

Equation of State for Carbon Dioxide

Youngil Kim

School of Architecture, Seoul National University of Technology Seoul 139-743, Korea

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Abstract

An equation of state (EOS) for carbon dioxide has been presented by Span and Wagner (1996). This equation of state is accurate but contains many terms. Some of the terms are complex exponential which become difficult for computation. Therefore a new simple equation of state with 30 terms is proposed. Bank of terms are suggested and an optimum set of terms is selected by a random search method. This new equation of state with less terms and simple exponential is simpler to use. The two equations of state are compared with the available experimental data. The results show that the new EOS is less accurate than Span and Wagner in gas and liquid regions but more accurate in the critical region.

Keywords: Carbon dioxide(CO₂), Equation of state(EOS), Random search method, Helmholtz free energy, Refrigerant

1. Introduction

Before the emergence of CFC, HCFC or HFC refrigerants, CO₂ played an important role as refrigerants in refrigeration system due to its environmentally friendly nature and ease of acquirability. However, after chlorofluorocarbon compounds have been developed in 1930s, CO₂ has transferred its role as refrigerants to these newly developed artificial compounds. Studies have indicated that chlorofluorocarbon compounds that are widely used as refrigerants in vapor-compression refrigeration cycles and as propellants are the major suspect to the depletion of the upper atmosphere ozone layer which protects the earth from the harmful radiation. Molina and Rowland (1974) first presented the theory that chlorofluorocarbons slowly migrate into the stratosphere where they decompose by action of sunlight and split off free chlorine molecules that react with ozone, thus reducing the concentration of ozone in the upper

atmosphere. Studies are being done to replace chlorofluorocarbon refrigerants with alternatives that have less or no ozone depletion and greenhouse warming potential, yet possess appropriate thermodynamic properties for a refrigeration cycle. Carbon dioxide which has zero ozone depletion potential and little greenhouse warming potential, re-emerged as a possible replacement for fluorocarbon refrigerants in 1989 and the intensity of research efforts has increased steadily since that time (Lorentzen and Pettersen, 1993).

Carbon dioxide has become an important substance both in industrial and scientific applications. In order to design components or run simulation programs using carbon dioxide as a working fluid, an accurate equation of state that describes thermodynamic properties of this substance becomes essential. Recently, an accurate equation of state for carbon dioxide has been presented by Span and Wagner (1996). This equation of state is accurate but contains many terms. Some of the terms are complex exponential which become difficult for computation. Therefore a new simple equation of state with 30 terms is proposed in

^{*}Corresponding author. Tel.: +82 2 970 6557, Fax.: +82 2 974 1480
E-mail address: yikim@snut.ac.kr

this study.

The fundamental equation used to describe all thermodynamic properties is the Helmholtz free energy. The Helmholtz free energy is represented by the summation of ideal and residual contributions.

$$\alpha(\delta, \tau) = \alpha^o(\delta, \tau) + \alpha^r(\delta, \tau) \tag{1}$$

where $\alpha = a/(RT)$ is dimensionless Helmholtz free energy, $\delta = \rho/\rho_c$ is reduced density, $\tau = T_c/T$ is inverse of reduced temperature. Superscript 'o' denotes ideal gas and superscript 'r', residual.

For critical parameters of carbon dioxide, the evaluation of Duschek et al. (1990) is used. The values are $T_c=304.1282$ K, $P_c=7.3773$ MPa, $\rho_c=467.6$ kg/m³ and $M=44.0098$ kg/kmol.

Instead of fitting experimental data, data to be fitted are generated using Span and Wagner EOS. The objective is to develop a simpler form of EOS for carbon dioxide using suggested bank of terms and an optimization process. If this method proves successful, then experimental data will be used to develop a new EOS for carbon dioxide.

2. Thermodynamic relations

Once the residual Helmholtz free energy is determined, other thermodynamic properties can be derived as shown in the following equations. The subscript variables denote differentiation with respect to that factor.

Compressibility factor

$$Z = 1 + \delta\alpha'_\delta \tag{2}$$

Internal energy

$$\frac{u}{RT} = \tau(\alpha'_\tau + \alpha''_\tau) \tag{3}$$

Entropy

$$\frac{S}{R} = -(\alpha_0 + \alpha r) + \tau(\alpha'_\tau + \alpha''_\tau) \tag{4}$$

Fugacity coefficient

$$\ln \phi = \alpha^r + Z - 1 - \ln Z \tag{5}$$

Second virial coefficient

$$B \cdot \rho_c = \lim_{\delta \rightarrow 0} \alpha'_\delta \tag{6}$$

Z is compressibility factor, u is internal energy, R is

gas constant, ϕ is fugacity coefficient and B is second virial coefficient.

