Description of Thermodynamic Properties of Liquids over Wide Ranges of Pressure and Temperature[1]

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ABSTRACT

A novel method for estimating the behavior of liquids at the moderate and high pressures within the range from a melting line to a critical isotherm has been developed on the base of the fluctuation thermodynamics (FT) - model. The knowledge of accurate data for the thermal ($P_S(T)$, $\rho^l(T)$) - properties along the liquid branch of the coexistence curve and the caloric (C_{P_0} (T), $W_0(T)$, $\rho_0(T)$) - properties along the initial supercritical isobar P_0 allow one to achieve a reasonable description of the complete set of thermodynamic properties (C_P, C_V, ρ, W, α_P, χ_T, h, s) at the arbitrary given values (P,T) in easy way.

Argon and carbon dioxide have been used to test the ability of the FT-model to represent the thermodynamic behavior of compressed liquids at low temperatures and high pressures up to 300 MPa (the initial isobar P_0 has been selected at the pressure 20 MPa for Ar and 30 MPa for CO_2). It appears to be the simple method able to predict a common crossing point of the $\alpha_P(P)$ - isotherms and a point of minimum of the $C_P(P)$ - isotherms experimentally observed for real liquids.

KEY WORDS: argon; carbon dioxide; coexistence curve; initial isobar; FT- model; isentrope;

1. INTRODUCTION

The fluctuational thermodynamics (FT)-model, introduced by Rogankov [1], [2], calls into question some suppositions of the conventional thermal or caloric (fundamental) equation of state (EOS)-methods and proposes an alternative concept of interpolation

between an arbitrary regular supercritical isobar P_0, selected far from the extended critical region and the singular CXS of pure substances in a whole fluid part of thermodynamic surface. The FT-model yields quantitatively accurate description and prediction of all thermodynamic properties in the fluid region (single-phase liquid and gas, including the classical as well as the extended critical areas). In this paper we shall consider the liquid state alone within the ranges from the melting temperatures up to the critical temperatures and from the liquid branch of the coexistence curves (CXS) up to the pressure 300 MPa for well-studied substances: carbon dioxide [3-5] and argon [6,7]. All thermodynamic properties are derived via the FT-model with a good accuracy from the set of experimental data along an initial supercritical isobar ($P_0>P_c$) and along the CXS. To illustrate the possibilities of FT - model we shall focus, also, on the problem of a crossing point of the $\alpha_P(P)$ - isotherms and a point of minimum of the $C_P(P)$ - isotherms. Up to now, there was no theoretical or empirical method in the literature (excluding the direct experiment itself) able to predict such behavior of liquids [8].

2. THE METHOD OF FT-MODEL

The foundation of FT-model has been described elsewhere [1,2]. In this paper we shall demonstrate that FT-model has also the remarkable extrapolation possibilities at least up to reduced pressures: $P/P_0 = 10 \div 15$ of a liquid state. From a thermodynamic viewpoint the inter - or extrapolating paths are the specific isentropes: s = const which connect each initial point (P_0, T_0) of a regular curve P_0 = const with the corresponding point (P_s, T_s) of the liquid branch of CXS. The critical point (P_c, T_c) and the points of spinodal have a higher

order of singularity than the ordinary singular points (P_S, T_S) along the binodal (CXS). We shall consider in this paper only the stable liquid phase relatively far from the critical point but it is appropriate to mention here that FT-model contains, in principle the possibility to take into account the properties of the extended critical region too. The choice of P_0=const as a regular line and the s = const as a characteristic path is not an arbitrary one. It is based on the FT-model which characterizes the presence of a special thermodynamic (**T**-) symmetry of real fluids (see below) different from the well-known symmetry of Ising-like systems, for example. From viewpoint of FT-model the only two directions which are singled out by the nature of CXS itself are the directions of critical isentrope s_C and critical isobar P_C.

The reduced slope A_S has a constant value A_0 along the isentrope in FT-model:

$$A_s = \frac{T}{P}\left(\frac{\partial P}{\partial T}\right)_s \approx \left[\frac{\rho C_P}{P\alpha_P}\right]_0 \tag{1}$$

For a simplicity we shall consider here only a zero - approximation for the another reduced slope of FT-model G_S (Gruneisen - parameter) along the isentropes in liquid phase, too:

$$G_s = \frac{\rho}{T}\left(\frac{\partial T}{\partial \rho}\right)_s \approx G_0 = \left[\frac{W^2\alpha_P}{C_P}\right]_0 \tag{2}$$

In other words, $A_0(T)$, $G_0(T)$ are the functions of temperature determined along the initial isobar P_0 and they have the finite values (A_0, G_0) for an each of isentropes. Such assumption will deteriorate, of course, the quality of description in general. But our main goal is to present an illustration of treatment by FT-model of liquid state in whole. From

this viewpoint, we have not attempted to select the "best" initial- or CXS-data for CO_2 and Ar or to present the "best" description and prediction of experimental data in the liquid phase. Accuracy of the FT-model predictions will discuss below.

