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**A Combination of Scale Equations with
a Classical Approach for the Numerical
Determination of the Helmholtz's Free
Energy of Carbon Dioxide in the
Neighborhood of the Critical Region**

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A-COMBINATION OF SCALE EQUATIONS WITH A CLASSICAL APPROACH FOR THE
NUMERICAL DETERMINATION OF THE HELMHOLTZ'S FREE ENERGY OF CARBON
DIOXIDE IN THE NEIGHBORHOOD OF THE CRITICAL REGION.

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ABSTRACT

The available data for state properties near the critical region are generally limited to the constants describing the critical point. In order to attain a better view of the associated phenomena an equation is developed for the Helmholtz's free energy, a very important and useful thermodynamic potential, commonly used for the generation of thermodynamic tables. The free energy is not directly measurable and more to that, the macroscopic thermodynamics only provides an existence postulate without any further information on the explicit form of this potential.

As far as developing an explicit form of the Helmholtz's potential, a mathematical formulation is proposed using the non-analytical power laws (scale equations) in order to proceed with a computer algorithm, which in turn could give detailed information of the critical behavior whenever a substance approaches its critical region. Even though the algorithm is presented for a particular substance (carbon dioxide), the results can easily be generalized to any other substances.

1. Introduction

The state of a pure fluid phase is completely determined by two independent intensive state properties. One of the fundamental postulates of classical thermodynamics is that for each pair of such properties there exists a unique characteristic state function or potential, such that all of the thermodynamic properties can be adequately described by the potential.

There are two fundamental reasons to select T and v as a pair of specially adequate independent specific thermodynamic variables, first of all T and v (temperature and specific volume) are easily measurable and the specific free energy function, the associated potential:

$$f = u - Ts = f(T, v) \quad (1)$$

represents a non-ambiguous function of T and v , for all the possible states of the fluid, including the two phase region.

The specific free energy is not directly measurable, however the entropy and all of the most important state properties may be expressed as functions of f and its derivatives, which in turn do only depend on (T, v) .

The purpose of this paper is to present an algorithm for the numerical calculation of the free energy as a function of the specific density ($\rho = 1/v$) and the thermodynamic temperature for a pure substance (T, ρ) , since the intention is to improve data in the neighborhood of the critical region, a combination of the analytical behavior, considering the IUPAC formulation (1) is used, combined with the non analytical or scale equations (2).

The polar coordinates of the scale equations are then transformed to develop an algorithm for calculating the most important thermodynamic properties.

2. The specific free energy

In addition to the zeroth law (state equation) the thermodynamic potentials provide an excellent tool for describing the behavior of compressible substances. In equilibrium thermodynamics, often called "thermostatistics", one of the most adequate functions for fully describing the state of a substance is that of Helmholtz or specific free energy function:

$$f = u - Ts = f(T, v) = f(T, \rho) \quad (2)$$

equation (2) may be successfully used in fully describing the fluid states of a substance (and even solid states). Thus, precise thermodynamic data may be generated in the two phase region between both branches of the coexistence curve.

However, the free energy is not directly measurable; although (T, ρ) are measurable, and, what is still more important, entropy and all of the main state properties may be expressed as functions of f and its derivatives, which in turn are only functions of (T, v) or (T, ρ) .

In order to save time and space, the following notation is adopted for the derivatives of f :

$$\begin{aligned} f_T &= (\partial f / \partial T)_v, \quad f_v = (\partial f / \partial v)_T; \\ f_{Tv} &= (\partial^2 f / \partial T \partial v), \text{ etc} \end{aligned} \quad (3)$$

Making use of the convention (3) and of the known thermodynamic relations, table I may be obtained, showing the

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various thermodynamic properties of state as a function of the specific free energy and its derivatives. The next step is to select a model function $\Psi = \Psi(T, \rho, \underline{a}) = f(T, \rho)$, where \underline{a} is a vector parameter, to be obtained with the aid of experimental data, Ahrendts & Baehr (3).