2.1 Equation of state by span and Wanger

The equation of state by Span and Wagner (1996) is valid up to pressures of 30 MPa and up to temperatures of 523 K. The estimated uncertainty of the equation ranges from $\pm 0.03\%$ to $\pm 0.05\%$ in the density, $\pm 0.03\%$ to $\pm 1\%$ in the speed of sound, and $\pm 0.15\%$ to $\pm 1.5\%$ in the isobaric heat capacity. Special interest has been focused on the description of the critical region and the extrapolation behavior of the formulation.

Span and Wagner EOS contains 42 terms. Among them, 8 terms are complex exponential which become difficult for computation. The bank of terms which was used in the optimization of the final equation of state contained a total of 860 terms. The resulting formulation for the residual part of the Helmholtz function is

$$\begin{aligned} ar(\delta, \tau) = & \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{34} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{\epsilon_i}} \\ & + \sum_{i=35}^{39} n_i \delta^{d_i} \tau^{t_i} e^{-\alpha_i(\delta-\epsilon_i)^2 - \beta_i(\tau-\gamma_i)^2} \\ & + \sum_{i=40}^{42} n_i \Delta^b \delta \tau^t e^{-C_i(\delta-1)^2 - D_i(r-1)^2} \end{aligned} \tag{7}$$

where $\Delta = \{(1 - \tau) + A_i[(\delta - 1)^2]^{1/(2\beta_i)}\}^2 + B_i[(\delta - 1)^2]^{a_i}$.

The argument in the exponential terms is a function of density and temperature, and this complicates the computation. The coefficients for Eq. (7) are given by Span and Wagner (1996) and will not be elaborated here. The ideal gas Helmholtz is given as

$$\alpha^o(\delta, \tau) = \ln \delta + b_1 + b_2 \tau + b_3 \ln \tau + \sum_{i=4}^8 b_i \ln[1 - e^{-r\theta_i}] \tag{8}$$

The coefficients for Eq. (8) are given in Table 1.

Table 1. Coefficients for Eq.(8)

i	b_i	θ_i
1	8.37304456	
2	-3.70454304	
3	2.50000000	
4	1.99427042	3.15163
5	0.62105248	6.11190
6	0.41195293	6.77708
7	1.04028922	11.32384
8	0.08327678	27.08792

2.2 A new equation of state

For the new equation of state, following form is proposed for the Helmholtz free energy.

$$\alpha^r(\delta, \tau) = \sum_{i,j,k} A_{ijk} \delta^i \tau^j \exp(-m_k \delta^k) \quad (9)$$

where

$$d_i = 0.9 + 0.1i \quad (i = 1, \dots, 141) \quad (10)$$

$$t_j = 0.1j \quad (j = 1, \dots, 300) \quad (11)$$

$$m_k = 0 \text{ if } k = 0, m_k = 1 \text{ if } k = 1, \dots, 6 \quad (12)$$

From a total of $141 \times 300 \times 7 = 296,100$ terms, a random search method is used to find an optimum set of terms that minimizes a score function S as defined in Eq. (13). z denotes any thermodynamic property as a function of two independent variables x and y , which in this case are τ and δ . Total uncertainty ω is obtained from the Gaussian error propagation formula. σ_x , σ_y , and σ_z denote the uncertainties of the variables x , y and z , respectively, which are obtained from experimental uncertainties.

$$S = \sum_{i=1}^N \left[\frac{z_{\text{exp},i} - z_{\text{calc},i}(x, y)}{w_i} \right]^2 \quad (13)$$

$$w_i^2 = \left[\sigma_z^2 + \left(\frac{\partial z}{\partial x} \right)^2 2\sigma_x^2 + \left(\frac{\partial z}{\partial y} \right)^2 2\sigma_y^2 \right] \quad (14)$$

Starting from an arbitrarily selected set of initial terms, the search algorithm looks for a better set of terms by interchanging terms that are not chosen. The new terms are chosen randomly and after a certain number of tries it increases the number of terms for interchange. Three constraints at the critical point are imposed by the Lagrange multiplier (Hust et al., 1967; De Reuck et al., 1979)

$$P_r = 1, \quad \left(\frac{\partial P_r}{\partial \delta} \right)_\tau = 0, \quad \left(\frac{\partial^2 P_r}{\partial \delta^2} \right)_\tau = 0 \quad (15)$$

