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Thermodynamic Properties of Carbon Dioxide Derived from the Speed of Sound

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Thermodynamic properties of CO_2 are derived from speed of sound in the temperature range 300 to 360 K (from 0 to 6 MPa), and 300 to 220 K (from 0 to 90% of the saturation pressure). The density, the specific heat capacity at constant pressure, and the specific heat capacity at constant volume are obtained by numerical integration of differential equations connecting the speed of sound with other thermodynamic properties. The set of differential equations is solved as the initial value problem, with the initial values specified along the isotherm at 300 K in terms of several accurate values of the density and the specific heat capacity at constant pressure. The density, the specific heat capacity at constant pressure and the specific heat capacity at constant volume are derived with the absolute average deviations of 0.018%, 0.19%, and 0.18%, respectively. The results of numerical integration are extrapolated to the saturation line for ρ, c_p, and c_v with the absolute average deviations of 0.056%, 2.31%, and 1.32%, respectively.

Keywords: Carbon dioxide, Density, Heat capacity, Speed of sound

INTRODUCTION

In this paper an attempt is made to derive accurate thermal and caloric properties of carbon dioxide from its speed of sound, on account of minimum experimental information. For that purpose, the set of differential equations connecting the speed of sound with other thermodynamic properties is solved as the initial value problem, with initial values (a few accurate data points of ρ and c_p) specified at a single temperature. The domain of integration is divided into a small number of isotherms and isobars in order to decrease requirements for sound-speed information also to minimum. This approach is consistent with an experimental practice in which measurements are usually performed at relatively small number of carefully selected *T-p* points.

The speed of sound is related to other thermodynamic properties (*e.g.*, ρ, c_p, c_v) through a set of partial differential equations. If gaseous phase is considered, this set of partial differential equations may be solved as a set of ordinary differential equations, but all the pressure derivatives must be estimated independently. There are many efficient and reliable methods for numerical solution of ordinary differential equations. However, accuracy of the solution depends on accuracy of the pressure derivatives as well, and this sensitivity is general for any thermodynamic function of this type. In the vicinity of the saturation line and especially the critical point, the pressure derivatives of the heat capacity at constant pressure and the thermal expansion coefficient may not be estimated accurately enough from an interpolation polynomial or from finite differences. Namely, it is well known that an interpolation polynomial estimates derivatives poorly in terminal points of an interval, especially if a function

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being differentiated shows high degree of nonlinearity.

A method of finite differences is probably the worst choice because function values at finite differences are usually obtained also from an interpolation polynomial. Therefore, this approach is as accurate as an interpolation polynomial used for evaluation of function values between the experimental points. If highly nonlinear functions are considered, a polynomial interpolation may not be the method of choice. In such cases a rational function approximation may represent a better solution. Generally speaking, an interpolation is the method of choice when plenty of experimental data points are available, but if it is not the case an approximation may give better results.

An accurate calculation of thermodynamic properties of carbon dioxide is more difficult than for many other technically interesting substances, because many technical processes take place around its critical point. The temperature and pressure ranges considered in this paper cover virtually the whole subcritical vapor phase from the ideal gas limit to the saturation line and from the triple point to above the critical point.

THEORY

The density and the specific heat capacity at constant pressure of a fluid at supercritical temperatures may be derived from its speed of sound if the following set of equations is solved [1]:

$$u^{-2} = \left(\frac{\partial \rho}{\partial p}\right)_T - \frac{T\alpha_p^2}{c_p} \tag{1}$$

$$\left(\frac{\partial \rho}{\partial T}\right)_p = -\rho\alpha_p \tag{2}$$

$$\left(\frac{\partial \alpha_p}{\partial T}\right)_p = -\alpha_p^2 - \frac{\rho}{T}\left(\frac{\partial c_p}{\partial p}\right)_T \tag{3}$$

where T is the temperature, p is the pressure, u is the speed of sound, ρ is the density, c_p is the specific heat capacity at constant pressure, and α_p is the thermal expansion coefficient. The set of partial differential Eqs. (1) to (3) may be solved simultaneously by numerical procedure in the range of T and p in which accurate speed of sound values are available. This set of equations may be solved as the initial value problem for the set of ordinary differential equations if all the pressure derivatives are estimated independently, without changing the nature of differentiation by mathematical or numerical way. The procedure of integration is stable if the initial values are specified at the lowest temperature of the range [2].

