

NUMERICAL IMPLEMENTATION OF THE ALTUNIN AND GADETSKII EOS AT THE CRITICAL REGION OF PURE CARBON DIOXIDE

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The development of equations of state (EoS) and their application to the correlation and the prediction of phase equilibrium properties is a wide research field. The Altunin and Gadetskii EoS was given to describe the thermodynamic properties of the pure carbon dioxide. The supercritical, the liquid and the gas states of carbon dioxide are represented accurately. Whereas, at the vicinity of the critical point, which is characterised principally by the divergence of compressibility, the Altunin and Gadetskii [1] EoS needs other corrective terms to stabilise fitting of the state and calculate accurately thermodynamic functions as the specific heat at constant volume or pressure and the sound celerity.

The original equation proposed by Altunin and Gadetskii and its tremendous importance in describing the carbon dioxide behaviour are analysed. A numerical implementation of the EoS, at the critical region, is performed by digitalizing corrective abacus given in the literature [2]. This work is followed by a numerical estimation of different thermodynamic functions as C_v , at the vicinity of the critical point, using limited development techniques. The domain of validation is showed when comparing results of the calculation and those determined experimentally and given by several authors.

I- INTRODUCTION

At present, even in the critical region, thermodynamic behaviour of pure components are most frequently modelled by classical equations of state, including commonly used cubic equations, such as the Redlich–Kwong and Peng–Robinson equations of state. Some non-classical models with theoretical or effective critical exponents are available, such as Bender model [3] and related models that incorporate crossover functions to connect the critical and non-critical regions [4]. Such models are currently used in a correlative rather than a predictive mode, since, in general, they require the critical locus as input as well as a number of adjustable parameters that can be determined only when extensive experimental data are available.

The critical point of a pure fluid is defined by the following conditions:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \text{ and } \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (1)$$

P , V , T and ρ denote respectively pressure, volume, temperature and density of the fluid.

Working near the critical point, the isothermal compressibility (k_T), at a few Celsius degrees from the critical temperature, is much higher than that of a perfect gas at the same density. The isothermal compressibility and the heat capacity at constant pressure of a fluid (C_p), are two well known physical properties that diverge to infinity in the vicinity of the critical point of a pure substance. Some studies developed by Bagatskii et al. [5], Voronel et al. [6] and by Lipa et al. [7] strongly suggest that the specific heat at constant temperature (C_v), also becomes infinitive at the critical point, which is in disagreement with the classical Van der

Waals theory. However, as pointed out by Sengers [8], the divergence of the C_v is weak compared to that of the k_T .

II- GOVERNING EQUATIONS

II-1 Complete equation of state:

The analytic Altunin and Gadestkii EoS is written as:

$$Z = \frac{P_A}{\rho RT} = 1 + \rho \sum_{i=0}^9 \sum_{j=0}^6 b_{ij} (\tau - 1)^j (\rho_r - 1) \quad (2)$$

Where $\rho_r = \rho/\rho_c$ and $\tau = T_c/T$. Z is the compressibility factor and R is the perfect gas constant. The c letter indicates the critical point and b_{ij} coefficients are given in the IUPAC tables [2]. A separate EoS was needed for the critical region within about ± 5 K of the critical temperature. The equation of Schofield et al [3] was chosen for use. This equation is in terms of two variables, r and θ , which may be regarded as polar coordinates centred on the critical point and are related to the density and the temperature by the set of equations:

$$\Delta T = \frac{(T - T_c)}{T_c} = r(1 - b^2\theta^2) \quad (3)$$

$$\Delta \rho = \frac{|\rho - \rho_c|}{\rho_c} = r^\beta g\theta \quad (4)$$

They are related to the pressure by the following parametric equation:

$$\Delta P = \frac{|P_s - P_c|}{P_c} = r^{\beta(\delta+1)} q(\theta) + c\Delta T + ar^{\beta\delta}\theta(1 - \theta^2) \quad (5)$$