The data that are to be fitted are generated with Span and Wagner EOS. Figure 1 shows the distribution of single-phase data generated for the fit. From an optimization process, thirty terms are chosen and the coefficients in Eq. (16) are given in Table 2.

$$\alpha^r(\delta, \tau) = \sum_{i=1}^{30} a_i \delta^i \tau^i \exp(-m_i \delta^{n_i}) \quad (16)$$

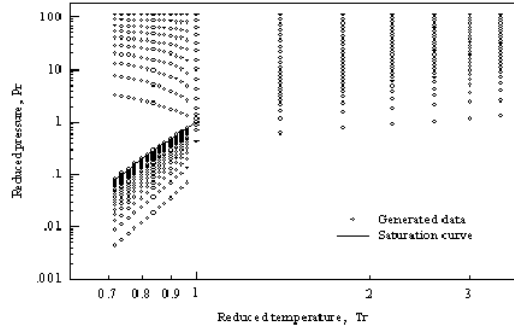


Fig. 1. Distribution of data to be fitted.

Table 2. Coefficients for Eq.(16)

i	a_i	d_i	t_i	m_i	n_i
1	33.8633836119084E+00	1.0	0.8	0	0
2	-42.5107601679589E+00	1.0	0.9	0	0
3	13.2333181388883E+00	1.0	1.5	0	0
4	-5.81979086093027E+00	1.0	2.0	0	0
5	-2.77959305544413E-01	1.5	5.1	0	0
6	.357828692610715E+00	2.0	0.5	0	0
7	.502011295316372E+00	2.1	2.9	0	0
8	-.433224010197574E+00	2.5	2.3	0	0
9	.785024502717065E-02	5.4	0.9	0	0
10	-.217445852349975E-02	6.1	0.6	0	0
11	.463960152694376E-05	1.0	24.4	1	1
12	-.161450283077738E+00	1.6	0.6	1	1
13	-.354234365287741E+00	2.5	0.8	1	1
14	.859239169914224E+00	3.6	2.3	1	1
15	-.749027753036816E+00	3.7	1.6	1	1
16	-.998311655008879E-02	5.2	3.1	1	1
17	.247828544813558E-03	9.7	0.8	1	1
18	.705252608291708E-05	10.7	2.2	1	1
19	.124194088430945E-01	1.7	11.4	1	2
20	.156030071557546E-01	2.4	8.6	1	3
21	-.382546248527141E-01	2.4	13.8	1	3
22	.729755322097156E-02	3.5	5.1	1	3
23	-.140757536497543E-02	2.3	0.2	1	4
24	.207580000636318E-02	2.9	27.1	1	4
25	.261888310538171E-02	4.5	17.5	1	4
26	.119645812491564E-01	1.3	10.4	1	5
27	-.110228135294275E-01	2.0	15.9	1	5
28	-.347274855359558E-03	11.8	3.8	1	5
29	-.707976507540442E-03	1.1	16.3	1	6
30	.783787974459364E-04	14.9	1.9	1	6

2.3 Experimental data

Several experimental measurements of various thermodynamic properties have been carried out for carbon dioxide. In this study, the experimental data are compiled only to compare the accuracy of the two equations of state. Table 3 lists the experimental data that have been compiled for comparison. Figure 2 shows the distribution of the experimental data.

Table 3. Experimental data for carbon dioxide.

Source	Type	N	T [K]	P [MPa]
Dusschek et al. (1990a)	T-P- ρ_g	42	217~304	
	T-P- ρ_f	50	217~304	
Dusschek et al. (1990b)	T-P- ρ	360	217~340	0.3~9.0
	T-B	7	220~340	
Gilgen et al. (1992)	T-P- ρ	264	220~360	0.5~13.5
Fenghour et al. (1995)	T-P- ρ	120	330~698	3.0~34.2
Abdulagatov et al. (1994)	T- ρ -C _v		280~355	

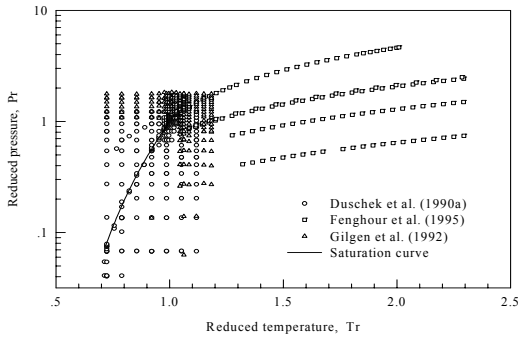


Fig. 2. Distribution of experimental data.