At subcritical temperatures, however, it is more convenient to use p/p_s (where p_s is the saturation pressure) as the second independent variable, than p itself [3]. In that way, it is possible to cover the whole temperature range from the critical point to the triple point, and the pressure range from the ideal gas limit to the saturation line. Now, recalling that [4]:

$$\left(\frac{\partial z}{\partial x}\right)_m = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_m \tag{4}$$

Eqs. (2) and (3) become:

$$\left(\frac{\partial \rho}{\partial T}\right)_{\frac{p}{p_s}} = \left(\frac{\partial \rho}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_{\frac{p}{p_s}} - \rho\alpha_p \tag{5}$$

$$\left(\frac{\partial \alpha_p}{\partial T}\right)_{\frac{p}{p_s}} = \left(\frac{\partial \alpha_p}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_{\frac{p}{p_s}} - \alpha_p^2 - \frac{\rho}{T}\left(\frac{\partial c_p}{\partial p}\right)_T \tag{6}$$

The procedure of solving the set of Eqs. (1), (5), and (6) is virtually the same as the one for the set of Eqs. (1) to (3), with the only difference that the negative step of integration is used. Therefore, the same set of initial values may be used for supercritical and subcritical temperature ranges.

Having calculated ρ and c_p in the temperature and pressure range of interest, the specific heat capacity at constant volume may be obtained from the equation:

$$c_v = c_p u^{-2}\left(\frac{\partial \rho}{\partial p}\right)_T^{-1} \tag{7}$$

When a gas (or vapor) phase is considered, it is convenient to choose the zero pressure as the lower limit of the pressure range. At this pressure an ideal gas density has value of zero, and the isobaric heat capacity may be obtained directly from the speed of sound [5].

RESULTS AND DISCUSSION

Supercritical Gas Phase

The initial values of ρ and c_p were specified at the isotherm of 300 K, in the pressure range 0.0 to 6.0 MPa, and the integration was performed up to 360 K. The temperature range was divided into seven isotherms (*i.e.*, 300, 310, 320, 330, 340, 350, and 360 K), while the pressure range was divided into seven isobars (*i.e.*, 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 MPa). The initial values, the reference values, as well as the sound-speed values were obtained from the fundamental equation of state for CO_2 [6]. The sound-speed values between the isotherms were estimated from a Lagrangian interpolation polynomial of the sixth-degree with respect to temperature. The pressure derivatives of ρ and c_p were estimated analytically from Eqs. (8) and (9), respectively.

$$\rho = \frac{a + bp + cp^2}{1 + dp + ep^2 + fp^3} \tag{8}$$

$$\ln c_p = \frac{a + bp + cp^2}{1 + dp + ep^2 + fp^3} \tag{9}$$

In Eqs. (8) and (9), parameters *a*, *b*, *c*, *d*, *e*, and *f* were obtained by solving a linear least-squares problem with iterative refinement of Björck [7]. The numerical integration of Eqs. (2) and (3), with respect to temperature, was performed by implicit multistep Adams-Moulton method with adaptive step size [8]. The method is very efficient, and it took only 86 steps to reach the upper limit of the temperature range.

One example of a multistep formula is known by the name of Adams-Bashforth, as:

$$X(t+h) = X(t) + \frac{h}{24}\left[55F(X(t)) - 59F(X(t-h)) + 37F(X(t-2h)) - 9F(X(t-3h))\right] \tag{10}$$

If the solution X has been computed at the four points t, $t - h$, $t - 2h$, and $t - 3h$, then Eq. (10) can be used to compute $X(t + h)$. If this is done systematically, the only one evaluation of F is required for each step. This represents a considerable saving over the fourth-order Runge-Kutta procedure; the latter requires four evaluations of F per step.

In practice, Eq. (10) is never used by itself. Instead, it is used as a predictor and then another formula is used as a corrector. The corrector usually employed with Eq. (10) is the Adams-Moulton formula:

$$X(t+h) = X(t) + \frac{h}{24}\left[9F(X^*(t+h)) + 19F(X(t)) - 5F(X(t-h)) + F(X(t-2h))\right] \tag{11}$$

Here, $X^*(t + h)$ is the predicted value of $X(t + h)$ computed from Eq. (10). Thus, Eq. (10) predicts a tentative value of $X(t + h)$, and Eq. (11) computes X value more accurately. The combination of the two formulas results in a predictor-corrector scheme.

