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Arch. Min. Sci. **63** (2018), 1, 27-41

Electronic version (in color) of this paper is available: http://mining.archives.pl

DOI 10.24425/118883

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FUNCTIONAL DEPENDENCIES OF THERMODYNAMIC AND THERMOKINETIC PARAMETERS OF REFRIGERANTS USED IN MINE AIR REFRIGERATORS. PART 2 – REFRIGERANT R404A

ZALEŻNOŚCI FUNKCYJNE PARAMETRÓW TERMODYNAMICZNYCH I TERMOKINETYCZNYCH CZYNNIKÓW CHŁODNICZYCH STOSOWANYCH W GÓRNICZYCH CHŁODZIARKACH POWIETRZA. CZĘŚĆ 2 – CZYNNIK CHŁODNICZY R404A

This paper deals with thermodynamic and thermokinetic properties of R404A refrigerant, which is one of the more commonly used in mine air compression refrigerators. Knowledge of these parameters is essential to analyze performance of such refrigeration equipment, to design it, or to estimate efficiency of air refrigerators using various refrigerants. These properties can be defined using 27 simple computational formulas, contained in 4 tables (Tables 2, 6, 10 and 12). The relationships determining thermodynamic and thermokinetic parameters of R404A occur in saturated liquid region, dry saturated vapor region, superheated vapor region and supercooled liquid region. The developed relationships were subjected to statistical verification. For this purpose, correlation coefficients, coefficients of determination, as well as absolute and relative deviations were determined by comparing results of the calculations with the corresponding results obtained by REFPROP 7 (Lemmon et al., 2002). Results of verification are contained in Tables 14 and 15.

Keywords: refrigerants, R404A, thermodynamic and thermokinetic parameters

Artykuł dotyczy właściwości termodynamicznych i termokinetycznych czynnika chłodniczego R404A, który jest jednym z częściej stosowanych w górniczych sprężarkowych chłodziarkach. Znajomość tych parametrów jest wymagana do analizy pracy takich chłodziarek, do ich projektowania, czy też do oceny efektywności pracy chłodziarek wykorzystujących różne czynniki chłodnicze. Wymienione właściwości określić można korzystając z utworzonych 27 prostych formuł obliczeniowych. Podano je w 4 tabelach (tabela 2, 6, 10 i 12). Przedstawione zależności określające parametry termodynamiczne i termokinetyczne czynnika chłodniczego R404A obowiązują w stanie cieczy nasyconej, w stanie pary nasyconej suchej, w stanie pary przegrzanej oraz w stanie cieczy przechłodzonej. Opracowane zależności poddano wery-

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fikacji statystycznej. W tym celu, porównując wyniki obliczeń z odpowiednimi wynikami uzyskanymi programem REFPROP 7 (Lemmon i inni, 2002) określono współczynniki korelacji, determinacji oraz odchyłki bezwzględne i względne. Rezultaty weryfikacji zamieszczono w tabelach 14 i 15.

Słowa kluczowe: czynniki chłodnicze, R404A, parametry termodynamiczne i termo-kinetyczne

1. Introduction

Air compression refrigerators, used to improve thermal working conditions in underground mine workings, utilize synthetic refrigerants, both single-component and multi-component ones. Currently, R407C, R404A, R507 and R134a are used most frequently. Part 1 of the study presents functional dependencies describing thermodynamic and thermokinetic parameters of R407C, whereas Part 2 deals with R404A. The basic thermodynamic and thermokinetic properties of this refrigerant are demonstrated in Table 1.

TABLE 1

Thermodynamic and thermokinetic properties of R404A (Lemmon et al., 2002)

Parameter	Value	
Group	**HFC**	
Chemical formula	52% 44% 4%	$C_2H_3F_3$ C_2HF_5 $C_2H_2F_4$
Molar mass [kg/kmol]	97,604	
Critical temperature [°C]	72,046	
Critical pressure [bar]	37,289	
Critical density [kg/m^3]	486,53	
Normal boiling point [°C]	–46,5	
Triple point temperature [°C]	–73,15	
ODP (Ozone Depletion Potential)	0	
GWP (Global Warming Potential)	3748	