Where q is a function of θ , given as follows:

$$q(\theta) = 36.98893 - 82.0796\theta^2 + 56.66053\theta^4. \quad (6)$$

The complete EoS is formed by combining equations (2) and (5) in such a way that one of the other is predominant in its appropriate region using a switching function $f(r)$.

$$P = f(r).P_A + [1 - f(r)].P_S \quad (7)$$

Where $f(r)$ is expressed by:

$$f(r) = 1 - \left[1 - \exp(-0,01/r^{n_1})\right] \left[1 - \exp(-0,05/r^{n_2})\right] \quad (8)$$

A and S indices notice respectively the analytic and the critical expressions of the pressure.

II-2 Constants:

Values of different constants needed to evaluate the pressure at the critical region P_S are:

$$n_1=3/2 ; n_2=3; a=0.065; \beta=0.347; \delta=4.576; g=1.491.$$

Concerning parameter c , its value depends on the relative temperature (T/T_c). We noticed that parameter $c= 240.435$ for $T > T_c$ and $c= -58.383$ for $T \leq T_c$.

II-3 Heat capacities and sound celerity:

Isochoric heat capacity is one of the important thermodynamic characteristics of fluids and fluid mixtures. The EoS does not sufficiently correctly reproduce the values and behaviour of C_v . The role of calorimetric measurements to develop an EoS is very important, especially near the critical and phase transition points. Isochoric heat capacity data contain direct information on second temperature derivatives of pressure $\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho$ [10]. For example, heat capacity at constant volume C_v is related to the EoS by:

$$C_v = \left[\frac{\partial U(T, V)}{\partial T} \right]_v \quad (9)$$

U is the internal energy.

$$\text{That gives: } C_v = C_{v0} - \int_0^p \frac{T}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2} \right)_p d\rho. \quad (10)$$

$$\text{Where } C_{v0} \text{ is the ideal gas heat capacity written as: } C_{v0} = C_{p0} - R \quad (11)$$

$$\text{and } C_{p0} = R \cdot \sum_{i=0}^7 \gamma_i \tau^i \quad (12)$$

Where $\tau = T/T_c$ and γ_i are tabulated constants in the IUPAC [2].

The heat capacity at constant pressure, C_p is related to C_v as follows:

$$C_p = C_v + \frac{T \left(\frac{\partial P}{\partial T} \right)_p^2}{\rho^2 \left(\frac{\partial P}{\partial \rho} \right)_T} \quad (13)$$

Finally, the sound velocity C of a pure component can be expressed by the relation:

$$C^2 = \left(\frac{\partial P}{\partial \rho} \right)_s. \quad (14)$$

And as a function of heat capacities we write:

$$C^2 = \frac{C_p}{C_v} \left(\frac{\partial P}{\partial \rho} \right)_T. \quad (15)$$

III- NUMERICAL TECHNIQUES

III-1 Implementation of the corrective pressure near the critical point:

The Newton-Raphson method is one of the better known algorithms for finding the root of an equation in the form $f(\theta)=0$. Equations (3) and (4) are combined to get a new function depending only in θ . Indeed, we write:

$$f(\theta) = \frac{\Delta T^\beta}{\Delta \rho} g\theta - (1 - b^2\theta^2)^\beta = 0 \quad (16)$$

Boundary values of θ are chosen as 1 and -1. The convergence criterion is fixed at very low error evaluation, less than 10^{-10} .

III-2 Evaluation of the pressure derivatives:

In numerical analysis, we are usually able to obtain the derivative of a function by the methods of elementary calculus. However, if a function is very complicated or known only from values eq.(7), it may be necessary to resort to numerical differentiation. Methods for approximating these partial derivatives on a discretised scheme are well established in literature [11]. In this study, the values of the partial derivatives of pressure are approximated by finite difference methods.