With initial values of X specified at a, three steps of a Runge-Kutta method can be performed to determine enough X values so that the Adams-Bashforth-Moulton procedure can begin. The fourth-order Adams-Bashforth and Adams-Moulton predictor and corrector formulas of the same order are used so that only one application of the corrector formula is needed.

An error analysis can be conducted after each step of the Adams-Moulton method. If $x_i^{(p)}$ is the numerical approximation of the ith equation in the system at $t + h$ obtained by predictor Eq. (10) and x_i is that from corrector Eq. (11) at $t + h$, then it can be shown that the single-step error for the ith component at $t + h$ is given approximately by:

$$\varepsilon_i = \frac{19}{270}\frac{\left|x_i - x_i^{(p)}\right|}{\left|x_i\right|} \tag{12}$$

Since an estimate of the error is available from the Adams-Moulton method, it is natural to use an adaptive procedure, that is, one that changes the step size. If the error analysis determines that halving of the step size is necessary on the first step of the Adams-Moulton formula after the Runge-Kutta method has been used to calculate the initial values, then the step size is halved. A retreat is made to the starting value (four steps), and new initial values are obtained with the new step sizes. This process is repeated until the error analysis allows at least one forward step by the Adams-Moulton formula. If the error analysis indicates that halving is required at some point within the interval [*a*,*b*], then the step size is halved. A retreat must be made to an appropriate previous value so that when the values needed by the Adams-Moulton formulas are calculated from the Runge-Kutta method with the new step size, the point at which the error was too large is computed by the Adams-Moulton formula and not the Runge-Kutta formula. Doubling the step size is handled in an analogous manner.

Relative deviations of ρ, c_p, and c_v, with respect to corresponding reference values, are given in Figs. 1, 2, and 3, respectively. The average absolute deviation of density is 0.005%, and the maximum relative deviation is +0.014%/-0.025%. The average absolute deviation of c_p is 0.15%, and the maximum relative deviation is +0.69%/-0.59%. The average absolute deviation of c_v is 0.16%, and the maximum relative deviation is +0.76%/-0.83%.

When the initial values of ρ were changed by +0.1%/-0.1%, the average absolute deviation of ρ, c_p, and c_v increased to 0.074%/0.079%, 0.21%/0.21%, and 0.24%/0.27%, respectively. When the initial values of c_p were changed by+0.1%/-0.1%, the average absolute deviation of ρ, c_p, and c_v increased to 0.010%/0.009%, 0.24%/0.31%, and 0.25%/0.33%, respectively. When the values of *u* were changed by +0.1%/-0.1%, the average absolute deviation of ρ, c_p, and c_v increased to 0.017%/0.015%, 0.36%/0.27%, and 0.43%/0.33%, respectively.

Subcritical Vapor Phase

The numerical integration of Eqs. (5) and (6) was performed in the temperature range 300 to 220 K, and the saturation pressure fraction (p/p_s) range 0.0 to 0.9. The initial values of ρ and c_p were also specified at the isotherm of 300 K. The temperature range was divided into seven isotherms (*i.e.*, 300, 290, 280, 260, 240, 230, and 220 K), while the saturation pressure fraction range was divided into seven values (*i.e.*, 0.00, 0.15, 0.30, 0.45, 0.60, 0.75, and 0.90). The initial values, the reference values, as well as the sound-speed values were also obtained from the fundamental equation of state for CO_2 [6].