One can easily obtain the relationship between density of mass ρ and reduced temperature $\overline{T} = (1 - T/T_0)$, taking into account the assumption (2) along the liquid isentrope:

$$\overline{T} = 1 - (\rho/\rho_0)^{G_0}, \tag{3}$$

where (ρ_0, T_0, G_0) are the values at the initial isobar P_0. The inter- and extrapolating paths are determined in FT-model by two equations of T-symmetry along an isentrope:

$$\sigma - \rho s = 0 \tag{4}$$

$$\overline{P} = A_0 \overline{T} + B_s \overline{T}^{3/2}, \qquad \overline{P} = C_0 \overline{\mu} + D_s \overline{\mu}^{-3/2} \tag{5}$$

Where (A_0, C_0) are the values of reduced slopes at the initial isobar P_0 and $\overline{P} = (1-P/P_0)$, $\overline{\mu} = (1-\mu/\mu_0)$ are the reduced pressure and chemical potential along the isentropes. The latter of eqs. (5) is important only for conception of T-symmetry but does not directly use in calculations. The linear relationship (4) between the densities ρ and σ (first derivatives of potential $P(\mu, T)$) is transformed into T - symmetrical eqs. (5) for the fields μ and T along the isentrope. To determine the coefficient B_s in the first of eqs. (5) one must have only the thermal CXS - data: ρ^l (T), $P_s(T)$ and the initial - data: $G_0(T)$, $A_0(T)$ of eqs. (35). The system of these equations is solved by iterations in the FT - model at the arbitrary round values (P,T) to obtain the coefficient B_s and the value of density $\rho(P,T)$ in this point of isentrope.

As the method of FT - model is not a conventional one we describe here the procedure of calculations in step-by-step form. Firstly, the reduced slopes (A_0, G_0) must be found directly by eqs. (1,2) along the isobar P_0 from the measurable initial - data. Recent developments of calorimetric high - pressure techniques for investigation of liquids (for instance, Alba et al. [9]) and direct measurements of the derivatives (α_P, C_P) are very helpful for the approach of FT - model. Our experience reveals that the simple polynomial equations are valid in general within the experimental uncertainties for representing initial - data in liquids over wide ranges of temperature:

$$\alpha_{P_0} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{P_0} = a_0 + a_1 T + a_2 T^2 + a_3 T^3, \tag{6}$$

$$W_0 = b_0 + b_1 T, \tag{7}$$

$$C_{P_0} = T\left(\frac{\partial s}{\partial T}\right)_{P_0} = c_0 + c_1 T + c_2 T^2 + c_3 T^3, \tag{8}$$

The values of initial density, specific entropy and enthalpy (ρ_0, s_0, h_0) along the isobar P_0 one can determined by integration of eqs. (6)…(8) from the reference point (ρ_0^0, s_0^0, h_0^0) at the temperature T_0^0 near (or at) the melting line to the limit point of liquids at the T_l near the maxima of $C_{P_0}(T)$ and $\alpha_{P_0}(T)$. Hence, the caloric values (h_0^0, s_0^0) at the melting line must be known in addition to the initial - data. To represent accurately the thermal CXS - data from the triple point up to the critical point we have used the equations proposed by Duschek et al [4] for CO_2 :

$$\ln\left(\frac{P_s}{P_c}\right) = \left(\frac{T_c}{T}\right)\left(d_0\overline{T} + d_1\overline{T}^{3/2} + d_2\overline{T}^2 + d_3\overline{T}^4\right), \tag{9}$$

$$\ln\left(\frac{\rho_s}{\rho_c}\right) = e_0\overline{T}^{2/6} + e_1\overline{T}^{3/6} + e_2\overline{T}^{7/6} + e_3\overline{T}^{9/6} \tag{10}$$

Coefficients of these auxiliary correlations for Ar and CO_2 must be found directly by eqs. (1,2) along the isobar P_0 and the values (B_s, ρ) can be determined by eqs. (3,5) at the round values (P, T). To predict the all other single - phase properties of liquid it is necessary to repeat the calculations at the small temperature step: $\Delta \leq 2K$ in the point: $\rho(P, T + \Delta T)$ belonged to the adjacent isentrope: $s + \Delta s$. Hence, the determination of the predicted values (C_P, α_P) at the point (P, T) is based on the evaluation of derivatives by simple finite differences:

$$C_P \approx T\left(\frac{\Delta s}{\Delta T}\right)_P, \qquad \alpha_P \approx -\frac{1}{\rho}\left(\frac{\Delta \rho}{\Delta T}\right)_P \tag{11}$$

The predicted value of a speed of sound W can be obtained by eq. (2). Then one can determine the predicted values (C_V, χ_T):

$$C_v = \frac{C_P}{1 + T\alpha_P G_0}, \qquad \chi_T = \frac{1 + T\alpha_P G_0}{\rho W^2} \tag{12}$$

At last, the predicted enthalpy h(P, T) follows from the numerical integration of the calculated density $\rho(P)$ along the isentrope.

3. RESULTS

3.1 Argon

Experimental (ρ_0, W_0) and derived α_{P_0} properties of liquid Ar, published by Street [6], have been used along the isobar: P_0=20 MPa (seven points at 10 K intervals between 90 and 150 K) . A comprehensive correlation and evaluation of data for Ar were reported by Rabinovich et al. [7]. From this work we have used measured C_{P_0} - and (ρ^l, P_s) - data.

