



THE THERMODYNAMIC PROPERTIES OF SUPERCRITICAL FLUIDS: CASE OF CARBON DIOXIDE ♦

A. Abbaci*, A. Acidi

*Faculté des Sciences, Département de Chimie, Université Badji-Mokhtar B.
P. 12, El-Hadjar, Annaba (23200); *Email: azzedineabbaci@hotmail.com
Tél: 213 38845376 Fax:213 38868510*

Abstract: A new fundamental equation of state that describes the behavior of the thermodynamic properties of carbon dioxide in the vicinity of the critical point is formulated. In this work, we present an equation of state based on the crossover model that takes into account not only the scaling laws at the critical point but also the classical behavior far away from the critical point. The equation of state is constructed based on the new pressure data measured by Duschek and co-workers. We give the comparison with different set of thermodynamic-property data available, such as the pressure data, the specific heat data.

Keywords: *carbon dioxide, crossover model, equation of state, specific heat, thermodynamic properties.*

INTRODUCTION

To reduce or to avoid the use of organic solvents in extraction processes, supercritical fluids carbon dioxide is used as an alternative key substance due to its technological importance, such as its suitability in the extraction of natural products. Depending on

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special condition of temperature and pressure, the limit between the liquid and vapor phases disappears and above these special temperature and pressure, called the critical temperature and pressure, carbon dioxide is classified as a supercritical fluid. These supercritical fluids combine distinctive properties that are distinct from either vapors or liquids under standard conditions. These supercritical fluids will have both the characteristics of vapors that are capable to penetrate anything as well as the characteristics of liquids that are capable to dissolve natural products or chemical compounds. It is the purpose of this paper to predict the behavior of the thermodynamic properties of carbon dioxide in the supercritical region.

The work described in this paper is part of a research effort to develop a comprehensive fundamental equation for the thermodynamic properties of carbon dioxide in the critical region that extends to the classical region. The formulated equation of state covers the entire range of temperatures and densities around the critical region and also can describe the behavior of the thermodynamic properties of carbon dioxide in the classical region far away from the critical region. Several analytic equations of state as well as non-analytical equations of state were proposed earlier. Among these equations, we mention the global equation of Huang et al. [1], James F. Ely [2] which represent a preliminary attempt to address this problem, and the equation of state formulated by Ely et al. [3], which are not suitable for an accurate representation of the thermodynamic properties of fluids in the near-critical region and it became our task to supplement the global equation of state with an equation of state for the near-critical region. For this purpose, Albright et al. [4] formulated a representative equation of state for the thermodynamic properties of carbon dioxide in the near-critical region with the aid of the so-called revised and extended scaled parametric equation of state [5]. Then came the equation of state formulated by Chen and coworkers [6], Abbaci [7, 8] and Abbaci et al. [9-11] which was not only valid in the critical region but also can describe the behavior of carbon dioxide in the vicinity of the critical region. Based on new and more accurate pressure data measured by Duschek and coworkers [12] with the additional data measured by Michels and coworkers [13-15], it has become our task to reformulate a new equation of state that represents the thermodynamic properties of carbon dioxide in the wider range of temperatures and densities around the critical region.

The development of our equation of state had to be based on the P - ρ - T data (P is pressure, ρ density and T temperature) reported by Duschek and coworkers [12] and Michels and coworkers [13-15] since they provide adequate P - ρ - T information in the near-critical region but not suitable for our purpose, for, the data measured by Duschek and coworkers do not cover the range of validity of our equation of state. The experimental P - ρ - T data reported by Michels and coworkers [13-15] do extend to higher temperatures. It is then possible to obtain a fundamental equation of state that represented P - ρ - T data of Duschek and coworkers [12] and Michels and coworkers [13-15] and the isochoric specific heat C_v data of Edwards [16] along two isochores. The comparison with different sets of P - ρ - T and caloric properties from different sources is then made; the results will be commented subsequently.

For this purpose we shall describe our new theoretically based crossover equation of state in the subsequent section, we then discuss the fundamental equation, the application to carbon dioxide and use it to analyze the available experimental data for CO_2 in the critical region. This work concludes with a discussion in last section.

