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Vorobiova, Hanna

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Kontakt/Contact

ZBW – Leibniz-Informationszentrum Wirtschaft/Leibniz Information Centre for Economics
Düsternbrooker Weg 120
24105 Kiel (Germany)
E-Mail: [rights\[at\]zbw.eu](mailto:rights[at]zbw.eu)
<https://www.zbw.eu/econis-archiv/>

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Hanna Vorobiova

MODIFICATION OF SCALED EQUATION OF STATE TO DETERMINE THE PRESSURE IN THE CO₂ CRITICAL REGION

The object of the research is carbon dioxide and its pressure distribution depending on the range of temperature and density in the region of the critical point. One of the most problematic areas of methods for finding thermodynamic parameters of a real gas is insufficient accuracy in calculations in the places of occurrence and rapid development of fluctuation phenomena, which are inherent in phase transitions of the first and second terms. For a more detailed and accurate description of the nature of the thermodynamic parameters in the region of the critical point, scaling and crossover equations of state were developed. Such equations, due to the presence of regular and scaling parts, allow describing the thermodynamic parameters of a real gas not only directly near the critical point, but also at some distance from it, maintaining a small error relative to experimental data. The article proposes an equation of state, which contains a scaling part described according to the rules of statistical physics, and a regular part in the form of a classical cubic equation of state. The equation is used to calculate the pressure of carbon dioxide in the region around the critical point from 300 K to 305 K. The article proposes a correlation equation for the scaling correction of the regular part (Redlich-Kwong-Aungier model) of the crossover equation of state, which is related to the scaling part the equation of state is a crossover function. The obtained results for the pressure in the critical region showed good agreement with the baseline data. The error relative to the experimental data is halved compared to the original model of the Redlich-Kwong-Aungier equation. The obtained results ensure the applicability of the proposed method in the temperature range from 300 K to 305 K. Due to the simplicity of the form of the regular equation of state and the small number of empirical coefficients for the large-scale equation of state, the obtained method can be used for practical problems of computational hydrodynamics without spending a lot of computing time.

Keywords: carbon dioxide, critical point, scale equation of state, real gas equation of state, cubic equation of state, phase transition, fluctuation phenomena, thermodynamic parameters, Redlich-Kwong-Aungier model.

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1. Introduction

It is now widely accepted that Widom's hypothesis that the free energy of a fluid in the neighborhood of its critical point can be expressed as a homogeneous function of two of the thermodynamic variables, is essentially correct. A parametric representation of the thermodynamic behavior, which automatically satisfies the so-called «scaling-law» relations, which follow from the hypothesis of homogeneity [1].

The singularities in the thermodynamic functions of fluids at their critical points cannot be described by the analytic, the classical cubic, equations of states used for preparing tables of these functions. They can be described by scaling equations, but these are accurate only close to the critical point. It is shown that Schofield's parametric version of the scaling equations can be combined with an analytic equation in such a way as to permit the accurate representation of the thermodynamic functions for all values of density and temperature. The method is

demonstrated for carbon dioxide and methane. The results are unsatisfactory near the critical point where the Helmholtz free energy, and hence the pressure, etc. are not analytic functions of p and T . The functions used to generate tables are everywhere analytic, and so lead to a classical (or van der Waals) critical point, which is only a qualitatively correct description of the real situation. The actual behaviour of the functions near the critical point is known to be essentially the same for all fluids, and is well described by the scaling equations, of which there are now several versions. These equations are useful only near the critical point since their form is quite inappropriate at other densities and temperatures; for example, the pressure is not zero at zero density [2]. Two-parameter cubic equation of state (EoS) models are popular due to better computational accuracies in modeling both liquid and vapor phases at high pressures [3]. EOS models are also not good for estimating operating conditions near the critical values due to the large variation in supercritical fluid (SCF)

density in this region [4]. EoS that contain a large number of terms with integral and fractional powers of density ρ and temperature T , including also exponential terms, are used to obtain reference tables on thermodynamic properties of single-component substances. The number of adjustable constants in these equations reaches 50–100 or more. The most well-known reference tables [5] are calculated for CO₂ by a multi-constant regular Span and Wagner EoS (SW EoS, 58 adjustable constants and 35 different power-law indices). Articles [6, 7] represent the thermal combined equation of state, including a new 11-constant EoS for the regular region and scaling 6-constant EoS for the critical region of states, a unified description of the thermal and caloric properties of carbon dioxide and for helium. In paper [8] proposes the crossover cubic-plus-association equation of state. Large deviations were observed in the description of the critical lines of solvating mixtures. The reason for this behavior might be related to the large quadrupolar moment of CO₂, which is not taken into account by the model developed in this work. Soave-Redlich-Kwong EoS was used as the regular part of the equation of state. Paper [9] was validated the procedure of combining the crossover method with the multiparameter equation of state using carbon dioxide as a working fluid. The relative simplicity of the procedure by removing the non-analytical terms of the original equation of state was achieved, but was leave a major part of the formulation (terms and coefficients) unaltered. To achieve fast convergence as departing from the critical point, 8th order crossover function that diminishes rapidly as departing from the critical point was proposed.