R404A, used as a long-term replacement for R502, and particularly as a replacement for R22, has become one of the most widely used refrigerants in both small and large systems. However, the (EU) Regulation No. 517/2014 of the European Parliament and Council of 16 April 2014 on fluorinated greenhouse gases and repealing the (EC) Regulation No. 842/2006, in force since 1 January 2015, restricts the use of many refrigerants due to their high GWP ratio. This also applies to R404A. The values of GWP for this refrigerant, provided in the literature, vary from 3748 (Lemmon et al., 2002) to 3943 (Myhre et al., 2013). Numerous studies point to potential replacements for R404A, which have similar parameters. (Minor and Gerstel, 2014) propose DR7 and Opteon XP40, while Mantecon and Ingenieria (2016) recommend R448A. A wider comparison of potential replacements for R404A has been presented in the paper (Mota-Babiloni et al., 2014). The authors point to R407A and R407F as medium-term replacements, and L40, DR7, N40 and DR33 as long-term replacements. Similar suggestions have been presented in the paper (Devecioglu et al., 2015) – DR33, L40, DR7 and R448A. Experimental comparison of R448A as a replacement for R404A has been presented in (Mota-Babiloni et al., 2015).

Knowledge of thermodynamic and thermokinetic properties of R404A is necessary both in calculations of refrigeration circuits as well as performance parameters of the equipment making up refrigerating circuits. Despite the fact that R404A will be completely withdrawn from use since 2020, numerous refrigeration devices using R404A (including mine refrigerators) still are, and will keep operating. Knowledge of the parameters of R404A is necessary, especially for comparative analysis of using new replacements with low GWP values.

2. Thermodynamic and thermokinetic properties of R404A

In order to determine numerical values of thermodynamic parameters of refrigerants, it is possible to use ready-made graphs and tables, which is associated with inaccuracy of reading, or to use computer programs such as REFPROP 9.1 (Lemmon et al., 2013) or CoolProp 6.1 (Bell et al., 2014). In numerical calculations, different types of state equations are used to describe the dependencies between parameters – Clapeyron equation, Martin-Hou equation, Redlich-Kwong equation, Benedict-Webba-Rubin equation, and Helmholtz equation, which is currently the most frequently used one (Butrymowicz et al., 2014). The literature also describes relationships defining parameters of refrigerants in a form that does not require numerical calculations, but they usually refer only to refrigerants in saturated liquid and dry saturated vapor regions. A complicated form of these formulas makes it impossible for them to be used in simple engineering calculations. In such cases, particular attention should be paid to the scope of a given relationship and, above all, to deviations from the source data.

In the case of R404A, several papers concentrate on its thermodynamic parameters. Using Artificial Neural Network (ANN) techniques, (Sozen et al., 2010) developed relationships describing enthalpy and entropy for the two-phase region, and enthalpy, entropy and specific volume for the superheated vapor region. For a refrigerant in the two-phase region, knowledge of temperature and degree of dryness is required, while in the superheated vapor region – temperature and pressure. (Kucuksille et al., 2009, 2011), using a variety of data mining techniques, obtained simple equations for determining enthalpy, entropy, specific volume, specific heat, dynamic viscosity coefficient, heat conduction coefficient, and density of refrigerants in saturated state. For the refrigerants R134a, R404A, R407C and R410A, appropriate formulas were developed. A drawback of the obtained relationships is a necessity to know two parameters of the refrigerant on the saturation line: temperature and pressure. Therefore, the authors of this paper have developed appropriate relationships allowing to determine thermodynamic and thermokinetic parameters of R404A in saturated state as functions of pressure only, within a wide range of its changes (0.5÷35.0 bar). The relationships in superheated vapor and supercooled liquid regions have also been defined where, in addition to pressure, knowledge of the second variable is required. It should be emphasized that the formulas which were created are characterized by high accuracy and simple form.