In equations of heat capacities (10 and 13) and that of sound velocity (15), both first and second derivatives of pressure are evaluated using centred discretisation. Variables dT and $d\rho$ are elementary steps of both temperature and density. Consequently, if we want to keep round-off errors down, we should use a large value of dT and $d\rho$. On the other hand, it can be shown that the truncation error is approximately proportional to h^p , where h is an elementary step and p is a positive integer. This must be sufficiently small for the truncation error to be tolerable.

The first derivatives are discretised in a centred manner with a double precision and a truncation error of (dT^2) as given in the following:

$$f'(x) = \frac{f(x-h) - f(x+h)}{2.h} + O(h^2) \quad (17)$$

$$\text{Therefore } \left(\frac{\partial P}{\partial T} \right)_\rho \approx \frac{P_{i+1,j} - P_{i-1,j}}{2.dT} \quad (18)$$

$$\text{And } \left(\frac{\partial P}{\partial \rho} \right)_T \approx \frac{P_{i,j+1} - P_{i,j-1}}{2.d\rho} \quad (19)$$

The second derivative of pressure is discretised in a centred scheme using two methods called three points and five points rules. The central difference formula for the second derivative, based on three points is written as:

$$f''(x) = \frac{f(x-h) - 2f(x) + f(x+h)}{h^2} + O(h^2) . \quad (20)$$

$$\text{Therefore } \left(\frac{\partial^2 P}{\partial T^2} \right)_\rho \approx \frac{P_{i+1,j} - 2.P_{i,j} + P_{i-1,j}}{dT^2} \quad (21)$$

To get more precision in calculation, we write the central difference formula for the second derivative, based on five points rule as:

$$f''(x) = \frac{f(x-2h) + f(x+2h) - f(x-h) + f(x+h)}{3h^2} + O(h^4) \quad (22)$$

That gives :

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_\rho \approx \frac{P_{i+2,j} + P_{i-2,j} - P_{i+1,j} + P_{i-1,j}}{3.\Delta T^2} \quad (23)$$

It must be recognized that numerical differentiation is subject to considerable error; the basic difficulty is that, while $f(x) - f(x+h)$ may be small, the values of derivatives $f'(x)$ and $f''(x)$, may be very large. Thus, we should choose the optimal elementary variations of temperature and density to stabilise numerical determination and to separate the appeared physical discontinuities (of the critical point) and those of the scheme (numerical instabilities).

VI – RESULTS

In figure 1, different isotherms near the critical point are given by both analytic and complete equations using expressions (2) and (7). Dashed lines deal with the analytic representation of the state and solid lines showed the full EoS. We notice that the analytic equation oscillated in the critical region and reproduced poorly the carbon dioxide state in this zone. Moreover, the validity of the analytic equation, in the critical region, is judged by drawing the relative error ε calculated as:

$$\varepsilon = \frac{P - P_A}{P} \quad (24)$$

Figure (2) shows the variation of relative error ε with density for different isotherms. We notice that ε is minor when the temperature T is close to that of the critical point. Far from the critical isotherm, error ε increases but can not exceed 2,5 %. Indeed, using the analytic equation of pressure P_A , gives a good approximation of the pressure except very close to the critical point. We conclude that comparison of the analytic equation with the complete EoS showed excellent agreement, which is best appreciated from figure (1), and numerical comparisons showed the disagreement to be generally about ± 1 per cent, with maximum difference of 2,5 per cent.