Thus, *the object of research* is carbon dioxide and its pressure distribution depending on the range of temperature and density in the region of the critical point. *The subject of research* an equation of state for carbon dioxide, which contains a scaling part described according to the rules of statistical physics, and a regular part in the form of a classical cubic equation of state. *The aim of presented article* is to determine the pressure of carbon dioxide in the region around the critical point from 300 K to 305 K.

2. Research methodology

The method for determination the near critical pressure was based on the modified Redlich-Kwong-Aungier (RKA) equation of state [10] as regular part and the scaling equation of state from [7]. As the crossover function between the regular and the scaling parts is used the classical function of the extinction probability of temperature and density fluctuations from [7]. In paper [11] was presented the method to determine the main thermodynamics properties in the two-phase region of the carbon dioxide. This method is based on Aungier-modified the Redlich-Kwong equation of state, which can predict fluid properties in the two-phase region with sufficient accuracy. Methodology from [11] was decided to applied and modified for using in the near critical region of CO₂.

Determination of the thermodynamics parameters of CO₂ in the near critical region can be divided into three steps: finding the pressure from the regular and from the scaling parts of equation of state in the near critical point region, finding the enthalpy in the near critical region, finding the entropy in the near critical region. Selected as the base data required to validate the method was used the data from the mini-REFPROP (Reference Fluid Thermodynamic

and Transport Properties) program. Mini-REFPROP is a free and abbreviated sample of the full version of the NIST REFPROP software. The program was developed by the National Institute of Standards and Technology (NIST), calculates the thermodynamic properties of only pure substances. For the calculation, the most accurate models close to the experimental data are used. For CO₂, mini REFPROP uses the Span-Wagner model [12], which describes the CO₂ operating range with high accuracy. However, the Span-Wagner model has drawbacks for practical application in computational fluid dynamics of 3D calculations: it requires a lot of time to calculate and determine thermodynamic relationships. The technique based on the use of the two-parameter equation of state requires less calculation time and uses fewer auxiliary parameters and coefficients. The two-parametric equation of state form is faster for the same processing and calculations.

Determination of pressure from the crossover equation of state in the CO₂ near critical point region

1. Determination of pressure from the regular part of the crossover equation of state in the CO₂ near critical point region.

The near critical point region pressure can be found with the RKA equation of state. The method, which is described below, can be used for density-based solvers, when the temperature and the density of a working fluid are known values and pressure is found from equation of state.

The original form of the two-parametric Aungier-modified Redlich-Kwong equation of state is used as the regular part of crossover equation of state:

$$P_{RKA} = \frac{R \cdot T}{V - b + c} - \frac{A(T)}{V \cdot (V + b)},$$

where

$$A(T) = a \cdot \left(\frac{T_{cr}}{T} \right)^n, \quad b = 0.08664 \cdot R \cdot T_{cr} / P_{cr},$$

$$c = \frac{R \cdot T_{cr}}{P_{cr} + \frac{a}{V_{cr} \cdot (V_{cr} + b)}} + b - V_{cr},$$

where R – the gas constant for a particular working fluid; T – the current temperature value; P_{RKA} – the current pressure value from the regular part of the equation of state; T_{cr} – the critical temperature of a working fluid; P_{cr} – the critical pressure of a working fluid; V_{cr} – the critical volume of a working fluid. Constants a and b are related to the gas critical pressure and critical temperature. Constant c is a correction to eliminate a known weakness of the Redlich-Kwong, model at the critical point, where it predicts a compressibility factor of 1/3. The optimum value for parameter n is correlated by R. H. Aungier:

$$n = 0.4986 + 1.1735 \cdot \omega + 0.4754 \cdot \omega^2,$$

where ω – the compressibility factor for a working fluid.

Scaled and shift parameters were added to the regular part of the crossover equation of state by analogy with methodology from paper [11] for achieving more accurate results for pressure. As temperature range from 300 K to 305 K contains several regions of working fluid, two-phases and supercritical, scaled parameters will be individual for both regions.