The sound-speed values between the isotherms were also obtained from a Lagrangian interpolation polynomial of the

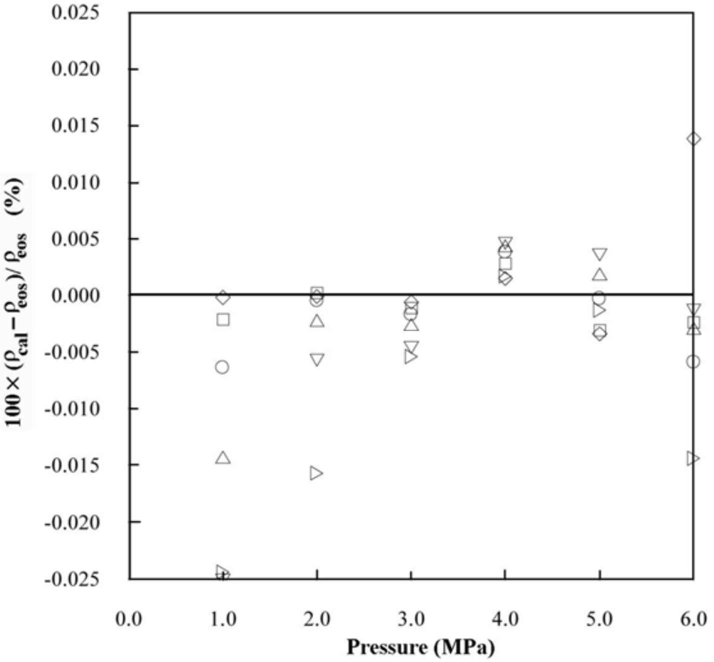

Fig. 1. Relative deviation of ρ *vs*. *p* at various temperatures, with respect to reference values [6]: (◇) 310 K, (□) 320 K, (○) 330 K, (△) 340 K, (▽) 350 K and (▷) 360 K.

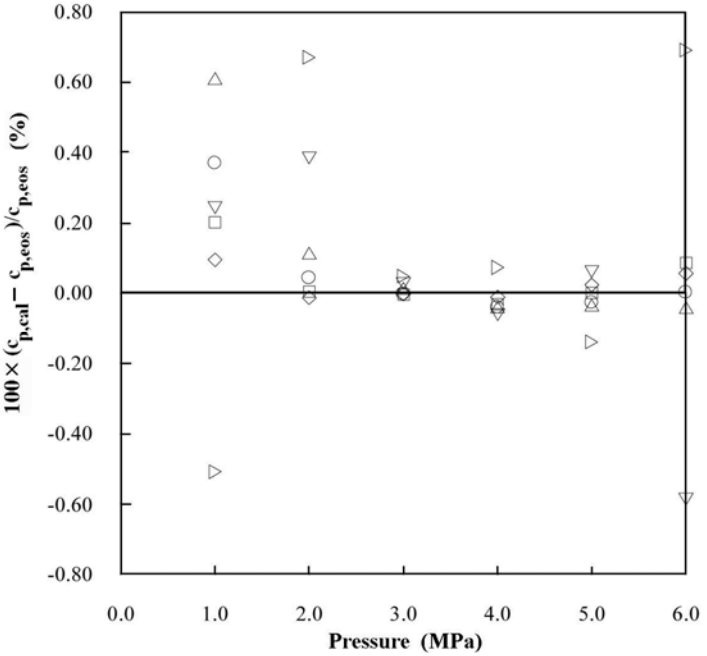

Fig. 2. Relative deviation of c_p *vs*. p at various temperatures, with respect to reference values [6]: (◇) 310 K, (□) 320 K, (○) 330 K, (△) 340 K, (▽) 350 K and (▷) 360 K.