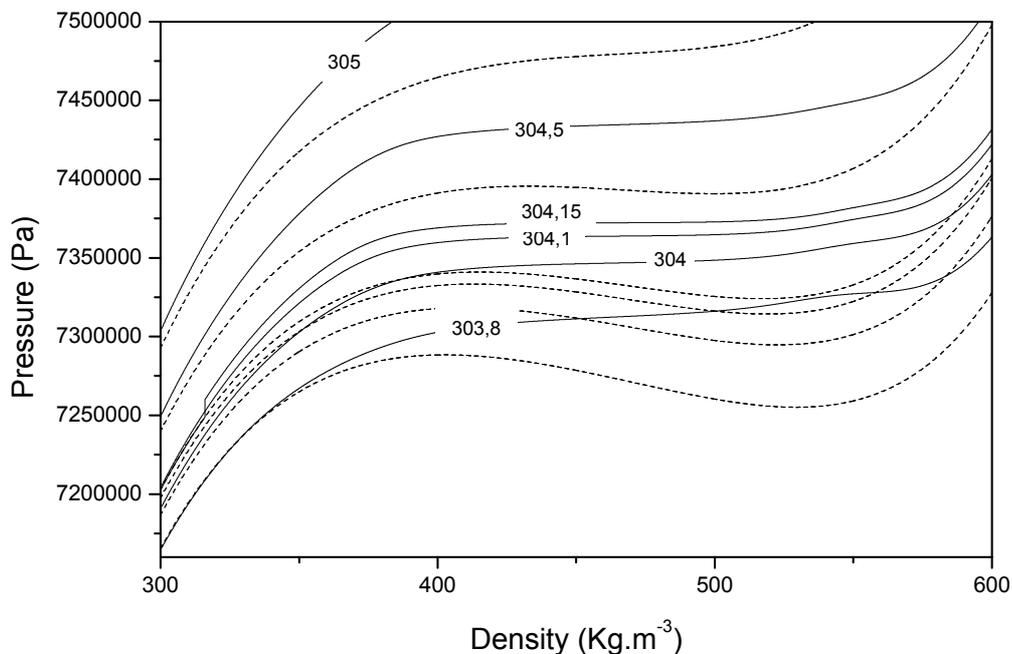


Figure (1) – Different isotherms of pure carbon dioxide near its critical point calculated using (eq. 2 : dashed line) and (eq. 7 : solid line).

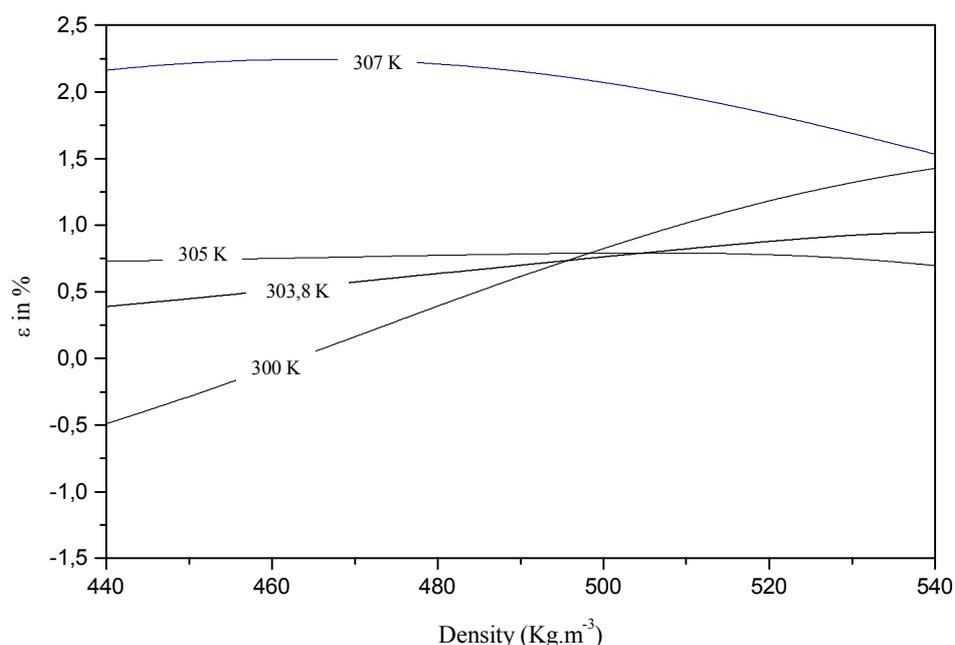


Figure (2) – Variation of error ϵ (eq. 24) as a function of density for different isotherms of pure carbon dioxide near its critical point.