3. Computational formulas for thermodynamic and thermokinetic parameters of R404A

On the saturation line, in order to unambiguously determine thermodynamic and thermokinetic parameters of a refrigerant, the knowledge of one independent variable is required, and in the case of superheated vapor region, supercooled liquid and saturated two-phase region – of two independent variables. Both input and output data of R404A parameters required for the analysis were obtained using REFPROP 7 (Lemmon et al., 2002). In order to obtain high accuracy, the sought thermodynamic and thermokinetic parameters were described using polynomials of degree 4, 5, 6, 8, 9, or 10, whose coefficients were determined using STATISTICA 12 (StatSoft, 2014). For this purpose, one of the least squares nonlinear estimation methods was used – the Levenberg-Marquardt method. The Levenberg-Marquardt method is a modification (extension) of the Gauss-Newton algorithm. Using the least squares loss function, as in the case of the Gauss-Newton algorithm, in order to find estimation of the least squares parameters, it is not necessary to calculate (or roughly estimate) partial derivatives of the second order, as in each iteration to calculate the gradient, a corresponding system of linear equations is solved (StatSoft, 2006).

To obtain the highest possible value of correlation coefficients and coefficients of determination, and at the same time possibly small deviations (absolute and relative) for individual relationships, the obtained coefficients of the polynomial were provided with the accuracy of up to 14 digits.

3.1. Saturated liquid region

For the refrigerant R404A in saturated liquid state, relationships describing basic thermodynamic and thermokinetic parameters as a function of pressure were determined: temperature T' [K], specific enthalpy h' [kJ/kg], specific entropy s' [kJ/(kg·K)], specific heat c_p' [kJ/(kg·K)], density ρ' [kg/m^3], specific volume v' [m^3/kg], thermal conductivity λ' [W/(m·K)], dynamic viscosity coefficient μ' [kg/(m·s)], Prandtl number Pr' [-], surface tension σ' [N/m].

Using REFPROP 7, for the pressures of 0.5 bar to 35 bar with a variability of 0.05 bar, the values corresponding to the saturated liquid parameters were read. A total of 690 data were used for the calculations for each of the analyzed property of the refrigerant.

The developed formulas for R404A in saturated liquid state are contained in Table 2.

TABLE 2

Computational formulas for thermodynamic and thermokinetic parameters of R404A in liquid saturated state

No.	Parameter	Unit	Formula	Formula No.
1	2	3	4	5
1	Temperature	[K]	$T' = \sum_{n=1}^{6} a_n \cdot \ln p^n + a_0$	(1)
2	Specific enthalpy	[kJ/kg]	$h' = \sum_{n=1}^{8} a_n \cdot \ln p^n + a_0$	(2)
3	Specific entropy	[kJ/(kg·K)]	$s' = \sum_{n=1}^{8} a_n \cdot \ln p^n + a_0$	(3)
4	Specific heat	[kJ/(kg·K)]	$c_p' = \sum_{n=0}^{9} a_n \cdot p^n$	(4)

1	2	3	4	5
5	Density	[kg/m³]	$\rho' = \sum_{n=0}^{8} a_n \cdot p^n$	(5)
6	Specific volume	[m³/kg]	$v' = \sum_{n=0}^{8} a_n \cdot p^n$	(6)
7	Thermal conductivity	[W/(m·K)]	$\lambda' = \sum_{n=0}^{9} a_n \cdot p^n$	(7)
8	Dynamic viscosity coefficient	[kg/(m·s)]	$\mu' = \sum_{n=1}^{9} a_n \cdot \ln p^n + a_0$	(8)
9	Prandtl number	[-]	$\mathrm{Pr}' = \sum_{n=0}^{10} a_n \cdot p^n$	(9)
10	Surface tension	[N/m]	$\sigma' = \sum_{n=1}^{10} a_n \cdot \ln p^n + a_0$	(10)

The determined coefficients of the polynomial for each property of the refrigerant are contained in Table 3 (temperature, specific enthalpy, specific entropy, specific heat), Table 4 (density, specific volume, thermal conductivity) and Table 5 (dynamic viscosity coefficient, Prandtl number, surface tension).