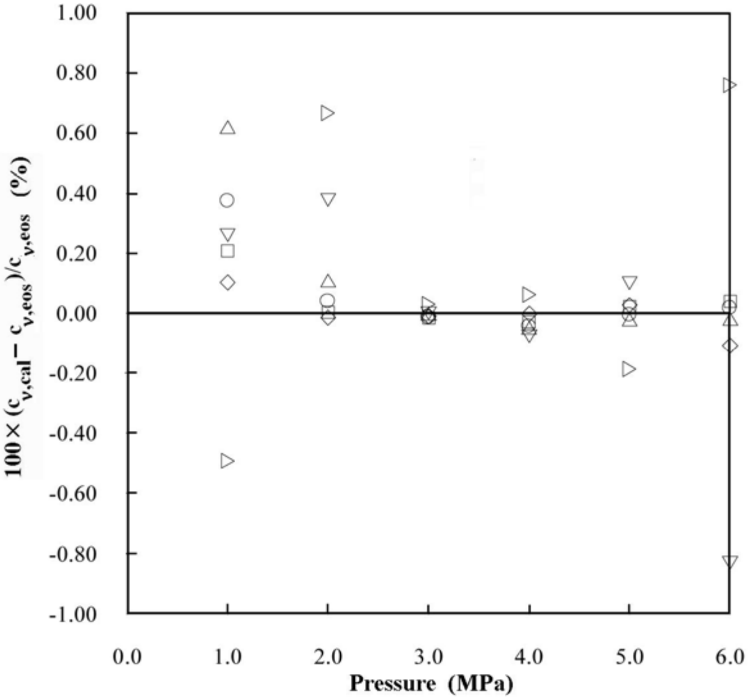

Fig. 3. Relative deviation of c_v *vs*. p at various temperatures, with respect to reference values [6]: (◇) 310 K, (□) 320 K, (○) 330 K, (△) 340 K, (▽) 350 K and (▷) 360 K.

sixth-degree with respect to temperature. The pressure derivatives of ρ, c_p, and α_p were estimated analytically from the following functions:

$$\rho = \frac{a + bp + cp^2}{1 + dp + ep^2 + fp^3} \qquad c_p = \frac{a + bp + cp^2}{1 + dp + ep^2 + fp^3}$$

$$\alpha_p = \frac{a + bp + cp^2}{1 + dp + ep^2 + fp^3} \tag{13}$$

in the temperature range 300 to 260 K, and from a Lagrangian interpolation polynomial of the sixth-degree in the temperature range 260 to 220 K. Parameters *a*, *b*, *c*, *d*, *e*, and *f* in Eqs. (13) were also obtained by solving a linear least-squares problem with iterative refinement of Björck [7]. The temperature derivatives of *p* were estimated from a Lagrangian interpolation polynomial of the sixth-degree. The numerical integration of Eqs. (5) and (6), with respect to temperature, was performed by Bulirsch-Stoer method with adaptive step size [9]. The method is very efficient, and it took only 26 steps to reach the lower limit of the temperature range.

The Bulirsch-Stoer method includes three key ideas. The first is Richardson's deferred approach to the limit. The idea is to consider the final answer of a numerical calculation as itself being an analytic function (if a complicated one) of an adjustable parameter like the step size *h*. That analytic function can be probed by performing the calculation with various values of *h*, none of them being necessarily small enough to yield the accuracy that we desire. When we know enough about the function, we fit it to some analytic form, and then evaluate it at that mythical and golden point $h = 0$.

The second idea has to do with what kind of fitting function is used. Bulirsch and Stoer first recognized the strength of rational function extrapolation in Richardson-type applications. That strength is to break the shackles of the power series and its limited radius of convergence, out only to the distance of the first pole in the complex plane. Rational function fits can remain good approximations to analytic functions even after the various terms in powers of *h* all have comparable magnitudes. In other words, *h* can be so large as to make the whole notion of the order of the method meaningless, and the method can still work superbly.

The third idea is to use a method whose error function is strictly even, allowing the rational function approximation to be in terms of the variable h^2 instead of just *h*.

A single Bulirsch-Stoer step takes us from *x* to $x + H$, where *H* is supposed to be quite a large-not at all infinitesimal-distance. That single step is a grand leap consisting of many (*e.g.*, dozens to hundreds) substeps of modified midpoint method, which are then extrapolated to zero step size.

The sequence of separate attempts to cross the interval *H* is made with increasing values of *n*, the number of substeps. Bulirsch and Stoer originally proposed the sequence:

$$n = 2, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, \ldots, \left(n_j = 2n_{j-2}\right), \ldots \tag{14}$$

For each step, we do not know in advance how far up this sequence we will go. After each successive *n* is tried, rational function extrapolation is attempted. That extrapolation returns both extrapolated values and error estimates. If the errors are not satisfactory, we go higher in *n*. If they are satisfactory, we go on to the next step and begin anew with $n = 2$.

Of course there must be some upper limit, beyond which we conclude that there is some obstacle in our path in the interval *H*, so that we must reduce *H* rather than just subdivide it more finely.

Relative deviations of ρ, c_p, and c_v, with respect to corresponding reference values are given in Figs. 4, 5, and 6, respectively. The average absolute deviation of density is 0.030%, and the maximum relative deviation is +0.097%/-0.105%. The average absolute deviation of c_p is 0.23%, and the maximum relative deviation is +0.86%/-0.67%. The average absolute deviation of c_v is 0.20%, and the maximum relative deviation is +0.66%/-0.67%.