Figure 3 shows that C_v of pure carbon dioxide is nearly independent of pressure in the high pressure region, indicating that the intermolecular interaction is not sensitive to pressure as the fluid is far from the critical region. In other words, the properties of the fluid far from the critical points do not vary with pressure considerably, which is similar to conventional liquids. The dependence of C_v in the critical region on temperature is more complex. The analytic equation can not produce the experimental data of Beck et al [12] at this region. Therefore, there exists a maximum in C_v versus temperature curve for CO_2 , as can be seen in figure 3.

As the temperature and the pressure approached the critical point, the compressibility is larger, and the clustering is more pronounced. The heat capacity results from the fact that the fluid absorbs energy as temperature rises. If clusters exist in the fluids, the degree of clustering should be decreased as temperature rises, i.e., some of the members in the clusters enter the bulk, which needs some additional energy. The results near the critical point are not sufficiently close to it using the analytic equation of Altunin. Whereas, the complete formulation of the pressure (7) can not give accurate calculation of the second derivatives as mentioned in (III-2). A longstanding, interesting question is whether the singular behaviour of C_v is related to that of the second derivative of pressure. More works will be made to recalculate coefficients of equations (5 and 6) by fitting an important number of experimental C_v data. Future corrections will conserve the good agreement obtained of the pressure estimation in the critical region and will give an accurate calculation of the second derivative of pressure as noticed in the C_v (eq. 10).

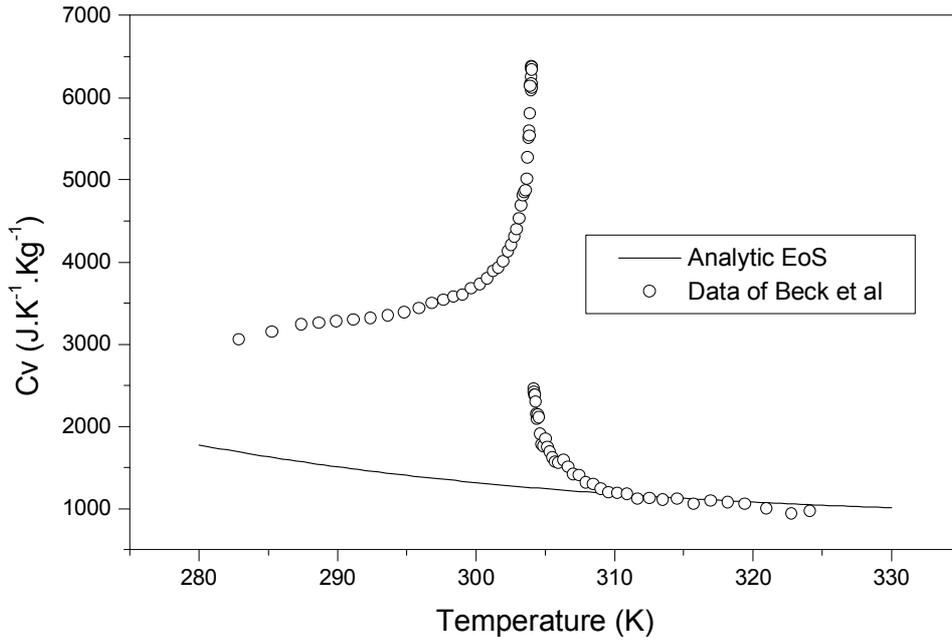


Figure (3) – Comparison of C_v experimental measurements [12] and those deduced from the analytic equation of state

The numerical integration of C_v using three or five points differentiation rules can produce exactly values of C_v at low and high density, figure 4. Both the two finite difference schemes give tolerable values of C_v when compared to that obtained from the analytic equation of pressure.