Scaled parameter can be found from correlation equation:

$$n_{2_ph} = -3.9245 \cdot E - 0.4 \cdot T^3 + 3.466 \cdot E - 0.1 \cdot T^2 - 1.0196 \cdot E + 0.2 \cdot T + 9.9872 \cdot E + 0.3;$$

$$n_{scr} = 2.3259 \cdot E - 0.5 \cdot T^4 - 2.7996 \cdot E - 0.2 \cdot T^3 + 1.2625 \cdot E + 0.1 \cdot T^2 - 2.528 \cdot E + 0.3 \cdot T + 1.8964 \cdot E + 0.5.$$

The modified equation of the coefficient $A(T)$ is presented below:

$$A(T)_{2ph} = a \cdot \left(\frac{T_{cr}}{T} \right)^{(n_{2ph}/n)}$$

$$A(T)_{scr} = a \cdot \left(\frac{T_{cr}}{T} \right)^{(n_{scr}/n)}$$

where index $2ph$ means parameters for two-phases region and scr – parameters for supercritical region.

Modified coefficients $A(T)_{2ph}$ and $A(T)_{scr}$ use in *RKA* equation of state instead of original form of coefficient $A(T)$.

2. Determination of pressure from the scaling part of the crossover equation of state in the CO_2 near critical point region.

The physical basis for the application of scaling equations of state, as well as the entire theory of scaling, consists in taking into account the collective interactions of developed fluctuations at the second-order phase transition point. It leads to a singular behavior of thermodynamic derivatives (in particular, heat capacity) with non-integer critical exponents, which was discovered in the experiment [7].

The scaling equation of state, which is presented below, explicitly represents the dependence of the pressure on corrections for the density and the temperature:

$$\begin{aligned} \frac{P_{scaled}}{P_{cr}} &= 1 - k(q_p - q)^\gamma \cdot \Delta\rho \cdot |\Delta\rho|^{\delta-1} \cdot 1 + \frac{\delta}{1+\delta} \Delta\rho + \\ &+ k \cdot (dT + q_p \cdot |\Delta\rho|^{1/\beta})^\gamma \cdot (\Delta\rho + \Delta\rho^2) - k \cdot dT \cdot |dT|^{\gamma-1} \times \\ &\times \Delta\rho^2 \cdot \frac{1}{2} + \frac{\gamma\beta}{1+2\beta} \frac{q_p \cdot |\Delta\rho|^{1/\beta}}{dT} + (M - a_p) dT. \end{aligned}$$

The equation contains three constants m , $M - a_p$, k and critical properties of the working fluid, which makes the equation more convenient for using. The values of critical exponents are taken from the 3D using model [12, 13]: $\beta = 0.3255$; $\gamma = 1.239$; $\Delta = (\gamma + \beta) / \beta = 4.806$. a_p is the Pokrovsky transformation constant [14]. $q = (m/k)1/\gamma$ – coefficient for the boundary curve (binodal) in the critical region.

$$dT = \frac{(T - T_{cr})}{T_{cr}},$$

$$\Delta\rho = \frac{(\rho - \rho_{cr})}{\rho_{cr}},$$

$$q_p = 4.0015 \cdot q,$$

where T and ρ – the current temperature and density values; T_{cr} and ρ_{cr} – the critical parameters of the carbon dioxide; q_p – coefficient of the curve containing the heat capacity C_v on the S -spinodal.

The essence of the scaling hypothesis of Widom is that the difference of the chemical potential from that on the critical isochore at the same temperature is an anti-symmetric function of a variable which is a simple combination of dT and $\Delta\rho$. The potential $\Delta\omega$, defined by Green, Cooper and Levelt Sengers [14], is a proportional to the difference of pressure of the fluid and the chemical potential and temperature and that of a point at the same coordinates, but on the plane tangent to the surface.

The regular part of equation of state (Redlich-Kwong-Aungier EoS – *RKA* EoS), which is connected with the scaling part of equation of state with the crossover function. As the crossover function between the regular and the scaling parts is used the classical function of the extinction probability of the temperature and of the density fluctuations from [7]:

$$Y = \exp(-\lambda \cdot dT^2 - \mu \cdot \Delta\rho^2),$$

where dT and $\Delta\rho$ have the meaning of the distance from the critical point, and the empirical coefficients λ and μ determine the area of influence of critical fluctuations.