The method is very sensitive to the initial conditions, and somewhat less sensitive to the changes in the speed of sound, in the case of subcritical vapor phase. Therefore, only the initial values of high accuracy should be used.

An attempt was made to calculate ρ, c_p, and c_v at the saturation line. Therefore, the values of the quantities obtained by the numerical integration were extrapolated, and corresponding results for saturated vapor are given in Figs. 7 to 9. The average absolute deviation of ρ, c_p, and c_v, with respect to corresponding reference values are 0.056%, 2.31%, and 1.32%, respectively.

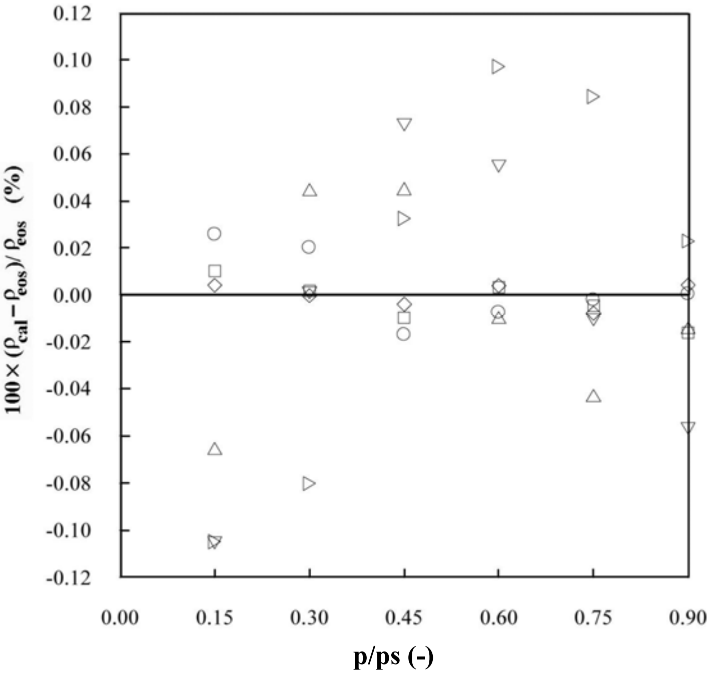

Fig. 4. Relative deviation of ρ *vs*. p/p_s at various temperatures, with respect to reference values [6]: (◇) 290 K, (□) 280 K, (○) 260 K, (△) 240 K, (▽) 230 K and (▷) 220 K.

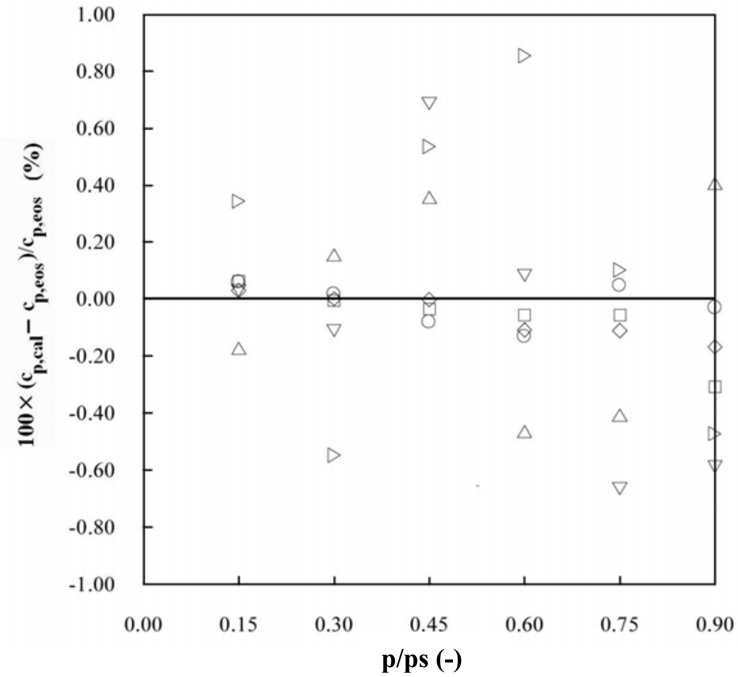

Fig. 5. Relative deviation of c_p *vs*. p/p_s at various temperatures, with respect to reference values [6]: (◇) 290 K, (□) 280 K, (○) 260 K, (△) 240 K, (▽) 230 K and (▷) 220 K.