TABLE 3

Coefficients of polynomials describing temperature, specific enthalpy, specific entropy, and specific heat of saturated liquid of the refrigerant R404A

No.	Coefficients	Formula			
		$T' = f(p)$	$h' = f(p)$	$s' = f(p)$	$c_p' = f(p)$
		(1)	(2)	(3)	(4)
1	a_0	2,26656656089798E+02	1,39155908034722E+02	7,57652250071433E-01	1,13628063383038E+00
2	a_1	2,07448767894318E+01	2,60693423122758E+01	1,14667256548885E-01	1,80552899686646E-01
3	a_2	2,25066441744582E+00	6,40159809618961E-01	1,36187127608066E-03	–8,34466777792953E-02
4	a_3	3,52121285108549E-01	2,73339507604666E+00	7,51510264197365E-03	2,15031075276533E-02
5	a_4	–1,24415838833123E-01	3,44578926709914E+00	9,80164472560737E-03	–3,05917176317592E-03
6	a_5	5,88513043810617E-02	–5,91534769429268E+00	–1,69275393743141E-02	2,56493379770086E-04
7	a_6	–7,93910818274909E-03	3,31525263921548E+00	9,47467262746237E-03	–1,29692260005755E-05
8	a_7	—	–8,16310635671909E-01	–2,33201116765914E-03	3,88467884645566E-07
9	a_8	—	7,56991210294063E-02	2,16040372224908E-04	–6,34373358038814E-09
10	a_9	—	—	—	4,35284391110640E-11

TABLE 4

Coefficients of polynomials describing density, specific volume and thermal conductivity of saturated liquid of the refrigerant R404A

No.	Coefficients	Formula		
		$\rho' = f(p)$	$v' = f(p)$	$\lambda' = f(p)$
		(5)	(6)	(7)
1	a_0	1,37724595711566E+03	7,25192238194906E-04	1,04877137873635E-01
2	a_1	–8,15266398400014E+01	4,52788525045687E-05	–1,41847373027602E-02
3	a_2	1,45089380334596E+01	–6,86169312529686E-06	3,42751110588146E-03
4	a_3	–1,85298543881228E+00	8,20774243977212E-07	–5,50726609396371E-04
5	a_4	1,43887723776435E-01	–5,83105743875901E-08	5,52021317430742E-05
6	a_5	–6,78414394872525E-03	2,46909753121693E-09	–3,48828609960489E-06
7	a_6	1,89054873425341E-04	–5,97763118593255E-11	1,38731575592158E-07
8	a_7	–2,85731554544348E-06	7,43834498524795E-13	–3,36221258630072E-09
9	a_8	1,79989565071609E-08	–3,45544392899228E-15	4,52898578919505E-11
10	a_9	—	—	–2,59578052462672E-13

TABLE 5

Coefficients of polynomials describing dynamic viscosity coefficient, Prandtl number and surface tension of saturated liquid of the refrigerant R404A

No.	Coefficients	Formula		
		$\mu' = f(p)$	$Pr' = f(p)$	$\sigma' = f(p)$
		(8)	(9)	(10)
1	a_0	3,56978445658089E-04	6,36208255560168E+00	1,29791677514392E-02
2	a_1	–1,26777960395296E-04	–2,16581447431669E+00	–2,31336311312520E-03
3	a_2	1,64259009241276E-05	7,81487919460013E-01	–3,14758633282321E-04
4	a_3	2,75858261766258E-06	–1,68267570172945E-01	5,28645729793096E-06
5	a_4	–6,60192735277160E-07	2,24782012638078E-02	–5,84805636884536E-05
6	a_5	–5,44662820059116E-06	–1,92768049743783E-03	–2,35625633384914E-05
7	a_6	5,82976158645952E-06	1,07855435046257E-04	9,13294587369533E-05
8	a_7	–2,58954560219114E-06	–3,91238776449392E-06	–7,20396516385538E-05
9	a_8	5,42519190913453E-07	8,86360873031563E-08	2,69908922548375E-05
10	a_9	–4,42026715277817E-08	–1,13931253218186E-09	–5,01147015885084E-06
11	a_{10}	—	6,34354112186225E-12	3,73389424564893E-07

3.2. Dry saturated vapor region

For the dry saturated vapor region, the same relationships were determined as for the refrigerant in saturated liquid state: temperature T'' [K], specific enthalpy h'' [kJ/kg], specific entropy s'' [kJ/(kg·K)], specific heat c_p'' [kJ/(kg·K)], density ρ'' [kg/m^3], specific volume v'' [m^3/kg], thermal conductivity λ'' [W/(m·K)], dynamic viscosity coefficient μ'' [kg/(m·s)], Prandtl number Pr'' [-], surface tension σ'' [N/m].