SPECIFICATION OF THE CROSSOVER MODEL

The so-called crossover model used earlier by Chen, Abbaci, Tang and Sengers CATS [7] is developed to give a new theoretically based equation of state for carbon dioxide in the critical region that incorporate the crossover from the scaled thermodynamic behavior asymptotically close to the critical point to the analytic classical thermodynamic behavior far away from the critical point. CATS [7] verified that their crossover model yields an accurate representation of the thermodynamic properties of several fluids in the critical region covering a large range of densities and temperatures around the critical point and extending into the far-critical region where analytic equations of state should be accurate. Hence, we decided to apply this crossover model to carbon dioxide.

FUNDAMENTAL EQUATION

Asymptotically close to the critical point the thermodynamic properties of fluids satisfy scaling laws with universal critical exponents and universal scaling functions [5]. Equations of state for fluids incorporating these scaling laws have been developed earlier. In previous works, a linear-model parametric equation of state revised to include a lack of vapor-liquid symmetry and extended to incorporate the first corrections beyond asymptotic scaling [17-19] has been used. The range of validity of such a scaled equation of state is still somewhat restricted and the agreement with the experimental data deteriorates very rapidly as soon as the scaled equations are extrapolated outside the near-critical region. On the other hand, outside the critical region the thermodynamic properties can be adequately represented by classical equations that are analytic everywhere. In order to combine the scaling laws near the critical point with classical equations one needs to use a certain mechanism that includes the crossover from scaled behavior near the critical point to analytic behavior far away from the critical point.

Starting from earlier work Nicoll et al. [20-22], we have developed a crossover model to represent the thermodynamic properties of fluids in the critical region [6-11]. This crossover model is based on the renormalization group theory of critical phenomena to include the cooperative effects associated with the long-range critical fluctuations up to a maximum microscopic wavenumber.

Let ρ be the density, T the temperature, P the pressure, μ the chemical potential and A/V the of Helmholtz free energy per unit volume. We make these properties dimensionless with the aid of the critical parameters [6-11]:

$$\tilde{\rho} = \rho/\rho_c, \quad \tilde{T} = -T_c/T, \quad \tilde{P} = PT_c/P_cT, \quad \tilde{\mu} = \mu\rho_cT_c/P_cT, \quad \tilde{A} = AT_c/P_cVT \quad (1)$$

In addition we define:

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \quad \Delta\tilde{T} = \tilde{T} + 1, \quad \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}) \quad (2)$$

and

$$\Delta\tilde{A} = \tilde{A} - \tilde{\rho}\tilde{\mu}_0(\tilde{T}) - \tilde{A}_0(\tilde{T}). \quad (3)$$

Here $\tilde{\mu}_0(\tilde{T})$ and $\tilde{A}_0(\tilde{T})$ are analytic background functions of T subject to the conditions that at the critical temperature $\Delta\tilde{\mu}(T = T_c) = 0$ and $\tilde{A}_0(T = T_c) = -1$.

Classical equations of state for the Helmholtz free energy density A imply that the classical part A_{cl} has an asymptotic expansion of the form:

$$\Delta \tilde{A}_{cl} = \frac{1}{2} t M^2 + \frac{1}{2} u_0 M^4 + \dots \quad (4)$$

Where t and M are temperature-like and density-like variables related to ΔT and $\Delta \rho$ in a manner to be specified below. In the sequel we find it convenient to write the coefficient u_0 of the M^4 term in (4) as $u_0 = u \Lambda$, where Λ is a dimensionless cutoff wave number [7]. In order to obtain a fundamental equation that can be applied in a large range of densities and temperatures around the critical point we retain six terms in the classical Landau expansion (4) for ΔA_{cl} :

$$\Delta \tilde{A}_{cl} = (1/2) t M^2 + (u_0/2!) M^4 + (a_{05}/5!) M^5 + (a_{06}/6!) M^6 + (a_{14}/4!) t M^4 + (a_{22}/2!2!) t^2 M^2 \quad (5)$$