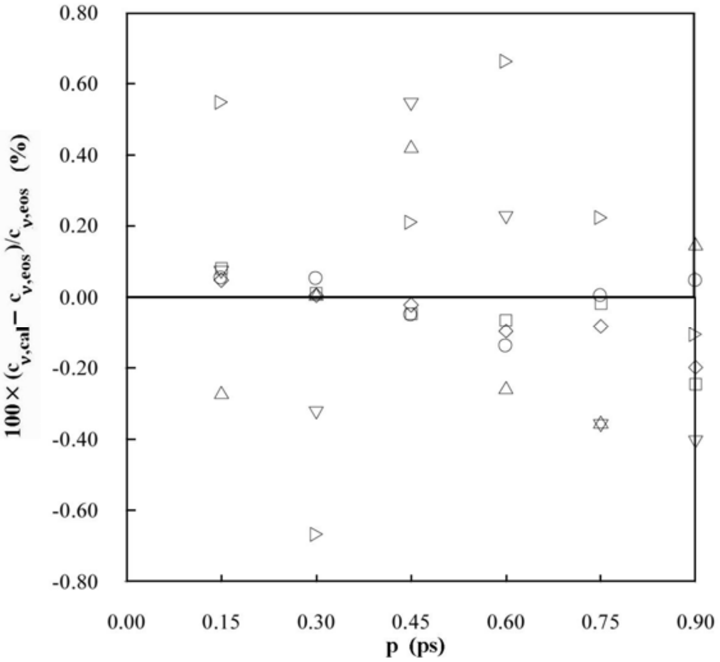

Fig. 6. Relative deviation of c_v *vs*. p/p_s at various temperatures, with respect to reference values [6]: (◇) 290 K, (□) 280 K, (○) 260 K, (△) 240 K, (▽) 230 K and (▷) 220 K.

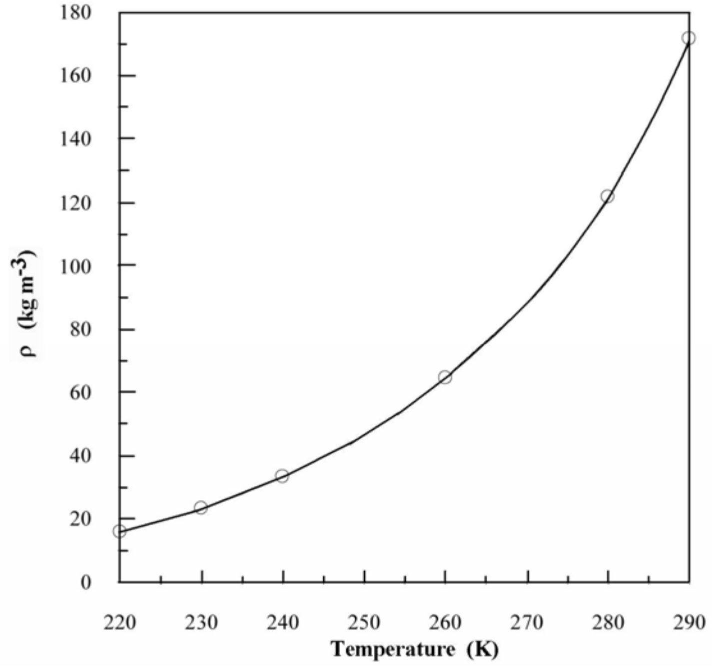

Fig. 7. Saturated vapor density *vs*. temperature: (○) this paper, (——) reference values [6].