The relationships (Table 6) were analyzed in the same way as for the refrigerant in the saturated liquid stage.

TABLE 6

Computational formulas of thermodynamic and thermokinetic parameters of the refrigerant R404A in dry saturated vapor state

No.	Parameter	Unit	Formula	Formula No.
1	Temperature	[K]	$T'' = \sum_{n=1}^{6} a_n \cdot \ln p^n + a_0$	(11)
2	Specific enthalpy	[kJ/kg]	$h'' = \sum_{n=1}^{8} a_n \cdot \ln p^n + a_0$	(12)
3	Specific entropy	[kJ/(kg·K)]	$s'' = \sum_{n=1}^{8} a_n \cdot \ln p^n + a_0$	(13)
4	Specific heat	[kJ/(kg·K)]	$c_p'' = \sum_{n=0}^{10} a_n \cdot p^n$	(14)
5	Density	[kg/m^3]	$\rho'' = \sum_{n=0}^{9} a_n \cdot p^n$	(15)
6	Specific volume	[m^3/kg]	$v'' = \sum_{n=1}^{9} a_n \cdot \ln p^n + a_0$	(16)
7	Thermal conductivity	[W/(m·K)]	$\lambda'' = \sum_{n=0}^{9} a_n \cdot p^n$	(17)
8	Dynamic viscosity coefficient	[kg/(m·s)]	$\mu'' = \sum_{n=0}^{9} a_n \cdot p^n$	(18)
9	Prandtl number	[-]	$\mathrm{Pr}'' = \sum_{n=0}^{10} a_n \cdot p^n$	(19)
10	Surface tension	[N/m]	$\sigma'' = \sum_{n=1}^{10} a_n \cdot \ln p^n + a_0$	(20)

The determined coefficients of the polynomial for each property of the refrigerant in dry saturated vapor state are contained in Table 7 (temperature, specific enthalpy, specific entropy, specific heat), Table 8 (density, specific volume, thermal conductivity) and Table 9 (dynamic viscosity coefficient, Prandtl number, surface tension).

TABLE 7

Coefficients of polynomials describing temperature, specific enthalpy, specific entropy, and specific heat of dry saturated vapor of the refrigerant R404A

No.	Coefficients	Formula			
		$T'' = f(p)$	$h'' = f(p)$	$s'' = f(p)$	$c_p'' = f(p)$
		(11)	(12)	(13)	(14)
1	a_0	2,27410426641056E+02	3,39783061494940E+02	1,64251763041994E+00	7,69989040497841E-01
2	a_1	2,06006572886799E+01	1,24605499333403E+01	–2,63746194962245E-02	–5,29026778556052E-02
3	a_2	2,25611235911456E+00	5,32270332066417E+00	1,56817328382986E-02	8,79346980973612E-02
4	a_3	3,77214728357499E-01	–3,74784444000637E+00	–1,06717475065130E-02	–3,17912840686778E-02
5	a_4	–1,52868513518368E-01	–5,54831220935182E+00	–1,56214222907762E-02	5,94459994936388E-03
6	a_5	6,94932104626961E-02	9,70196932604655E+00	2,74095159320188E-02	–6,52474575552540E-04
7	a_6	–9,32648090982757E-03	–5,44515648883569E+00	–1,53866016729331E-02	4,43228143042173E-05
8	a_7	—	1,34287982208833E+00	3,79365913617968E-03	–1,88495955896429E-06
9	a_8	—	–1,24741452948463E-01	–3,52065478311403E-04	4,88440472337277E-08
10	a_9	—	—	—	–7,05092484167395E-10
11	a_{10}	—	—	—	4,34849974911910E-12

TABLE 8

Coefficients of polynomials describing density, specific volume and thermal conductivity of dry saturated vapor of the refrigerant R404A