As shown by Chen et al. [7] the theoretically predicted asymptotic behavior can be recovered from this expansion by the following transformation:

$$\Delta \tilde{A}_r = (1/2) t M^2 \mathbf{T} \mathbf{D} + (u_0/2!) M^4 \mathbf{D}^2 \mathbf{U} + (a_{05}/5!) M^5 \mathbf{D}^{5/2} \mathbf{V} \mathbf{U} + (a_{06}/6!) M^6 \mathbf{D}^3 \mathbf{U}^{3/2} + (a_{14}/4!) t M^4 \mathbf{T} \mathbf{D}^2 \mathbf{U}^{1/2} + (a_{22}/2!2!) t^2 M^2 \mathbf{T}^2 \mathbf{D} \mathbf{U}^{-1/2} - (1/2) \mathbf{T}^2 \mathbf{K} \quad (6)$$

where the functions \mathbf{T} , \mathbf{D} , \mathbf{U} , \mathbf{V} and \mathbf{K} are defined by

$$\begin{aligned} \mathbf{T} &= Y^{(2-1/\nu)/\omega}, \quad \mathbf{D} = Y^{-\eta/\omega}, \quad \mathbf{U} = Y^{1/\omega} \\ \mathbf{V} &= Y^{(2\omega_a-1)/2\omega}, \quad \mathbf{K} = \nu/\alpha \bar{u} \Lambda \left[Y^{-\alpha/\nu\omega} - 1 \right] \end{aligned} \quad (7)$$

In terms of a crossover function Y to be determined from

$$1 - (1 - \bar{u}) Y = \bar{u} \left(1 + \Lambda^2 / \kappa^2 \right)^{1/2} Y^{1/\omega} \quad (8)$$

with

$$\kappa^2 = t \mathbf{T} + 1/2 u \Lambda M^2 \mathbf{D} \mathbf{U}, \quad (9)$$

and

$$\bar{u} = u / u^* \quad (10)$$

In these expressions ν , η , ω and ω_a are universal critical exponents, u^* is also a universal constant. The values of the universal critical-region parameters are specified in table 1.

Table 1. Universal critical-region constants

ν	0.630
η	0.033
$\alpha = 2 \dots 3\nu$	0.110
Λ	0.510

The crossover model depends parametrically on the variable κ^2 defined by eq. (9). For small values of κ one recovers from eq. (6) the scaled critical behavior, while for large values of κ the crossover function Y approaches unity and eq. (6) reduces to the classical Landau expansion eq. (5).

In order to apply the crossover model of eq. (6) to fluids we need to introduce a proper translation to fluids variables [6-11]. This is accomplished by the

$$t = c_t \Delta \tilde{T} + c \left(\partial \Delta \tilde{A}_r / \partial M \right)_t, \quad (11)$$

$$M = c_\rho (\Delta \tilde{\rho} - d_1 \Delta \tilde{T}) + c \left(\partial \Delta \tilde{A}_r / \partial t \right)_M \quad (12)$$

with the corresponding transformation for $\Delta \tilde{A}_r$:

$$\Delta \tilde{A} = \Delta \tilde{A}_r - c \left(\frac{\partial \Delta \tilde{A}_r}{\partial M} \right)_t - \left(\frac{\partial \Delta \tilde{A}_r}{\partial t} \right)_M \quad (13)$$

where c , c_t , c_ρ and d_1 are system-dependent constants. Finally, the pressure is deduced from eq. (3) as:

$$\tilde{P} = \Delta \tilde{\mu} + \Delta \tilde{\rho} \Delta \tilde{\mu} - \Delta \tilde{A} - \tilde{A}_0(\tilde{T}) \quad (14)$$

APPLICATION TO CARBON DIOXIDE

The crossover model as applied to carbon dioxide contains the following system-dependent parameters: The critical parameters T_c , ρ_c , and P_c to be deduced either from an asymptotic analysis of the thermodynamic–property data near the critical point or reported by several experiments. The crossover parameters \bar{u} and Λ , the scaling-field parameters c , c_t , c_ρ and d_1 , the classical parameters a_{05} , a_{06} , a_{14} , a_{22} and the background parameters \tilde{A}_j which can be determined by fitting the crossover model to the P - ρ - T data of Duschek et al. [12] associated with those of Michels et al. [9, 11], and finally the caloric background $\tilde{\mu}_i$ which can be determined from experimental speed of sound data or specific heat data. In this work, we used the values of the system dependent parameters as found earlier [6]. Actually, the coefficients $\tilde{\mu}_i$ ($i = 0, 1$) are related to the zero-point values of energy and entropy and are not considered here. A survey of the available experimental information for the thermodynamic properties of carbon dioxide can be found in the work of Duschek et al. [12]. The primary experimental information used for the comparison with the thermodynamic surface in the critical region is provided by the P - ρ - T data reported by Duschek et al. [12] and those of Michels et al. [9-11] that extends beyond the data of Duschek et al..