The crossover equation of state has form:

$$\frac{P}{P_{cr}} = (1 - Y) \cdot \frac{P_{RKA}}{P_{cr}} + Y \cdot \frac{P_{scaled}}{P_{cr}},$$

where P_{RKA} – pressure, which was found from regular part (*RKA* EoS) of crossover equation of state; P_{scaled} – pressure, which was found from scaling part of crossover equation of state; Y – crossover function of the extinction probability of the temperature and of the density fluctuations.

Analysis of the equations for the temperature and for the density corrections showed that when the temperature and the density are reached the critical values, the corrections are equal to zero. In this regard, it was decided to add conditions to achieve critical parameters: the temperature and the density corrections will be equal to $1 - E - 0.5$, when the current temperature and density are reached critical point parameters.

3. Research results and discussion

The error between the base data and the values calculated using the Redlich-Kwong-Aungier equation of state in original form show significant difference with density rises for whole temperature diapason from 300 K to 305 K. A scaled parameters n_{2ph} and n_{scr} were included into the equation of the coefficient $A(T)$ of the Redlich-Kwong-Aungier model to refine pressure values over the whole temperature range. This *RKA* modification was included to crossover equation of state and pressure distribution for wide density and temperature ranges was refined and results of crossover equation were close to base data. Visualization of isotherms shows similar trends for scaled EoS and base data except of isotherms for 305 K.

The results of validation of the method are described below in Tables 1–5 and in Fig. 1–5.

Method, which was presented above can be used for the pressure determination in wide density diapason and for temperature from 300 K to 305 K in near critical region. As seen from results, relative error reduced significantly for temperature 300–304.11 K. Relative error for results of scaled equation from temperature 304.13 K to 305 K is

also reduced in comparison with original Redlich-Kwong-Aungier model. Next step of the method developing can be found ways of improvement isotherms trends in supercritical region from 304.13 K to 305 K for achieving similar isotherms behaviour with baseline data isotherms.

The main limitation of the presented method is using crossover equation of state in critical point. Parameters dT and Δp here are equal to zero and, as assumption, these parameters can be set $1 \cdot E-0.5$ for calculation in critical point for correct crossover equation computing.

Table 1

Pressure results, where *RKA original* – results for original RKA equation, *RKA corr* – results for modified RKA equation from section 1, *RKA scaled* – results for scaled equation of state from section 2. Temperature – 300 K

<i>T, K</i>	<i>P, Pa mini-NIST</i>	<i>Ro, kg/m³ mini-NIST</i>	<i>v, m³/kg mini NIST</i>	<i>P, Pa RKA original</i>	<i>rel err, %</i>	<i>P, Pa RKA corr</i>	<i>rel err, %</i>	<i>P, Pa RKA scaled</i>	<i>rel err, %</i>
300	6713100	679.24	0.0015	9643340	44	7657488	14	6340862	-6
300	6808600	690	0.0014	10093395	48	8054420	18	6669545	-2
300	7415300	730	0.0014	12167873	64	9926961	34	8220123	11
300	8561800	770	0.0013	14982936	75	12533900	46	10378825	21
300	10479000	810	0.0012	18706533	79	16043871	53	13285293	27
300	13457000	850	0.0012	23557640	75	20675807	54	17120816	27
300	17835000	890	0.0011	29805582	67	26699324	50	22108651	24
300	24003000	930	0.0011	37781461	57	34446111	44	28523458	19
300	32406000	970	0.0010	47956387	48	44386841	37	36754982	13
300	43573000	1010	0.0010	60880183	40	57072477	31	47259454	8
300	58127000	1050	0.0010	77385764	33	73335501	26	60726220	4
300	76787000	1090	0.0009	98586414	28	94289578	23	78077460	2
300	100360000	1130	0.0009	126098151	26	121550945	21	100651516	0
300	129750000	1170	0.0009	162370264	25	157568935	21	130476585	1

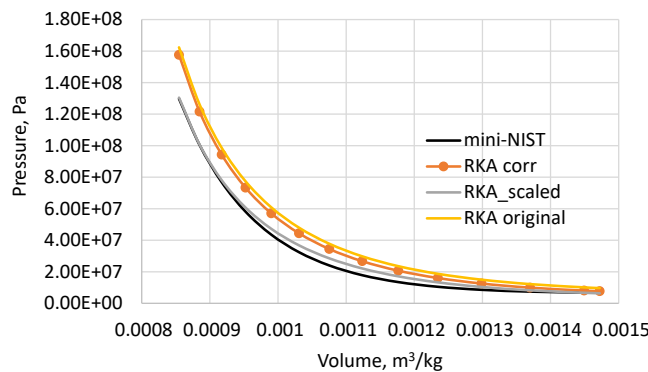


Fig. 1. Isotherms for different RKA modifications. Temperature 300 K

Table 2

Pressure results, where *RKA original* – results for original RKA equation, *RKA corr* – results for modified RKA equation from section 1, *RKA scaled* – results for scaled equation of state from section 2. Temperature – 304 K