Coefficients of eqs. (6-10) are given in table I. The accuracy of the FT-model predictions was determined by statistical comparisons of its results with experimental data on the single-phase density and velocity of sound (78 points on ρ and W from [6]) within the ranges from 90 to 150 K and from 1 to 300 MPa. Besides, the results of FT - model predictions on density and isobaric heat capacity C_P have been compared with the whole volume of table data, presented in [7] up to the pressure 100 MPa (426 points). As the inter- and extrapolating description by FT - model has nothing to do with a fitting procedure and has, in fact, a sense of prediction we did not consider it worthwhile to calculate the conventional standard deviations (AAD, BIAS, RMS). The statistics attribute used in this paper is only PAD (percentage average deviation). We have obtained the following values of PAD for liquid Ar: PAD(ρ[6]) = 0.28, PAD(ρ[7]) = 0.11, PAD(W[6])=1.69, PAD(C_P[7])=0.91. The FT - model provides the reasonable accuracy of predictions for most practical purposes in the whole liquid region of this substance.

The results of FT - model predictions are shown in figures 1-3 on α_P, C_P and C_V, respectively. There is a common crossing point of $\alpha_P(P)$ - isotherms at the parameters: $\alpha_P = 2.8\ kK^{-1}$, P = 63 MPa, as is seen in figure 1. Street [6] has not found the common crossing point at the same $\alpha_P(P)$ isotherms. Irregular crossing of these isotherms in his work suggests that temperature dependence of thermal. EOS is incorrect. In consequence of presence of a such crossing point there are the points of minima at the $C_P(P)$ - isotherms predicted by FT - model, as is seen in figure 2. The $C_V(P)$ - isotherms predicted by FT - model are shown in figure 3. The thermal EOS fails often to give even qualitatively correct values of C_V.

3.2 Carbon dioxide

A comprehensive correlation and evaluation data for CO_2 were reported by Altunin [3] and recently by Span and Wagner [5].Unfortunately, thermal EOS [3] fails to represent the correct behavior of $C_P(T)$ - isobars near the melting line. The discrepancies between the calculated and measured values of C_P, obtained in old but relatively accurate measurements of Popov and Sayapov [3] can be as large as 10 to 15 % within the range from 220 to 260 K. Taking into account this fact one can consider the heat capacities of the above - named works as unreliable ones at low temperatures of liquid phase. In this paper, the direct experimental data on α_{P_0} (Alba et al. [9]) and C_{P_0} (Popov and Sayapov [3]) for liquid CO_2 have been used along the isobar: P_0 = 30 MPa as well as the derived data on W [3]. Along the CXS we have used the accurate (ρ^l, P_S) - data, obtained by Duschek et al. [4]. Coefficients of eqs. (6-10) are given in table II. In this case the accuracy of the FT - model predictions was only determined by comparisons of its results with data on single - phase density, published in [3-5]. We have obtained the following values of PAD for liquid CO_2: PAD(ρ[3]): 0.365 %, PAD(ρ[5]): 0.244 %, respectively.

The results of FT -model predictions of caloric properties along the liquid branch of CXS are shown in figure 4. There is a common crossing point of $\alpha_P(P)$ - isotherms at the parameters: α_P=1.64 kK^{-1}, P=91 MPa ,as is seen in figure 5. It is interesting that value α_P predicted by FT - model coincides, practically, with the result of Alba et al. [9]: α_P=1.633 kK^{-1} but the pressure of crossing differs from the measured value P=125 MPa [9]. Besides,

FT - model does not predict the points of minima at the $C_P(P)$ - isotherms for CO_2 as is seen in figure 6. Alba et al [9] have found such minima, by mistake, in region of a solid phase.

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FIGURE CAPTIONS

Fig.1 $\alpha_P(P)$ - isotherms for liquid argon at 10 deg intervals from 100 to 150 K, predicted by FT - model. The parameters of a crossing point are approximately: α_P=2.8 K^{-1}, P = 63 MPa.