A decision must be made concerning the values of the critical parameters. A survey of the critical–parameter values reported for CO₂ is also included in the work of Duschek et al. [12]. For a reason of consistency of our work, the critical parameters for carbon dioxide are those measured by Duschek et al. [12], which are as follows:

$$T_c = (304.136 \pm 0.015) \text{ K}, \rho_c = (467.6 \pm 0.6) \text{ kg.m}^{-3}, P_c = (7.3773 \pm 0.0030) \text{ MPa} \quad (15)$$

The values of the system-dependent parameters adopted for CO₂ in this work are presented in Table 2. The range of validity of our crossover equation is determined by:

$$\tilde{\chi}_r^{-1} \leq 2.38 \quad (16)$$

with the additional restriction that the temperature T should be within the range:

$$291 \text{ K} \leq T \leq 373 \text{ K} \quad (17)$$

and the density ρ within the range:

$$193 \text{ kg/m}^3 \leq \rho \leq 712 \text{ kg/m}^3 \quad (18)$$

Table 2. System-dependent constants for carbon dioxide

Parameters' nature	Parameters values
Crossover parameters	$\bar{u} = 0.39803$, $\Lambda = 1.4214$
Scaling parameters	$c_t = 1.5951$, $c_\rho = 2.4145$, $c = -0.02590$
Classical parameters	$a_{05} = -0.27063$, $a_{06} = 1.14228$, $a_{14} = 0.39839$, $a_{22} = 0.30116$
Pressure background parameters	$\tilde{A}_0 = -1$, $\tilde{A}_1 = -6.0079$, $\tilde{A}_2 = 4.5139$, $\tilde{A}_3 = -1.9509$, $\tilde{A}_4 = 5.1371$, $d_1 = -0.3323$
Caloric background parameters	$\tilde{\mu}_2 = -13.730$, $\tilde{\mu}_3 = -7.9191$, $\tilde{\mu}_4 = 32.249$, $\tilde{\mu}_5 = -93.274$

A comparison between the experimental P - ρ - T data of Duschek et al. and Michels et al. for temperature above 340 K and the values calculated from our equation is presented in figure 1 and plotted in the form of pressure deviations as a function of the reduced inverse compressibility $\tilde{\chi}_T^{-1}$ along various isotherms. The equation reproduces the data within the estimated experimental accuracy. Finally, we made a comparison with the P - ρ - T data reported by Ely et al. for pure carbon dioxide [23]. From the comparison we found that the maximum percent deviation to be of 0.20 %. This value shows that the data of Ely et al. are in excellent agreement with those of Duschek et al. [12]. In figure 2, we also present the liquid-vapor prediction from the present equation and compared to the data reported by Duschek et al. [24]. As can be seen from the figure, the agreement is excellent.