<i>T, K</i>	<i>P, Pa mini-NIST</i>	<i>Ro, kg/m³ mini-NIST</i>	<i>v, m³/kg mini NIST</i>	<i>P, Pa RKA original</i>	<i>rel err, %</i>	<i>P, Pa RKA corr</i>	<i>rel err, %</i>	<i>P, Pa RKA scaled</i>	<i>rel err, %</i>
1	2	3	4	5	6	7	8	9	10
304	7355500	530.3	0.0019	7680052	4	7636805	4	6165410	-16
304	7372300	570	0.0018	8150699	11	8101703	10	6540735	-11
304	7448800	610	0.0016	8920872	20	8865828	19	7157635	-4
304	7655300	650	0.0015	10074409	32	10013088	31	8083850	6
304	8095700	690	0.0014	11716321	45	11648492	44	9404159	16
304	8918200	730	0.0014	13965861	57	13891315	56	11214853	26
304	10309000	770	0.0013	16970379	65	16888910	64	13634897	32

Continuation of the Table 2

1	2	3	4	5	6	7	8	9	10
304	12501000	810	0.0012	20899560	67	20810984	66	16801299	34
304	15783000	850	0.0012	25975331	65	25879464	64	20893226	32
304	20498000	890	0.0011	32470399	58	32367066	58	26130852	27
304	27033000	930	0.0011	40719848	51	40608894	50	32784714	21
304	35840000	970	0.0010	51201391	43	51082647	43	41240472	15
304	47451000	1010	0.0010	64471348	36	64344681	36	51947289	9
304	62492000	1050	0.0010	81374058	30	81239322	30	65586812	5
304	81683000	1090	0.0009	103037370	26	102894431	26	83069597	2
304	105830000	1130	0.0009	131098687	24	130947419	24	105717571	0
304	135840000	1170	0.0009	168039924	24	167880203	24	135534457	0

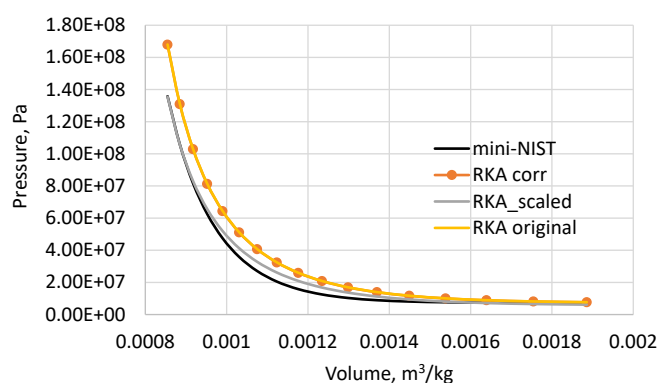


Fig. 2. Isotherms for different RKA modifications. Temperature 304 K

Table 3

Pressure results, where *RKA original* – results for original RKA equation, *RKA corr* – results for modified RKA equation from section 1, *RKA scaled* – results for scaled equation of state from section 2. Temperature – 304.11 K

<i>T</i> , K	<i>P</i> , Pa <i>mini-NIST</i>	<i>Ro</i> , kg/m ³ <i>mini-NIST</i>	<i>v</i> , m ³ /kg <i>mini NIST</i>	<i>P</i> , Pa <i>RKA original</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA corr</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA scaled</i>	<i>rel err</i> , %
304.11	7374200	502.09	0.0020	7506855	2	7500811	2	6049032	-18
304.11	7375900	530	0.0019	7705694	4	7699052	4	6215664	-16
304.11	7395500	570	0.0018	8182669	11	8175137	11	6600021	-11
304.11	7475700	610	0.0016	8956703	20	8948242	20	7224170	-3
304.11	7686300	650	0.0015	10114375	32	10104949	31	8158012	6
304.11	8131700	690	0.0014	11760736	45	11750309	45	9486358	17
304.11	8960000	730	0.0014	14015069	56	14003610	56	11305512	26
304.11	10358000	770	0.0013	17024775	64	17012251	64	13734474	33
304.11	12557000	810	0.0012	20959587	67	20945971	67	16910277	35
304.11	15847000	850	0.0012	26041512	64	26026776	64	21012155	33
304.11	20571000	890	0.0011	32543353	58	32527468	58	26260349	28
304.11	27116000	930	0.0011	40800301	50	40783245	50	32925472	21
304.11	35934000	970	0.0010	51290251	43	51271997	43	41393340	15
304.11	47557000	1010	0.0010	64569702	36	64550231	36	52113235	10
304.11	62612000	1050	0.0010	81483307	30	81462595	30	65767067	5
304.11	81817000	1090	0.0009	103159316	26	103137343	26	83265707	2
304.11	105980000	1130	0.0009	131235720	24	131212467	24	105931552	0
304.11	136000000	1170	0.0009	168195331	24	168170779	24	135769047	0