No.	Coefficients	Formula		
		$\rho'' = f(p)$	$v'' = f(p)$	$\lambda'' = f(p)$
		(15)	(16)	(17)
1	a_0	4,69835801745614E-02	1,84677450100487E-01	8,11178359891879E-03
2	a_1	5,63530190311826E+00	–1,73898478003280E-01	2,82019825982088E-03
3	a_2	–3,42028140298342E-01	8,07429110010910E-02	–7,06920435431416E-04
4	a_3	8,18365201531940E-02	–2,49089400344961E-02	1,21833088515820E-04
5	a_4	–1,06409941156177E-02	5,87938355986300E-03	–1,27464276837250E-05
6	a_5	8,57974267701066E-04	–1,45948951746503E-03	8,38999877667568E-07
7	a_6	–4,25031596457310E-05	5,33454756137698E-04	–3,49510542622932E-08
8	a_7	1,26258208444692E-06	–1,79846645302972E-04	8,95749113730857E-10
9	a_8	–2,06103778692196E-08	3,48682622661943E-05	–1,28987890837223E-11
10	a_9	1,42494623229520E-10	–2,76255459671168E-06	7,99959837002893E-14

3.3. Superheated vapor region

For the refrigerant R404A in superheated vapor state, the authors developed four relationships describing thermodynamic parameters: specific enthalpy as a function of pressure and temperature: $h = f(p,t)$, specific enthalpy as a function of pressure and specific entropy: $h = f(p,s)$, specific entropy as a function of pressure and temperature: $s = f(p,t)$, temperature as a function of pressure and specific enthalpy: $T = f(p,h)$.

TABLE 9

Coefficients of polynomials describing dynamic viscosity coefficient, Prandtl number and surface tension of dry saturated vapor of the refrigerant R404A

No.	Coefficients	Formula		
		$\mu'' = f(p)$	$Pr'' = f(p)$	$\sigma'' = f(p)$
		(18)	(19)	(20)
1	a_0	8,95554359739614E-06	7,85602572089583E-01	1,31899428160687E-02
2	a_1	1,55528928352342E-06	–5,04704556436273E-02	–2,45337787212936E-03
3	a_2	–3,70279522192208E-07	4,85218645041743E-02	–2,77294233973954E-04
4	a_3	6,16645799186998E-08	–1,56001925386761E-02	7,63622008634168E-07
5	a_4	–6,28969298384910E-09	2,76427395619049E-03	–5,73563542287303E-05
6	a_5	4,03056081439239E-10	–2,95521642582208E-04	–2,26952433974978E-05
7	a_6	–1,62893268234041E-11	1,98255043194716E-05	8,90135978558169E-05
8	a_7	4,03454032515508E-13	–8,38753827565172E-07	–7,04240227397136E-05
9	a_8	–5,59618140267256E-15	2,17073348665435E-08	2,64415808604930E-05
10	a_9	3,33445246803155E-17	–3,13668944286168E-10	–4,91737057392738E-06
11	a_{10}	—	1,93898951802684E-12	3,66899197250496E-07

Data for the analyses were obtained by reading the values of the specific enthalpy and specific entropy for the pressure of 0.5 to 35 bar with a variability of 0.1 bar, and for the temperature from the dry saturated vapor temperature to 100°C with a variability of 1°C. A total of 24097 data were used to develop each formula. The formulas are contained in Table 10 and the coefficients for the equations in Table 11.

TABLE 10

Computational formulas for the thermodynamic parameters of the refrigerant R404A in superheated vapor state

No.	Parameter	Unit	Formula	Formula No.
1	Specific enthalpy as a function of pressure and temperature	[kJ/kg]	$h = \sum_{n=1}^{6}(a_n \cdot p + b_n \cdot t + c_n)^n$	(21)
2	Specific enthalpy as a function of pressure and specific entropy	[kJ/kg]	$h = \sum_{n=1}^{4}(a_n \cdot \ln p + b_n \cdot \ln s + c_n)^n$	(22)
3	Specific entropy as a function of pressure and temperature	[kJ/(kg·K)]	$s = \sum_{n=1}^{5}(a_n \cdot \ln p + b_n \cdot t + c_n)^n$	(23)
4	Temperature as a function of pressure and specific enthalpy	[K]	$T = \sum_{n=1}^{4}(a_n \cdot p + b_n \cdot h + c_n)^n$	(24)

TABLE 11

Coefficients of polynomials describing thermodynamic parameters of superheated vapor of the refrigerant R404A