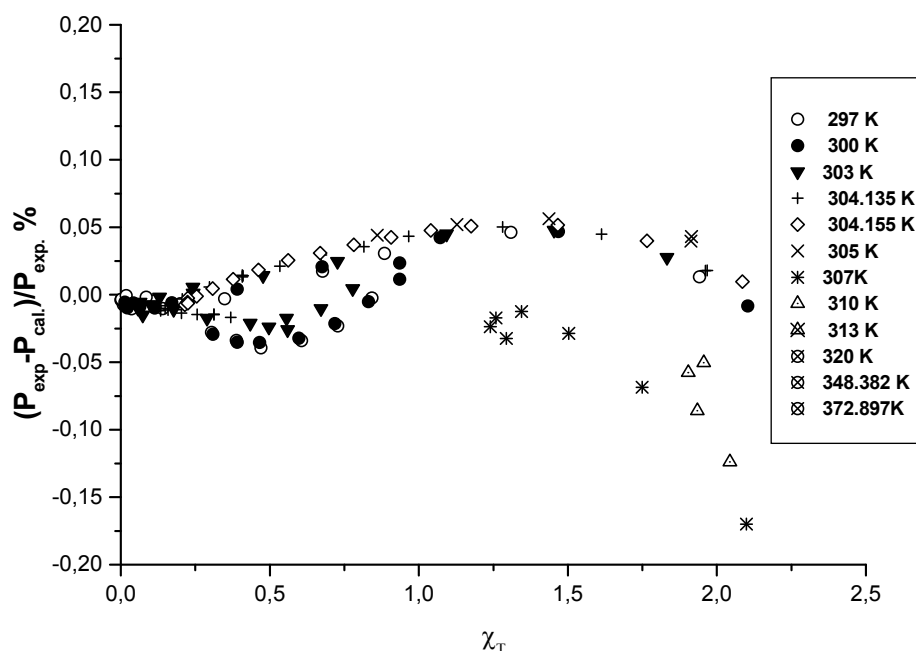


Figure 1. Percentage differences between the experimental pressures data of Duschek et al. and Michels et al. and the values calculated from the present equation as a function of the temperature

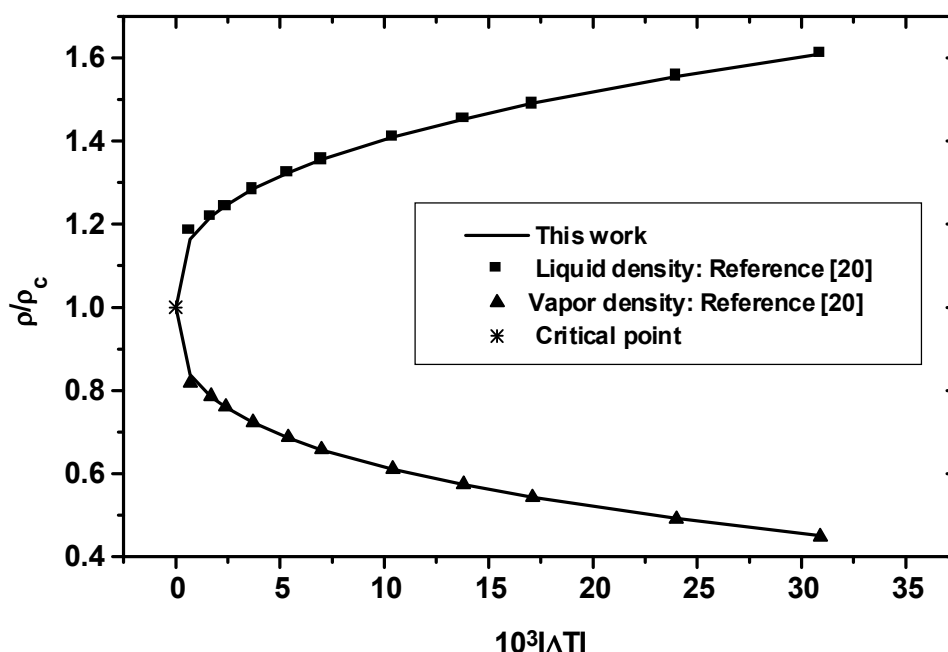


Figure 2. Liquid-vapor densities, the data points are those of Duschek et al. [24] and the curve are the values predicted from the present equation

CALORIC PROPERTIES

In previous work [8 - 11], the analytic background coefficients $\tilde{\mu}_2$ and $\tilde{\mu}_3$ were determined by fitting the equation of state to the speed of sound, for speed-of-sound data are more sensitive to the choice of coefficients $\tilde{\mu}_i (i > 1)$ so that these constants can be determined more accurately. However, in this work, we used the reliable C_v data measured by Edwards [16] along two isochores, that is the off-critical isochore at $\rho = 434 \text{ kg/m}^3$ and the critical isochore at $\rho = 467 \text{ kg/m}^3$ to complete the formulation of our fundamental equation of state for CO_2 . The equation reproduces correctly the behavior specific-heat data of Edwards [16]. Figures 3 and 4 show the comparison of the experimental data reported by Edwards and Buckingham and the calculated from the crossover model. Specific heat data for carbon dioxide have been reported also by Amirkhanov and coworkers at different isochores [25]. A comparison is made based on the caloric parameters deduced from Edwards data, and the deviations are found to be very low at all isochores.