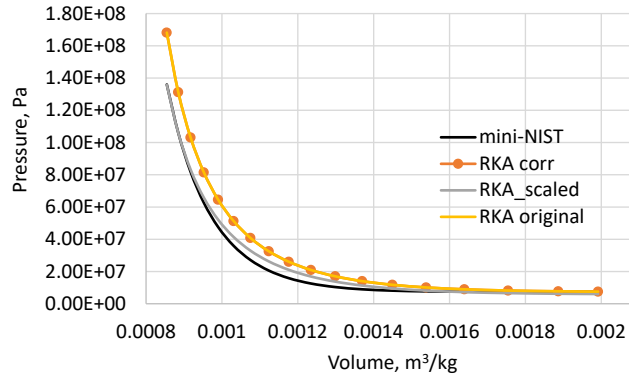


Fig. 3. Isotherms for different RKA modifications. Temperature 304.11 K

Table 4

Pressure results, where *RKA original* – results for original RKA equation, *RKA corr* – results for modified RKA equation from section 1, *RKA scaled* – results for scaled equation of state from section 2. Temperature – 304.13 K

<i>T</i> , K	<i>P</i> , Pa <i>mini-NIST</i>	<i>R₀</i> , kg/m ³ <i>mini-NIST</i>	<i>v</i> , m ³ /kg <i>mini NIST</i>	<i>P</i> , Pa <i>RKA original</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA corr</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA scaled</i>	<i>rel err</i> , %
304.13	559370	10	0.1000	559678	0	559678	0	451262	-19
304.13	2506600	50	0.0200	2510964	0	2510964	0	2024562	-19
304.13	4029700	90	0.0111	4044402	0	4044402	0	3260955	-19
304.13	5183900	130	0.0077	5213343	1	5213343	1	4203459	-19
304.13	6024600	170	0.0059	6068748	1	6068748	1	4893163	-19
304.13	6606400	210	0.0048	6659746	1	6659746	1	5369678	-19
304.13	6982400	250	0.0040	7034180	1	7034180	1	5671579	-19
304.13	7203600	290	0.0034	7239533	0	7239533	0	5837154	-19
304.13	7316900	330	0.0030	7323524	0	7323524	0	5904875	-19
304.13	7363500	370	0.0027	7334817	0	7334817	0	5913980	-20
304.13	7376200	410	0.0024	7323916	-1	7323916	-1	5905191	-20
304.13	7377600	450	0.0022	7344070	0	7344070	0	5921441	-20
304.13	7377600	490	0.0020	7452340	1	7452340	1	6008737	-19
304.13	7379600	530	0.0019	7710850	4	7710850	4	6217171	-16
304.13	7399700	570	0.0018	8188481	11	8188481	11	6602279	-11
304.13	7480600	610	0.0016	8963217	20	8963217	20	7226940	-3
304.13	7692000	650	0.0015	10121640	32	10121640	32	8160964	6
304.13	8138200	690	0.0014	11768810	45	11768810	45	9489058	17
304.13	8967600	730	0.0014	14024014	56	14024014	56	11307404	26
304.13	10367000	770	0.0013	17034663	64	17034663	64	13734856	32
304.13	12567000	810	0.0012	20970499	67	20970499	67	16908275	35
304.13	15859000	850	0.0012	26053544	64	26053544	64	21006677	32
304.13	20585000	890	0.0011	32556615	58	32556615	58	26250029	28
304.13	27132000	930	0.0011	40814926	50	40814926	50	32908612	21
304.13	35951000	970	0.0010	51306405	43	51306405	43	41367772	15
304.13	47577000	1010	0.0010	64587582	36	64587582	36	52076235	9
304.13	62634000	1050	0.0010	81503168	30	81503168	30	65715080	5
304.13	81842000	1090	0.0009	103181485	26	103181485	26	83194061	2
304.13	106010000	1130	0.0009	131260632	24	131260632	24	105833958	0
304.13	136030000	1170	0.0009	168223584	24	168223584	24	135636767	0