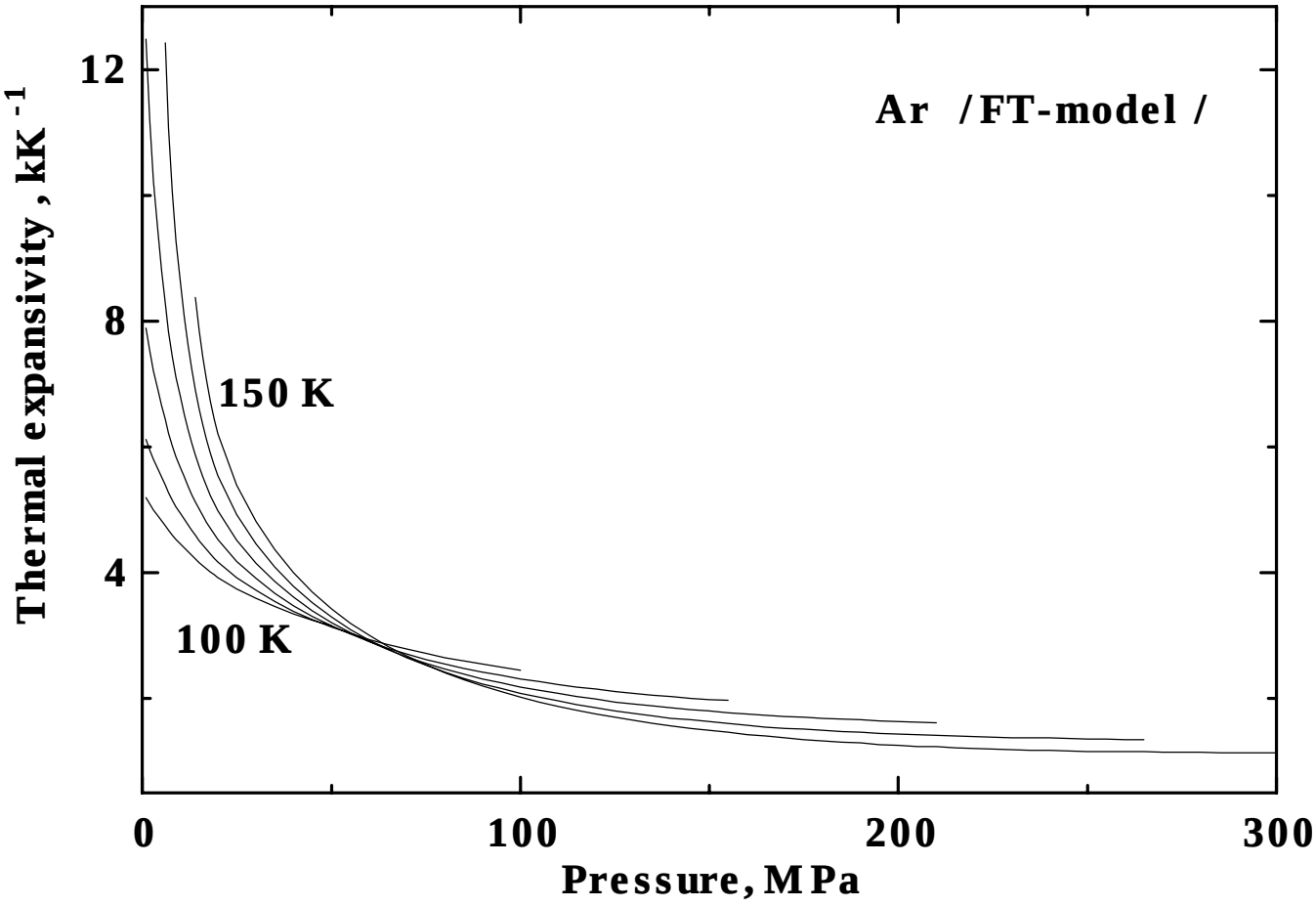
Fig.2 $C_P(P)$ - isotherms for liquid argon at 10 deg intervals from 100 to 150 K, predicted by FT - model. Isotherms from 110 to 150 K have the points of minima.

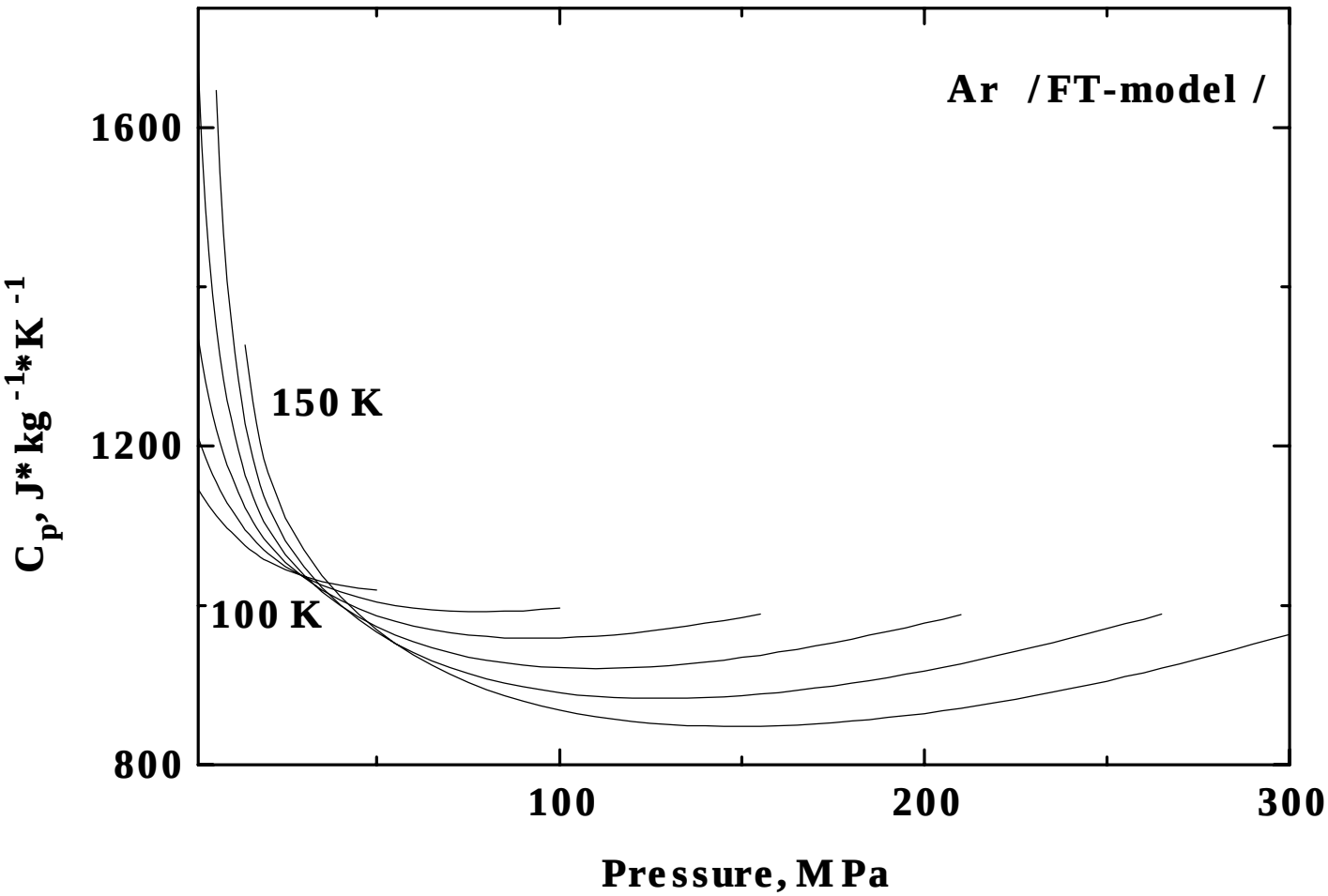
Fig.3 $C_V(P)$ - isotherms for liquid argon at 10 deg intervals from 100 to 150 K, predicted by FT - model.