No.	Coefficients	Formula			
		$h = f(p,t)$	**$h = f(p,s)$**	**$s = f(p,t)$**	**$T = f(p,h)$**
		(21)	**(22)**	**(23)**	**(24)**
1	a_1	–1,61447546392564E+01	1,11158970841813E+01	2,30551999958680E+02	–1,93462756056163E+02
2	a_2	–8,58136329467770E-03	2,10259014814250E-01	9,42733212785861E-01	–5,45318990684276E-07
3	a_3	1,93495300210842E-02	5,60011689169090E-02	–9,82720639724708E-02	5,78298359882372E-03
4	a_4	–8,67814297226799E-02	2,10508138833602E-01	–4,32608603352939E-01	2,65755992255702E-02
5	a_5	–7,60352668124328E-02	—	–2,75041360479625E-01	—
6	a_6	–3,95461111371696E-02	—	—	—
7	b_1	2,51517783958237E+00	2,40481406797838E+02	–3,44768974437698E+00	–3,33817805492781E+02
8	b_2	5,32804825659345E-02	5,35791535204568E+00	–1,35382927371767E-02	1,02242359478704E-01
9	b_3	–8,00667474672958E-03	1,42162833766823E+00	1,52664111581301E-03	6,15666410252490E-03
10	b_4	1,79488599029534E-02	5,21366723572646E+00	5,22951892334805E-03	1,49987730833413E-02
11	b_5	2,56000599132325E-02	—	3,32350014002661E-03	—
12	b_6	1,71258936591605E-02	—	—	—
13	c_1	2,63180855942421E+03	1,30262084987531E+02	4,94254347804191E+03	9,41918066769461E+05
14	c_2	4,35730795650912E+01	6,18677869802833E+00	–5,77037749331619E+01	5,80426042510737E+02
15	c_3	–1,60767279670175E+01	1,32814155260488E+00	–2,02217186159046E+01	–1,08555133404352E+02
16	c_4	–5,60006045782348E-01	–1,18607908765026E+00	–8,63364011319460E-01	–5,38422789769136E+00
17	c_5	–1,40255352344797E+00	—	–1,14975776869262E+00	—
18	c_6	–1,44685245591227E+00	—	—	—

3.4. Supercooled liquid region

For the refrigerant R404A in supercooled liquid state, the authors developed three relationships describing thermodynamic parameters: specific enthalpy as a function of pressure and temperature: $h = f(p,t)$, specific entropy as a function of pressure and temperature: $s = f(p,t)$, temperature as a function of pressure and specific enthalpy: $T = f(p,h)$.

Data for the analyses were obtained by reading the values of the specific enthalpy and specific entropy for the pressure of 0.5 to 35 bar with a variability of 0.1 bar, and for the temperature from –100°C to the saturated liquid temperature to with a variability of 1°C. A total of 46156 data were used to develop each formula. The formulas are contained in Table 12 and the coefficients for the equations in Table 13.

4. Statistical verification of computational formulas of thermodynamic and thermokinetic parameters of R404A

The developed formulas describing the parameters of R404A were subjected to statistical verification by determining correlation coefficients and coefficients of determination (Table 14),

TABLE 12

Computational formulas for the thermodynamic parameters of the refrigerant R404A in supercooled liquid state

No.	Parameter	Unit	Formula	Formula No.
1	Specific enthalpy as a function of pressure and temperature	[kJ/kg]	$h=\sum_{n=1}^{6}(a_n\cdot p+b_n\cdot t+c_n)^n$	(25)
2	Specific entropy as a function of pressure and temperature	[kJ/(kg·K)]	$s=\sum_{n=1}^{6}(a_n\cdot p+b_n\cdot t+c_n)^n$	(26)
2	Temperature as a function of pressure and specific enthalpy	[K]	$T=\sum_{n=1}^{5}(a_n\cdot p+b_n\cdot h+c_n)^n$	(27)

TABLE 13

Coefficients of polynomials describing thermodynamic parameters of supercooled liquid of the refrigerant R404A