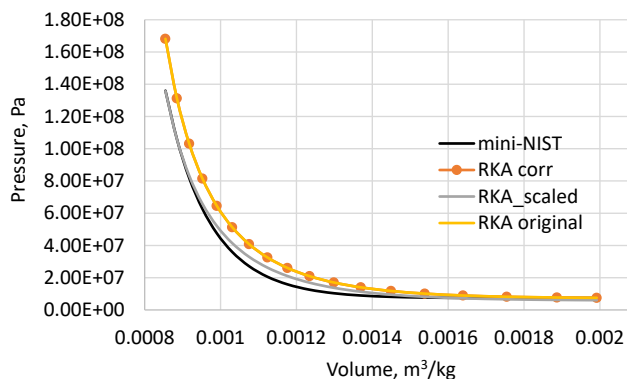


Fig. 4. Isotherms for different RKA modifications. Temperature 304.13 K

Table 5

Pressure results, where *RKA original* – results for original RKA equation, *RKA corr* – results for modified RKA equation from section 1, *RKA scaled* – results for scaled equation of state from section 2. Temperature – 305 K

<i>T</i> , K	<i>P</i> , Pa <i>mini-NIST</i>	<i>R₀</i> , kg/m ³ <i>mini-NIST</i>	<i>v</i> , m ³ /kg <i>mini NIST</i>	<i>P</i> , Pa <i>RKA original</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA corr</i>	<i>rel err</i> , %	<i>P</i> , Pa <i>RKA scaled</i>	<i>rel err</i> , %
305	7533700	500	0.0020	7704301	2	7624128	1	6148481	-18
305	7536700	510	0.0020	7769236	3	7686244	2	6205323	-18
305	7540500	520	0.0019	7845739	4	7759892	3	6264781	-17
305	7545400	530	0.0019	7934946	5	7846208	4	6334467	-16
305	7551900	540	0.0019	8037759	6	7946100	5	6415113	-15
305	7560500	550	0.0018	8155718	8	8061098	7	6507953	-14
305	7571700	560	0.0018	8289839	9	8192224	8	6613815	-13
305	7586300	570	0.0018	8441032	11	8340396	10	6733438	-11
305	7604900	580	0.0017	8611274	13	8507576	12	6868408	-10
305	7628500	590	0.0017	8801012	15	8694228	14	7019097	-8
305	7658100	600	0.0017	9011776	18	8901878	16	7186739	-6
305	7694600	610	0.0016	9246267	20	9133209	19	7373499	-4
305	7739500	620	0.0016	9503853	23	9387619	21	7578891	-2
305	7794000	630	0.0016	9787446	26	9668001	24	7805251	0
305	7859800	640	0.0016	10098255	28	9975569	27	8053560	2
305	7938500	650	0.0015	10437359	31	10311408	30	8324692	5
305	8032000	660	0.0015	10807351	35	10678103	33	8620736	7
305	8142500	670	0.0015	11211422	38	11078833	36	8944257	10

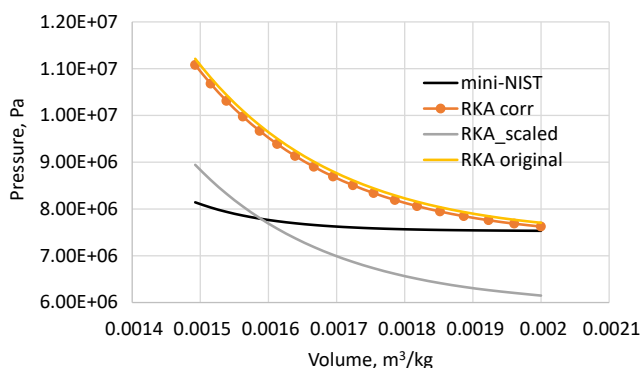


Fig. 5. Isotherms for different RKA modifications. Temperature 305 K

4. Conclusions

The crossover equation of state with modified Redlich-Kwong-Aungier model as regular part presented here refined accuracy with base data in prediction of the pressure in critical region of CO₂, than original forms of analytical cubic equation of state. The equation was validated for wide density range and for near-critical temperature region from 300 K to 305 K. Regular part of crossover equation was modified by scaled parameters for both phases of working diapason of CO₂ – two-phases region and supercritical. Results were compared with Span and Wagner equation from mini-REFPROP, which was selected as the base data. Comparison analysis between crossover equation and base data showed appropriate agreement and similar isotherm trends.