In order to obtain the free energy of measurable variables, the process consists of three steps:

$$a) \quad u - u_0 = \int_{\rho_0}^{\rho} (P/\rho^2)(\partial P/\partial T)_{\rho} d\rho \quad (4)$$

$$b) \quad s - s_0 = \int_{\rho_0}^{\rho} (-1/\rho^2)(\partial P/\partial T)_{\rho} d\rho \quad (5)$$

$$c) \quad f - f_0 = u - u_0 - T(s - s_0) \quad (6)$$

Where the sub-index "o" refers to an arbitrary level of reference. From the expressions (4) to (6), it may be easily noted that a state equation is needed. To proceed further, the use of the scale equations is proposed in the next section, along with adequate subroutines, the handling is carried on by a digital computer.

3. The non-analytical state equation.

As previously mentioned, the following scale equations are proposed to be used as a substitution to the state equation for the region, where the classical behavior does not reproduce the actual phenomena (2):

$$\Delta p = \frac{\rho - \rho_c}{\rho_c} = r^{\beta} \theta g \quad (7)$$

$$\Delta p = \frac{P - P_c}{P_c} = r^{\beta(\delta+1)} q\theta + C_1 \Delta T + \frac{ar^{\beta\delta}(1-\theta)^2}{T_c} \quad (8)$$

$$\Delta T = \frac{T - T_c}{T_c} = r^{\beta(1-b^2\theta^2)} \quad (9)$$

The function $q(\theta)$ represents a polynomial of the form:

$$q(\theta) = I_0 + I_2 \theta^2 + I_4 \theta^4 + c \left| 1 - b^2 \theta^2 \right|^{2-\alpha} \quad (10)$$

Where T_c , ρ_c and P_c , are the critical values of temperature density and pressure respectively. All of the constants are listed in table 2.

Equations (7) to (10) are non linear, and the elimination of the polar coordinates is quite elaborated and leads to a very long expression:

$$\begin{aligned} \Delta p = & \frac{1}{2} X \cdot \left[I_0 + I_2 \cdot \left(\frac{\Delta \rho}{(1/2)gX} \right) \right] \\ & + I_4 \cdot \left[\left(\frac{\Delta \rho}{(1/2)gX} \right)^4 + c \right]^{1-b^2} \\ & \cdot \left\{ \left(\frac{\Delta \rho}{(1/2)gX} \right) \right\}^{2-\alpha} + c_1 \Delta T + a \left(\frac{1}{2} X \right)^{\delta} \\ & \cdot \frac{\Delta \rho}{1/2gX} \cdot \left\{ 1 - \left(\frac{\Delta \rho}{1/2gX} \right)^2 \right\} \end{aligned} \quad (11)$$

Where the following substitutions have been made:

$$X = \Delta T + \Delta t \quad (12)$$

$$\Delta t = \left\{ \Delta T + \left\{ (\Delta T)^2 + \frac{4b^2}{g^2} (\Delta \rho)^2 \right\}^{1/2} \right\} \quad (13)$$

(11) is therefore a state equation for CO2 in the critical region, with P as a function of (T, ρ) , which is to be processed in a computer so as to obtain the state properties described in table 1.

The flow chart is shown in figure 1, the subroutines DEU and DES, correspond to the numerical integration of the internal energy and entropy, from the basic state equations incorporating the non-analytical behavior as given by the scale equations.

4. Acknowledgements.

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5. References

- 1) Angus, S., Armstrong, B. and K.M. de Reuck, editors IUPAC: INTERNATIONAL THERMODYNAMIC TABLES OF THE FLUID STATE, CARBON DIOXIDE, Pergamon Press, London, N.Y. (1973)
- 2) Chapela, G.A. and Rowlinson, J.S., "Accurate representation of thermodynamic properties near the critical point", J. Chem. Society, 70: 584-593 (1974)
- 3) Ahrendts, J. und Baehr, H.D., "Die direkte Verwendung von Messwerten beliebiger thermodynamischer Zustandsgroessen zur Bestimmung Kanonischer Zustandsgleichungen", Forsch. Ing.-Wes. 45 Nr. 1 (1979)

Table 1.

STATE PROPERTIES AS FUNCTIONS OF THE SPECIFIC FREE ENERGY f
AND ITS DERIVATIVES FOR A PURE COMPRESSIBLE SUBSTANCE.