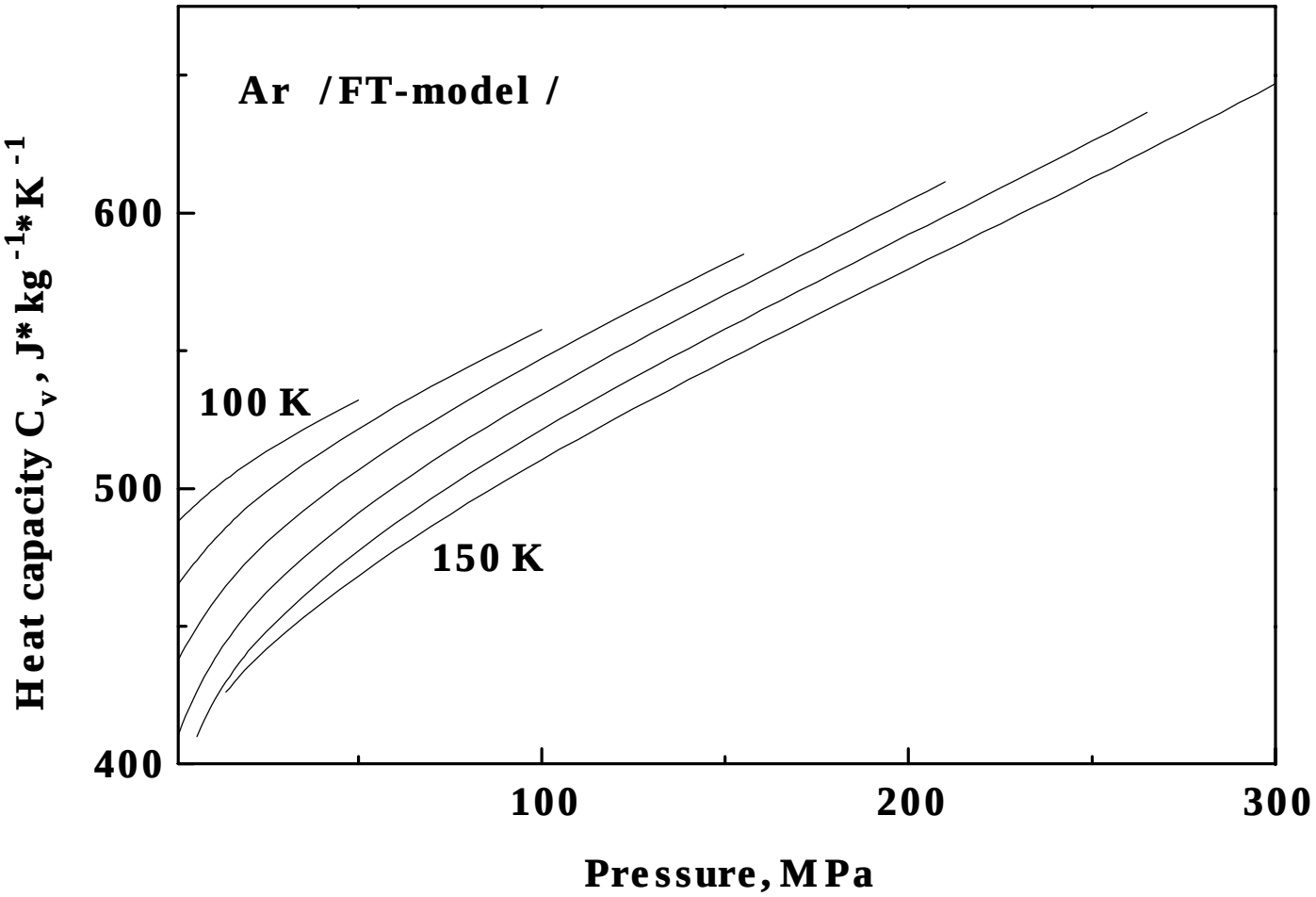
Fig.4 Caloric data of saturated liquid CO_2, predicted bt FT - model on the base of measurements on C_P [3] and α_P [9] at the initial isobar $P_0 = 30$ MPa.