Table 4. Percentage absolute error deviation.

	N	Span	This work
Gas	411	0.1433	0.1888
Critical	167	0.5771	0.3956
Liquid	164	0.4036E-2	0.1959E-1
Average	742	0.2415	0.2013

3. Results

Comparisons are made between the experimental data and the predictions by the two EOS's. For a given set T_r and P_r , the percentage absolute error deviation (PAED) of calculating δ is calculated. N indicates the total number of the data set.

$$PAED(\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{\delta_{calc} - \delta_{exp}}{\delta_{exp}} \right| \quad (17)$$

Reduced density δ is a function of temperature and pressure. By varying the pressure with the temperature fixed, one gets a constant temperature line. Since the slope of a constant temperature line differs greatly depending on its phase, all measurements are divided into three regions (critical: $2/3 < \delta < 1.5$ and $Tr < 1.25$; gas: $\delta < 1$; liquid: $\delta > 1$: the overlapping region is considered as critical) as proposed by Platzter et al. (1990). Table 4 shows the PAED of two EOS's. The

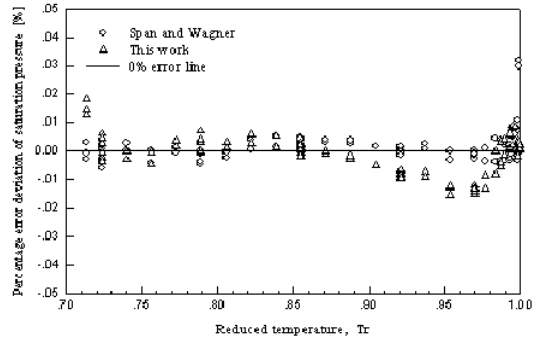


Fig. 3. Deviation of saturated pressure.

average of error is calculated by averaging the errors of three regions.Span and Wagner EOS shows better accuracy in gas and liquid regions but in critical region, the prediction by this work EOS is better. Considering that special treatment has been done by Span and Wagner to better predict properties in the critical region, the capability of this work EOS in this region is quite promising.

Large deviations in the critical region are expected since the slopes of constant temperature line are relatively flat near the critical region. This will augment the error of estimating density for a given temperature and pressure set.

Saturated properties are obtained by imposing the Maxwell condition at vapor-liquid equilibrium.

$$\phi_f = \phi_g \quad (18)$$

Ninety two sets of saturated pressure data are collected (Dusschek et al., 1990a) and deviations between these values and the saturation pressures predicted by two EOS's are shown in Fig. 3. Percentage absolute error deviation of estimating saturated pressure are 0.0032% and 0.0051% for Span et al. and this work, respectively.

4. Conclusions

A new equation of state for carbon dioxide has been developed. From a suggested 296,100 terms, optimum 30 terms has been selected by a random search method. The data to be fitted have been generated with Span and Wagner EOS.

Comparisons are made between the experimental data and the predictions by the two EOS's for the single and two-phase regions. For a single-phase region, percentage absolute error deviation using

Span and Wagner EOS are 0.1433% for gas, and 0.5771% for critical, 0.0040% for liquid region. With this work EOS, they become 0.1888%, 0.3956 and 0.0196%. For a two-phase region, PAED for estimating saturated pressure becomes 0.0032% and 0.0051% for Span et al. and this work, respectively.

Though the accuracy has been sacrificed somewhat with less terms, a search method used in this work is efficient in optimizing an equation of state.

Nomenclature

A	: Helmholtz free energy
b	: Coefficient
B	: Second virial coefficient
i, j, k	: Indices
m, n	: Indices
M	: Molecular weight
P	: Pressure
R	: Universal gas constant
s	: Entropy
S	: Score function
T	: Absolute temperature
u	: Internal energy
w	: Total uncertainty
x, y, z	: Variables
Z	: Compressibility factor

Greek Symbols

α	: Dimensionless Helmholtz free energy
δ	: Reduced density
θ	: Coefficient
ρ	: Density
σ	: Uncertainty
τ	: Inverse of reduced temperature,
ϕ	: Fugacity coefficient

Subscript

c	: Critical
f	: Saturated liquid
g	: Saturated vapor
s	: Saturated

Superscript

o	: Ideal
r	: Residual

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