State Property	relationship with f
Pressure p	$-f_v$
Specific entropy s	$-f_T$
Specific internal energy u	$f - Tf_T$
Specific enthalpy $h \equiv u + pv$	$f - Tf_T - vf_v$
Specific heat at const. vol.	$-Tf_{TT}$
Specific heat at const. pressure	$-T(f_{TT} - f_{Tv}^2/f_{vv})$
Velocity of sound $a = v[-(\partial p/\partial v)_s]^{1/2}$	$v(f_{vv} - f_{Tv}^2/f_{TT})^{1/2}$
Joule-Thomson coefficient $\alpha_h = (\partial T/\partial p)_h$	$-(v + Tf_{Tv}/f_{vv})/c_p$

Table 2. PARAMETER VALUES FOR THE SCALE EQUATION (2)

Constant	Value	Constant	Value
b^2	1.4402	c for $T > T_c$	240.4358
α	0.065	c for $T < T_c$	-58.38316
β	0.347	I_0	36.98893
g	1.4918	I_2	-82.07936
δ	4.576	I_4	56.66053
c_1	6.98		

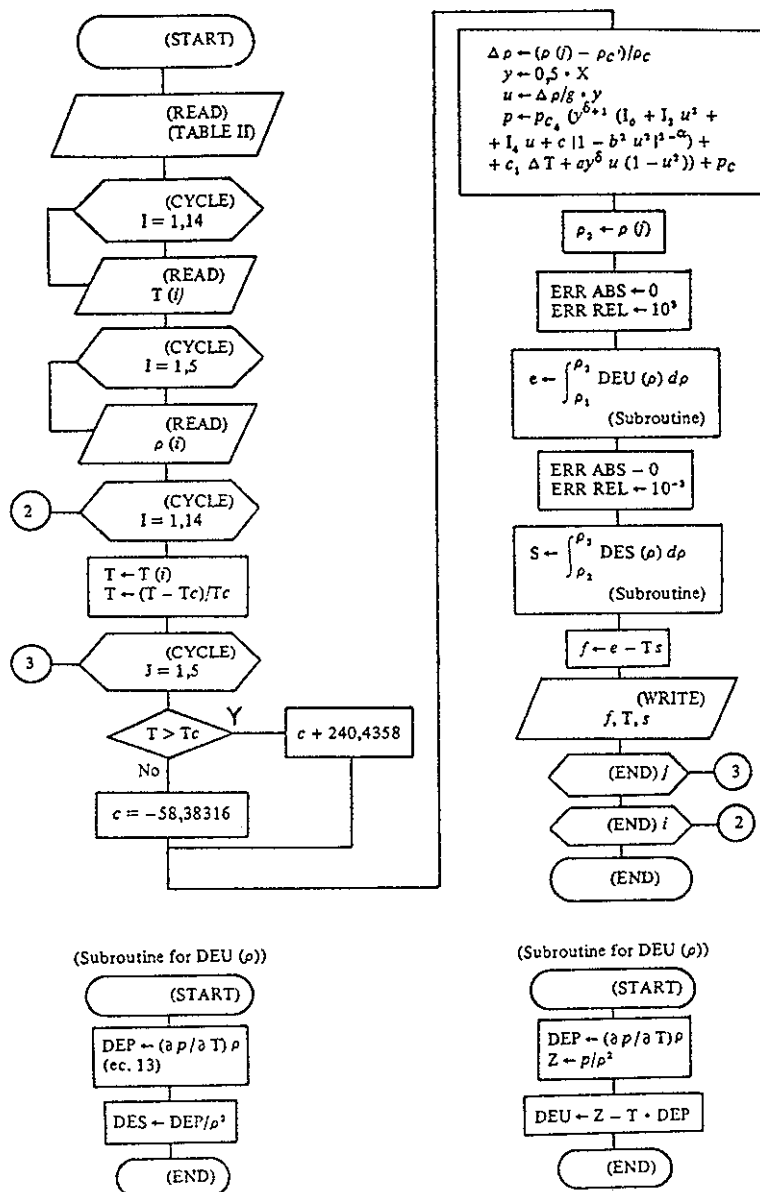


Fig. 1. FLOW DIAGRAM FOR THE NUMERICAL CALCULATION OF THE SPECIFIC FREE ENERGY