The present method of regular EoS modification requires two additional parameters in comparison with the original form of equation – the scaled parameters for pressure in 2-phases and supercritical regions. Equations for each of these parameters are presented here in convenient form and described in regions from 300 K to 305 K for isotherms from minimal to maximum specific volumes for each corresponding temperatures.

The modification in regular part of crossover equation saves original form of Redlich-Kwong-Aungier model and the crossover equation of state gives ability to determine pressure values in region of critical point of CO₂ with significantly reduced relative error in comparison with analytical cubic equation of states.

References

- Schofield, P. (1969). Parametric representation of the equation of state near a critical point. *Physical Review Letters*, 22 (12), 606–608. doi: <http://doi.org/10.1103/physrevlett.22.606>
- Chapela, G. A., Rowlinson, J. S. (1974). Accurate representation of thermodynamic properties near the critical point. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 70, 584–593. doi: <http://doi.org/10.1039/f19747000584>
- Hasan, O., Sandler, S. I. (1998). *Modeling vapor-liquid equilibria: cubic equations of state and their mixing rules*. Cambridge University Press, 19–25.
- Lee, S., Joonhyeon, J., Wonsoo, K., Tong-Seek, C. (2008). A new model approach for the near-critical point region: 1. Construction of the generalized van der Waals equation of state. *The Journal of Physical Chemistry B*, 112 (49), 15725–15741. doi: <http://doi.org/10.1021/jp8002855>
- Span, R., Wolfgang, W. (1996). A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *Journal of physical and chemical reference data*, 25 (6), 1509–1596. doi: <http://doi.org/10.1063/1.555991>
- Bezverkhii, P. P., Martynets, V. G., Matizen, E. V. (2009). Equation of state for He4, including a regular and a scalar part. *Low Temperature Physics*, 35 (10), 471–474. doi: <http://doi.org/10.1063/1.3253391>
- Bezverkhii, P. P., Martynets, V. G., Matizen, E. V. (2007). A scaling equation of state near the critical point and the stability boundary of a liquid. *Journal of Engineering Thermophysics*, 16 (3), 164–168. doi: <http://doi.org/10.1134/s1810232807030083>
- Vinhal, A. P. C. M., Yan, W., Kontogeorgis, G. M. (2019). Modeling the critical and phase equilibrium properties of pure fluids and mixtures with the crossover cubic-plus-association equation of state. *Journal of Chemical & Engineering Data*, 65 (3), 1095–1107. doi: <http://doi.org/10.1021/acs.jced.9b00492>
- Kolawole, A., Hutton-Prager, B. (2020). Modeling the solubility of Alkyl Ketene Dimer in supercritical carbon dioxide: Peng-Robinson, group contribution methods, and effect of critical density on solubility predictions. *Fluid Phase Equilibria*, 507, 112415. doi: <http://doi.org/10.1016/j.fluid.2019.112415>
- Aungier, R. H. (1995). A fast, accurate real gas equation of state for fluid dynamic analysis applications. *Journal of Fluids Engineering*, 117 (2), 277–281. doi: <http://doi.org/10.1115/1.2817141>
- Vorobieva, H. (2021). Modification of the Redlich-Kwong-Aungier Equation of State to Determine the Degree of Dryness in the CO₂ Two-phase Region. *Journal of Mechanical Engineering*, 24 (4), 17–27. doi: <http://doi.org/10.15407/pmach2021.04.017>
- Span, R., Wolfgang, W. (1996). A new equation of state for carbon dioxide covering the fluid region from the triple point temperature to 1100 K at pressures up to 800 MPa. *Journal of physical and chemical reference data*, 25 (6), 1509–1596. doi: <http://doi.org/10.1063/1.555991>
- Anisimov, M. A., Rabinovich, V. A., Sychev, V. V. (1990). *Termodinamika kriticheskogo sostoiianiia individualnykh veshchestv*. Moscow: Energoatomizdat, 192.
- Patashinskii, A. Z., Pokrovskii, V. L. (1982). *Fluktuatsionnaia teoriia fazovykh perekhodov*. Moscow: Nauka, 381.

Hanna Vorobiova, Postgraduate Student, Department of Aircraft Engine Design, National Aerospace University «Kharkiv Aviation Institute», Kharkiv, Ukraine, e-mail: vorobyovaanna1610@gmail.com, ORCID: <https://orcid.org/0000-0002-4181-8269>