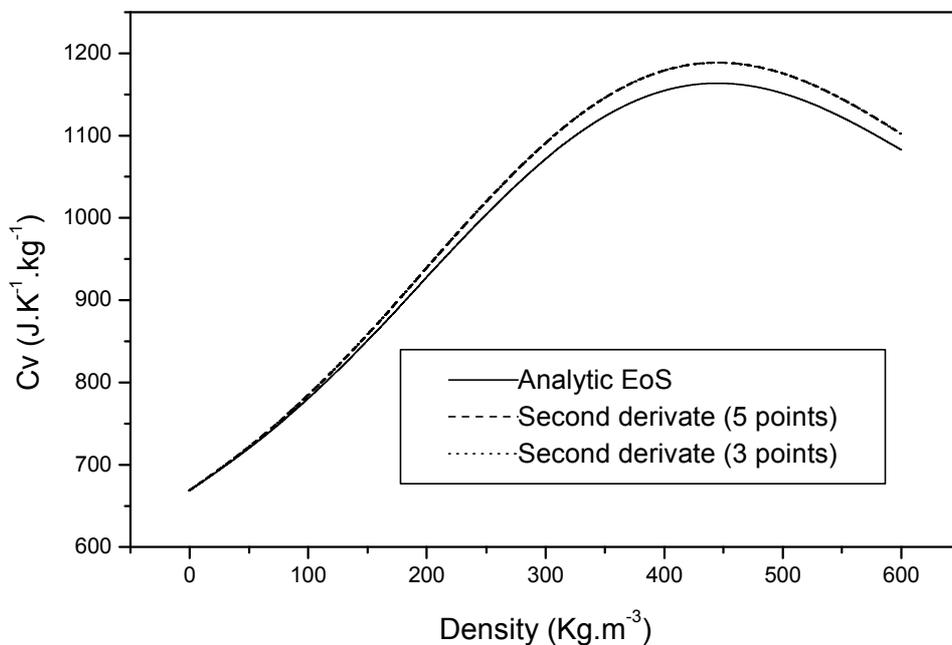


Figure (4)- Comparison between C_v deduced from the analytic EoS and the discretised one using 3 and 5 points rules.

When the isochoric heat capacity is determined, the isobaric capacity can be deduced by calculating first derivatives of pressure (eq. 18 and eq. 19). From figure (5), we conclude that C_p is nearly independent of density in both low and high density regions. When the reduced density (ρ/ρ_c) tends to 1, C_p exceeds high values and numerical calculation diverges.