Fig.5 $\alpha_P(P)$ - isotherms for liquid carbon dioxide at 10 deg intervals from 230 to 290 K, predicted by FT - model. The parameters of a crossing point are approximately: $\alpha_P = 1.64$ kK^{-1}, P = 91 MPa

Fig.6 $C_P(P)$ - isotherms for liquid carbon dioxide at 10 deg intervals from 230 to 290 K, predicted by FT - model.


Ar /FT-model /
150 K
100 K
Thermal expansivity , kK -1
12
8
4
0
100
200
300
Pressure, MPa


Ar /FT-model /
1600
1200
800
150 K
100 K
100
200
300
Pressure, MPa
C_p, J* kg^{-1}* K^{-1}


Ar /FT-model /
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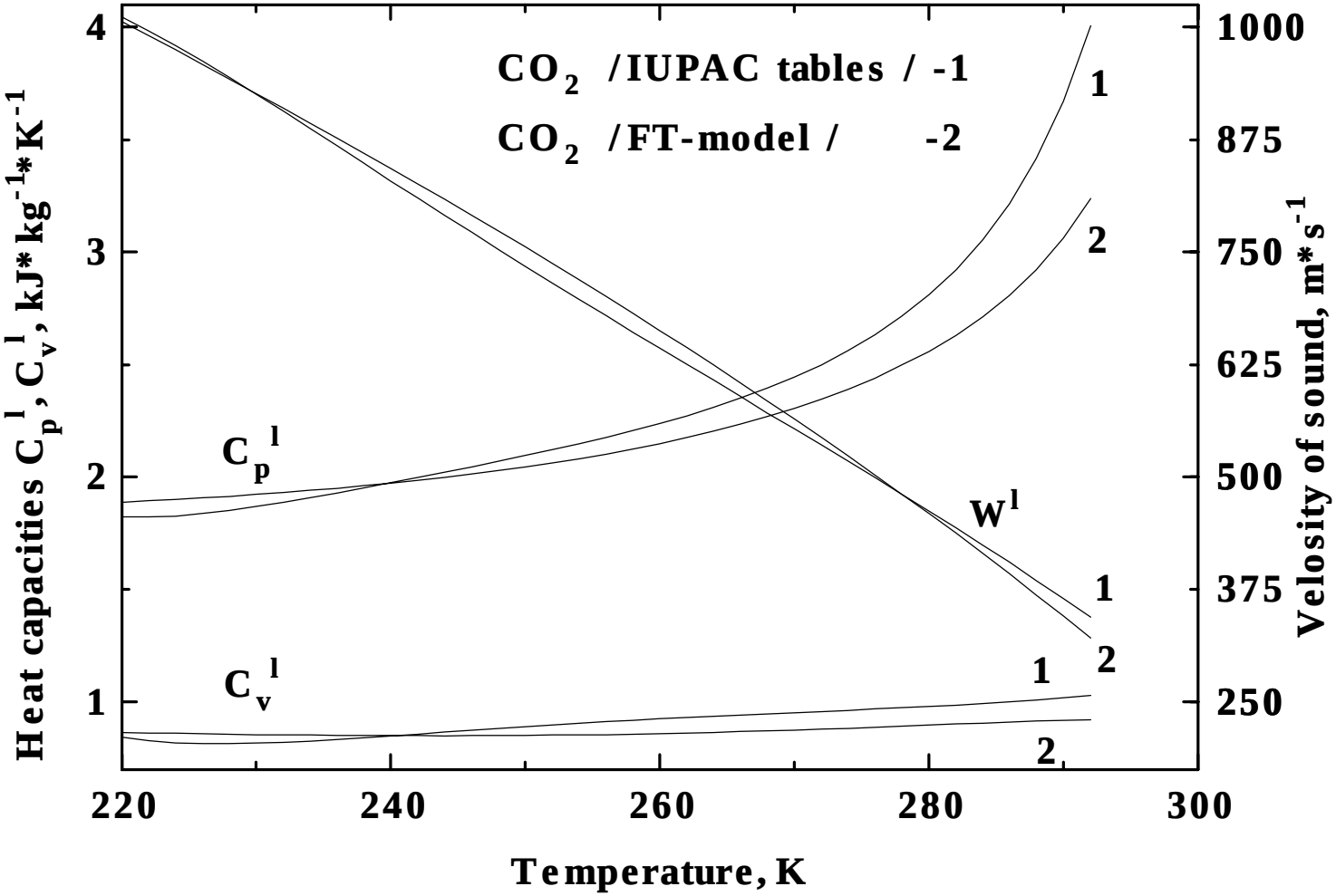
150 K
600
500
400
100
200
300
Heat capacity C_v, J* kg^{-1}* K^{-1}
Pressure, MPa