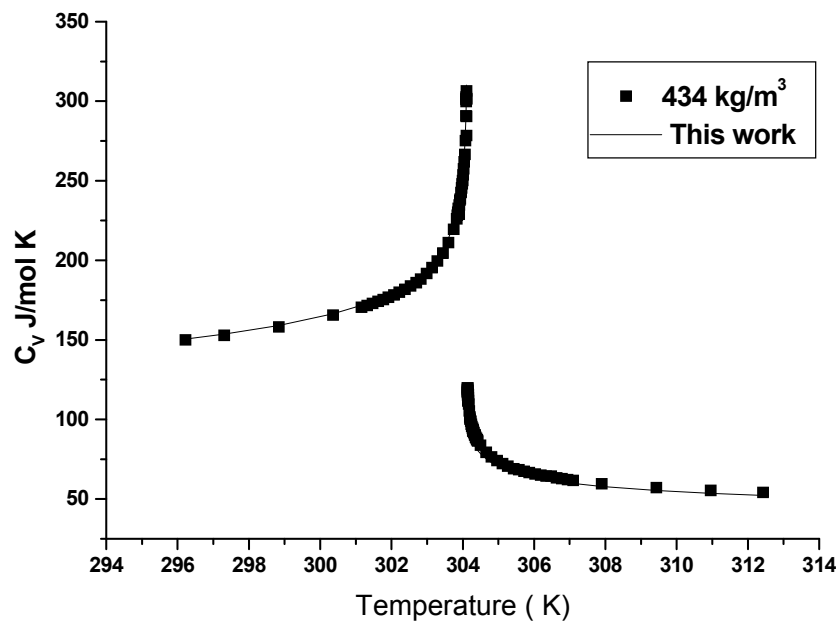


Figure 3. Specific heat at constant volume of carbon dioxide at $\rho = 434 \text{ kg/m}^3$. The data points indicate the experimental data reported by Edwards and Buckingham [16] and the solid curves represent the values calculated from the crossover model

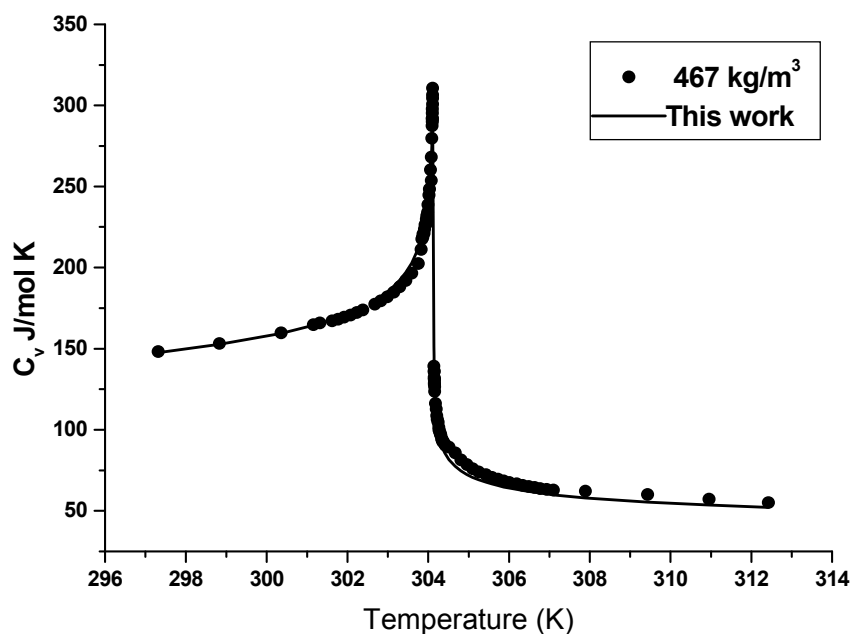


Figure 4. Specific heat at constant volume of carbon dioxide at $\rho = 467 \text{ kg/m}^3$. The data points indicate the experimental data reported by Edwards and Buckingham [16] and the solid curves represent the values calculated from the crossover model

DISCUSSION

We have formulated a new fundamental equation based on the crossover model in conjunction with the newly measured pressure data reported by Duschek et al.. Despite of the fact the pressure data of Michels et al. are old compared to those reported by Duschek et al., they remain one of the most accurate data to date.

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