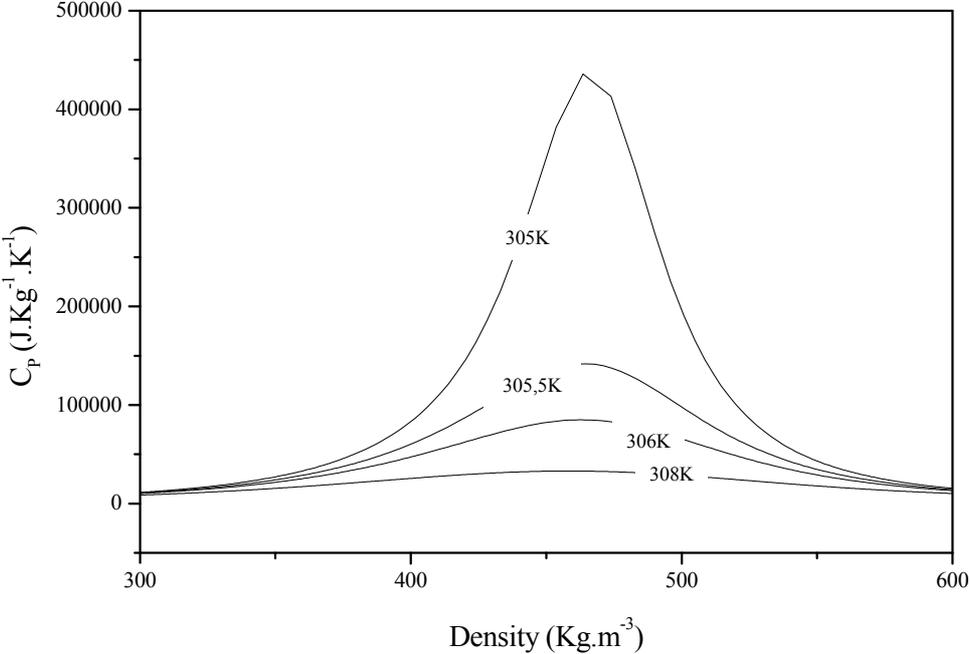


Figure (5)– Variation of heat capacity C_p as a function of density at different isotherms

The sound celerity C is an important parameter in fluid dynamics simulation where its accurate estimation is a necessary step in calculation.

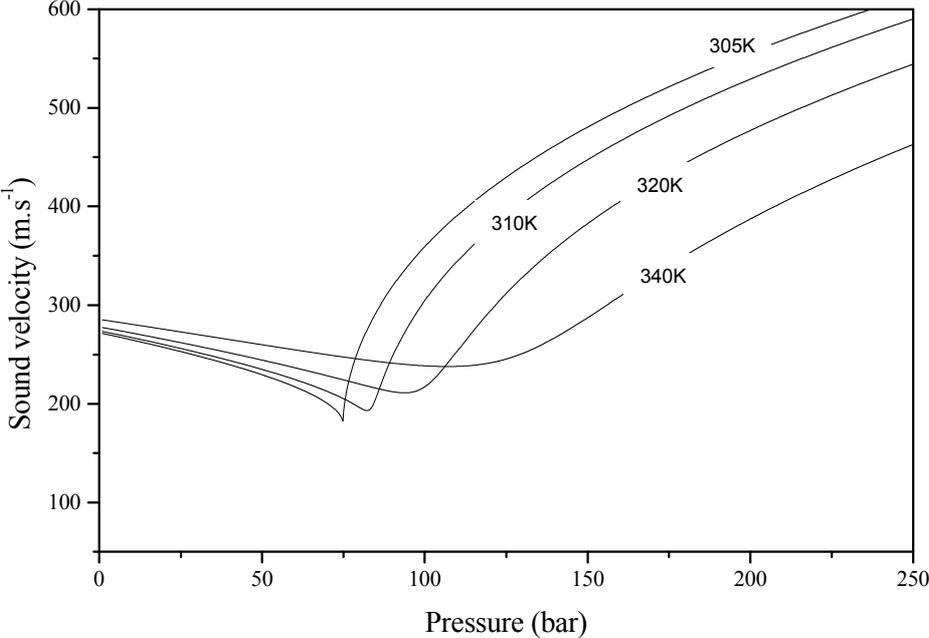


Figure (6)– Variation of the sound velocity as a function of pressure at different isotherms

Therefore, many researchers have studied fluid dynamics at high density using different expressions of C [13] and [14]. Their results show that shock wave capture in high compressible regions, which is often referred to an important increasing of both C_v and C_p , creates numerical problems and the divergence of calculations. Therefore, figure 6 shows the behaviour of the sound celerity at the critical region and the abrupt discontinuities when the pressure is close to that of the critical point. Here, the complete equation as presented by Altunin et al. [1] can not offer accurate value of the parameter C and the variation of derivatives of pressure versus temperature is so perturbed and gives an erroneous function.

V- CONCLUSION

In this contribution, we have considered the integration of heat capacities and sound celerity from the equation of Altunin in the supercritical domain and also at the critical region. The numerical integration evaluates derivatives of the pressure using different high order finite difference techniques. The obtained results showed a good agreement of calculations with the analytic EoS. In contrast, calculation of derivatives of pressure using the complete equation of state diverges. Therefore, estimation of coefficients of this equation will be undertaken by fitting experimental data of heat capacities at the critical region of carbon dioxide.

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