CO2 /IUPAC tables / -1
CO2 /FT-model / -2
Heat capacities Cp l, Cv l, kJ* kg-1* K-1
Velosity of sound, m* s-1
Temperature, K
Cp l
Cv l
W l
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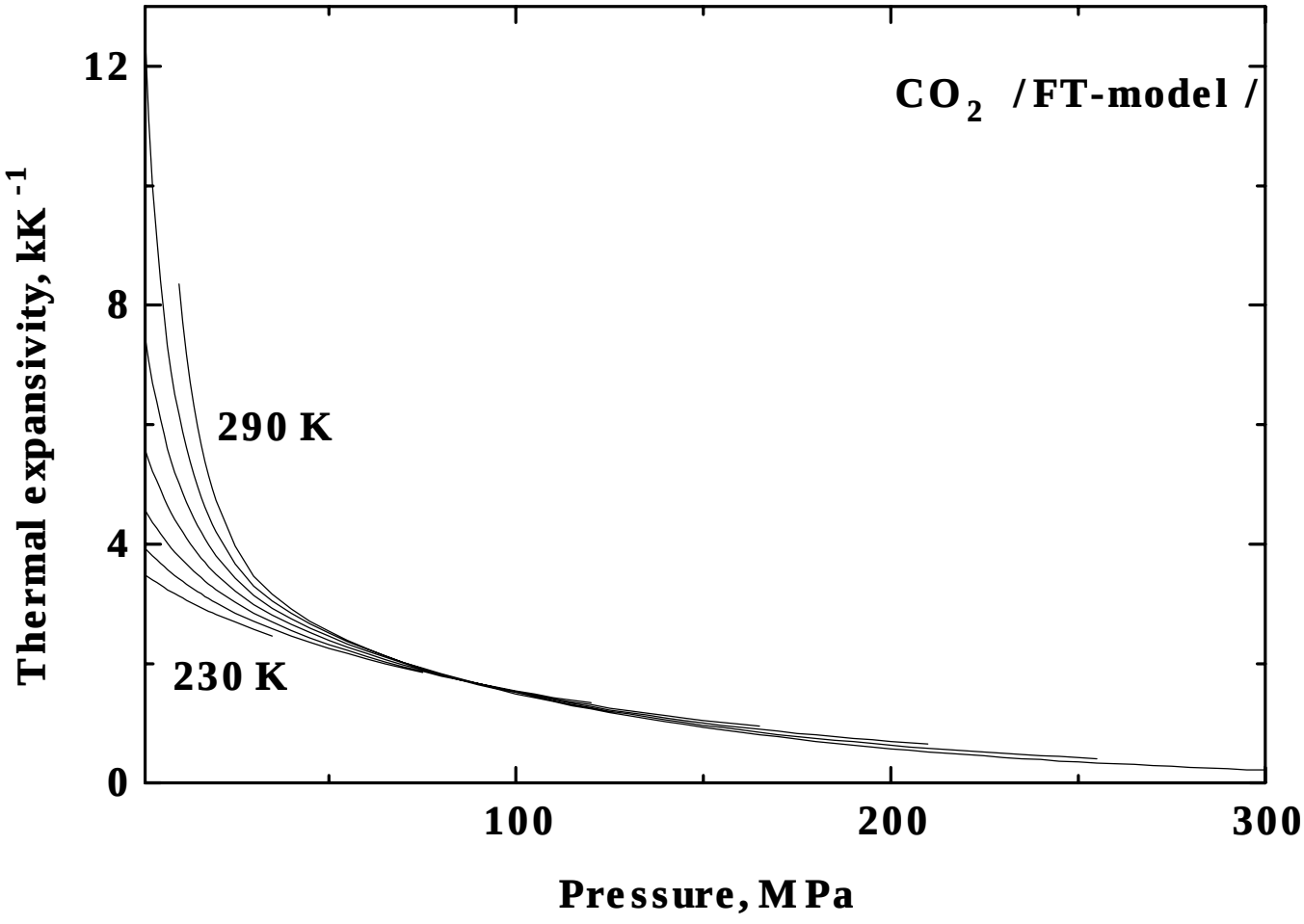
2
4
3
2
1
1000
875
750
625
500
375
250
220
240
260
280
300


CO2 /FT-model /
290 K
230 K
Thermal expansivity, kK -1
Pressure, MPa
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4
8
12
100
200
300