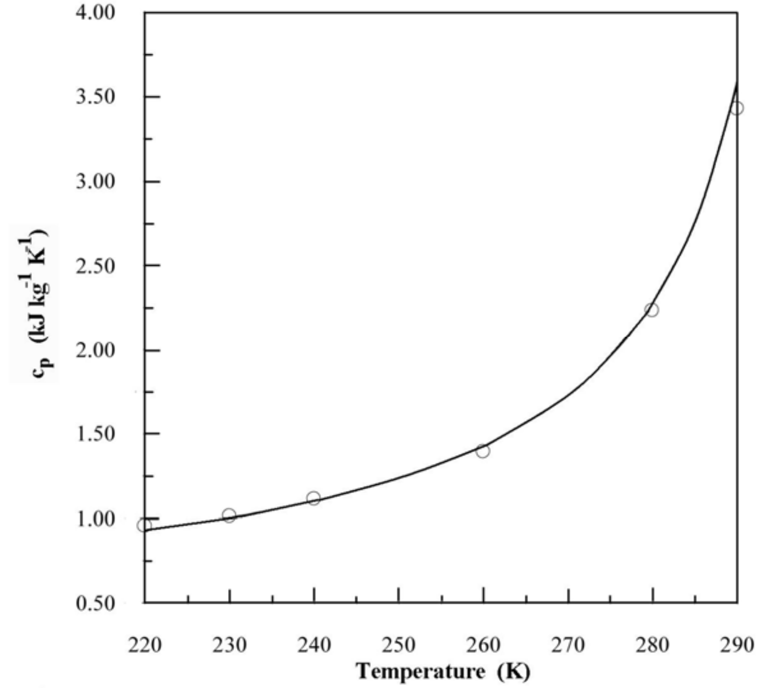

Fig. 8. Saturated vapor c_p *vs*. temperature: (○) this paper, (——) reference values [6].

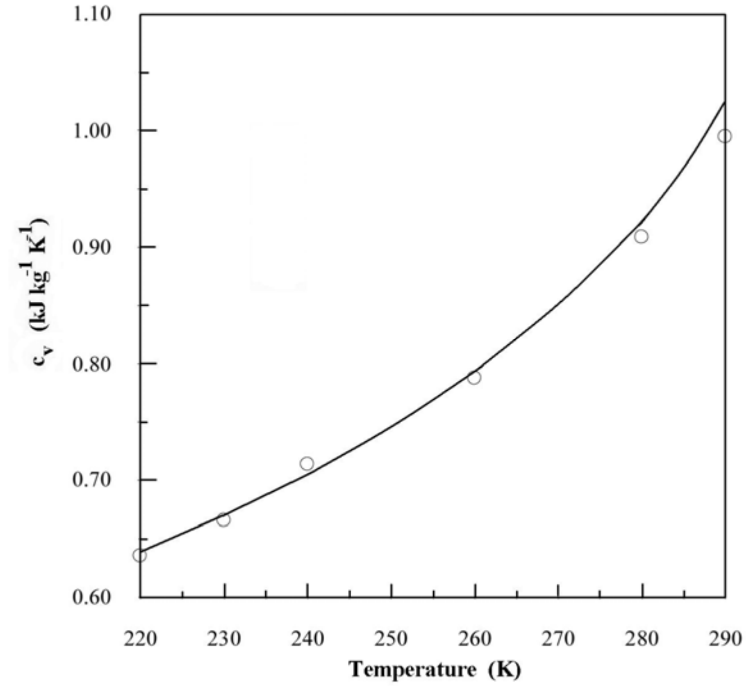

Fig. 9. Saturated vapor c_v *vs*. temperature: (○) this paper, (——) reference values [6].

CONCLUSIONS

The results obtained should be estimated taking into account the temperature and the pressure range considered, as well as dependency on the experimental information. In this paper it has been demonstrated (on the example of carbon dioxide) that, on the basis of just a few accurate initial data points, it is possible to derive quite precisely thermal and caloric properties of a substance from its speed of sound, from the ideal gas limit to the saturation line, and from the triple point quite above the critical point. Moreover, all the calculations are based on standard numerical methods of solving ordinary differential equations, polynomial interpolation, and the least-squares approximation.

The nature of the equations connecting the speed of sound with other thermodynamic properties is such that even a small uncertainty of the initial values, the sound-speeds, and the pressure derivatives propagates considerable error into the results, especially into the heat capacity. At subcritical conditions, these uncertainties may even prevent obtaining any reasonable result. In order to avoid this situation, only the state-of-the-art methods of higher order of approximation to ordinary differential equations should be used. However, accuracy of the pressure derivatives estimation is probably the most critical issue, with the biggest potential for improvements. An attempt in that direction is made in this paper by introducing derivative estimation from a rational function rather than from an interpolation polynomial.

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