4	1.9
	150.2	131.9634	4	-2.4		198.9	135.3249	4	2.1
	100.1	132.8719	4	-3.1		149.7	136.0811	4	1.4
	49.88	133.7691	3	-2.7		99.64	136.8424	2	0.1
				49.84	137.5926	2	-2.0		

Table II - Perfect-gas heat capacities, second and third acoustic virial coefficients of HFC-227ea determined from isotherm fits. Uncertainties are one standard deviation.

$T$ (K)	$c_p^o/R$	$\beta_a$ (cm <sup>3</sup> /mol)	$\gamma_a$ (cm <sup>3</sup> /mol·kPa)
270.022	15.350 ± 0.007	-1415.9 ± 2.4	-0.614 ± 0.020
280.022	15.704 ± 0.005	-1292.6 ± 1.2	-0.476 ± 0.006
290.047	16.030 ± 0.008	-1191.8 ± 2.4	-0.298 ± 0.020
299.928	16.339 ± 0.010	-1102.5 ± 2.0	-0.190 ± 0.010
309.967	16.671 ± 0.013	-1018.9 ± 2.2	-0.137 ± 0.010
329.948	17.300 ± 0.007	-873.1 ± 1.1	-0.086 ± 0.004
349.951	17.820 ± 0.007	-752.6 ± 0.6	-0.070 ± 0.001
369.993	18.337 ± 0.012	-656.1 ± 1.0	-0.041 ± 0.002

Table III - Coefficients for the residual part  $\phi^r$  regressed from speed of sound data.

$n$	$a_n$	$t_n$	$d_n$
1	6.582354133·10 <sup>-1</sup>	-0.5	2.0
2	5.650210429·10 <sup>-2</sup>	0.0	1.0
3	-3.45848603·10 <sup>-1</sup>	0.0	3.0
4	8.934278078·10 <sup>-4</sup>	0.0	6.0
5	1.561128939·10 <sup>-3</sup>	1.5	6.0
6	8.380824041·10 <sup>-1</sup>	1.5	1.0
7	-2.20543052·10 <sup>+0</sup>	2.0	1.0
8	-7.81026567·10 <sup>-2</sup>	2.0	2.0

## Figure captions

Fig 1a. Measured ideal-gas heat capacities of HFC-227ea as a function of  $T$ .

Fig 1b. Deviations of  $c_p^o$  from eq. (2), calculated as  $\Delta c_p^o / c_p^o = (c_{p_{\text{exp}}}^o - c_{p_{\text{calc}}}^o) / c_{p_{\text{calc}}}^o$ .

Measured values from Ref. [6] are also shown.

Fig.2. Measurements and “square-well” fit to the second acoustic virial coefficient  $\beta_a$  as a function of temperature.

Fig.3. Deviations of the measurements of the second density virial coefficient  $B$  of Ref. [8-10] from the model square well potential fitted with the parameters:  $b_{0B} = 184.527 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $\varepsilon/k_B = 499.55 \text{ K}$ ,  $r_B = 1.318$ . The zero line refers to the present work.

Fig. 4. Density validation of the Helmholtz free energy equation (6) as function of pressure and inside the fitting range.

Fig. 5. Density validation of the Helmholtz free energy equation (6) as function of temperature and inside the fitting range.

Fig. 6. Density validation of the Helmholtz free energy equation (6) as function of pressure and outside the fitting range.

Fig. 7. Density validation of the Helmholtz free energy equation (6) as function of temperature and outside the fitting range.