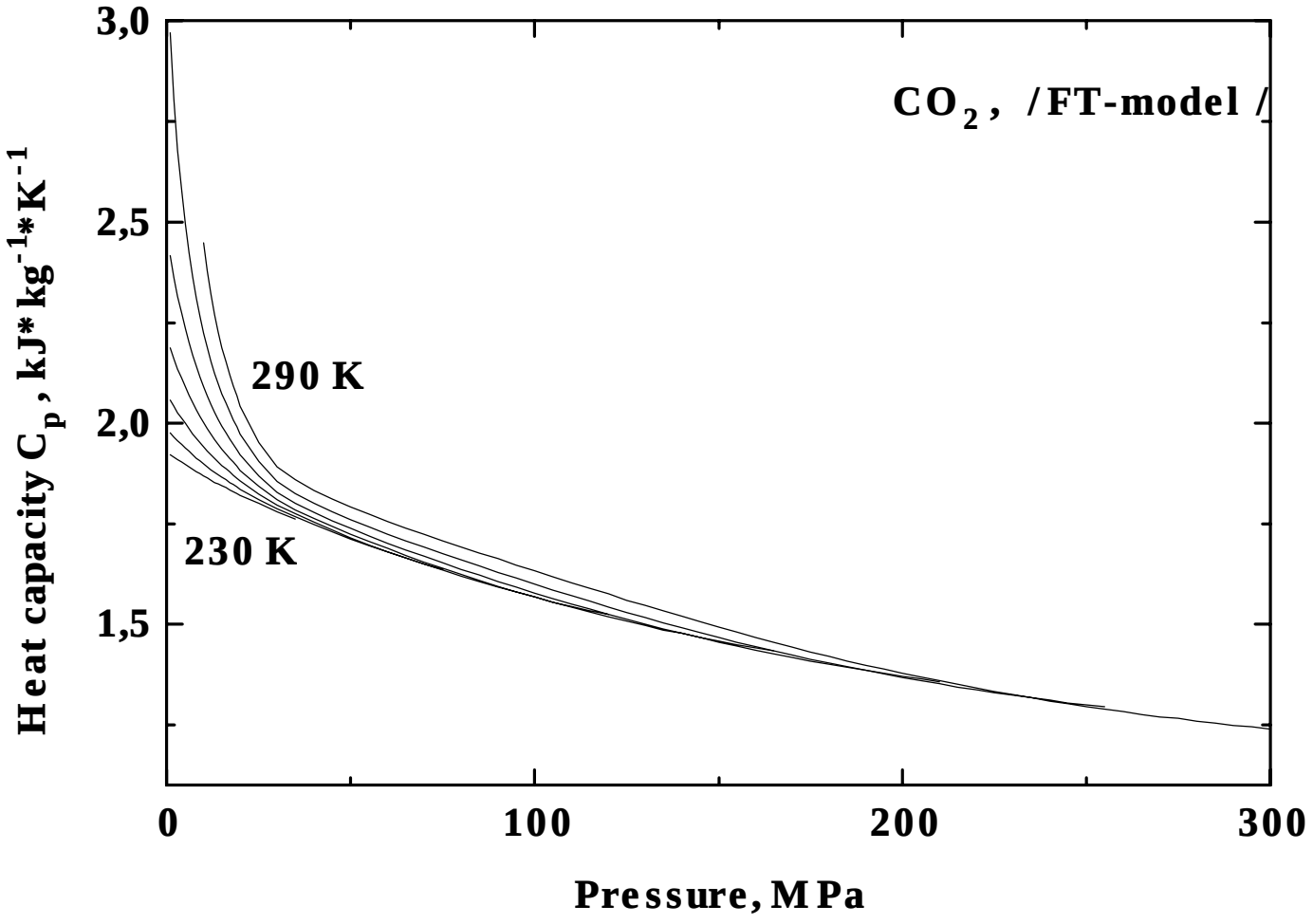
3,0
2,5
2,0
1,5
0
100
200
300
Heat capacity C_p, $kJ*kg^{-1}*K^{-1}$
Pressure, MPa
CO_2, /FT-model /
290 K
230 K

Table I. Coefficients of initial- and CXS- data for argon.

Properties	Coeff.	i = 0	i = 2	i = 3	i = 4
α_{P0} (K^{-1})	a_i	$6.0843 \cdot 10^{-3}$	$-5.8103 \cdot 10^{-5}$	$3.0952 \cdot 10^{-7}$	$5.5556 \cdot 10^{-10}$
W_0 ($m \cdot s^{-1}$)	b_i	1405.8	-5.4896		
C_{P0} ($J \cdot kg^{-1} \cdot K^{-1}$)	c_i	237.94	21.632	$-1.9798 \cdot 10^{-1}$	$6.3365 \cdot 10^{-4}$
P_S (Pa)	d_i	-5.74288	0.23141	1.3171	-2.79651
ρ^l ($kg \cdot m^{-3}$)	e_i	1.27129	0.26555	-1.15092	0.91552
$T_c = 150.86$ K, $\rho_c = 535.70$ $kg \cdot m^{-3}$, $P_c = 4.8979$ MPa					
$T^0_0 = 90$ K, $\rho^0_0 = 1431.2$ $kg \cdot m^{-3}$, $s^0_0 = 1.354$ $kJ \cdot kg^{-1} \cdot K^{-1}$, $h^0_0 = 84.47$ $kJ \cdot kg^{-1}$					

Table II. Coefficients of initial- and CXS- data for carbon dioxide.

Properties	Coeff.	i = 0	i = 1	i = 2	i = 3
α_{P0} (K^{-1})	a_i	$-1.8106\cdot10^{-3}$	$3.5437\cdot10^{-5}$	$-1.1622\cdot10^{-7}$	$1.9571\cdot10^{-10}$
W_0 ($m\cdot s^{-1}$)	b_i	2589.5	-6.5695		
C_{P0} ($J\cdot kg^{-1}\cdot K^{-1}$)	c_i	-2988.1	60.042	$-2.5483\cdot10^{-1}$	$3.6486\cdot10^{-4}$
P_S (Pa)	d_i	-7.057346	1.932188	-1.63612	-3.312470
ρ^l ($kg\cdot m^{-3}$)	e_i	1.778227	-0.4253792	-0.2671606	0.2652934
$T_c = 304.136$ K, $\rho_c = 467.6$ $kg\cdot m^{-3}$, $P_c = 7.3773$ MPa					
$T^0_0 = 225$ K, $\rho^0_0 = 1204.0$ $kg\cdot m^{-3}$, $s^0_0 = 2.656$ $kJ\cdot kg^{-1}\cdot K^{-1}$, $h^0_0 = 411.5$ $kJ\cdot kg^{-1}$					