No.	Coefficients	Formula		
		$h=f(p,t)$	$s=f(p,t)$	$T=f(p,h)$
		(25)	(26)	(27)
1	a_1	1,80738488490748E+01	1,02188848335934E+01	–7,65816534257380E+00
2	a_2	–1,09254239861645E-01	3,97104454086450E-02	1,03008645073297E-01
3	a_3	–2,10813823757872E-02	–7,01419731511928E-03	1,10507915950042E-02
4	a_4	–7,68928513153763E-03	–2,82058202899844E-03	6,17225320516499E-04
5	a_5	–3,48200418173251E-03	–1,43205201700350E-03	–3,22484156758068E-03
6	a_6	–1,55859992756645E-03	–8,41035779729922E-04	—
7	b_1	–9,05957464556919E+01	–4,87319162983095E+01	1,44437268008011E+01
8	b_2	5,38551408684314E-01	–1,88421889644897E-01	–1,80368144726043E-01
9	b_3	1,15550250925986E-01	3,38256889429956E-02	–1,94783658064590E-02
10	b_4	4,82122478524765E-02	1,40042077711670E-02	–9,08034560785994E-04
11	b_5	2,60878064319194E-02	7,40767160448585E-03	5,65941136528487E-03
12	b_6	1,69191697104068E-02	6,37077346649203E-03	—
13	c_1	2,45029921690494E+03	3,51604493564486E+03	1,19859821300475E+04
14	c_2	3,10510203343116E+01	–5,28709953651019E+01	–5,89947611492851E+01
15	c_3	–1,61836270697630E+01	–1,94468778418287E+01	–2,48021618625257E+01
16	c_4	–5,79308941499325E+00	–5,81059689243440E+00	3,56657808940597E-01
17	c_5	–2,52374412877928E+00	–2,49087425782797E+00	–2,51163869415836E+00
18	c_6	–8,26814551464307E-01	–9,85655899213133E-02	—

as well as absolute and relative deviations between the values from REFPROP 7 (Lemmon et al., 2002) and the calculated ones (Table 15).

TABLE 14

Correlation coefficients and coefficients of determination of computational formulas of thermodynamic and thermokinetic parameters of R404A

No.	Formula		Region	Correlation coefficient R [-]	Coefficient of determination R^2 [-]
1	$T' = f(p)$	(1)	Saturated liquid	0,9999999771	0,9999999542
2	$h' = f(p)$	(2)	Saturated liquid	0,9999973908	0,9999947815
3	$s' = f(p)$	(3)	Saturated liquid	0,9999980801	0,9999961603
4	$c_p' = f(p)$	(4)	Saturated liquid	0,9999296938	0,9998593926
5	$\rho' = f(p)$	(5)	Saturated liquid	0,9999888338	0,9999776678
6	$v' = f(p)$	(6)	Saturated liquid	0,9999964783	0,9999929567
7	$\lambda' = f(p)$	(7)	Saturated liquid	0,9999642225	0,9999284463
8	$\mu' = f(p)$	(8)	Saturated liquid	0,9999994801	0,9999989602
9	$\mathrm{Pr}' = f(p)$	(9)	Saturated liquid	0,9998537843	0,9997075900
10	$\sigma' = f(p)$	(10)	Saturated liquid	0,9999999898	0,9999999796
11	$T'' = f(p)$	(11)	Dry saturated vapor	0,9999999643	0,9999999287
12	$h'' = f(p)$	(12)	Dry saturated vapor	0,9998517829	0,9997035878
13	$s'' = f(p)$	(13)	Dry saturated vapor	0,9998526028	0,9997052274
14	$c_p'' = f(p)$	(14)	Dry saturated vapor	0,9999789722	0,9999579448
15	$\rho'' = f(p)$	(15)	Dry saturated vapor	0,9999999477	0,9999998954
16	$v'' = f(p)$	(16)	Dry saturated vapor	0,9999999949	0,9999999898
17	$\lambda'' = f(p)$	(17)	Dry saturated vapor	0,9999958139	0,9999916279
18	$\mu'' = f(p)$	(18)	Dry saturated vapor	0,9999951517	0,9999903034
19	$\mathrm{Pr}'' = f(p)$	(19)	Dry saturated vapor	0,9999841645	0,9999683293
20	$\sigma'' = f(p)$	(20)	Dry saturated vapor	0,9999999901	0,9999999802
21	$h = f(p,t)$	(21)	Superheated vapor	0,9999355693	0,9998711428
22	$h = f(p,s)$	(22)	Superheated vapor	0,9993992312	0,9987988233
23	$s = f(p,t)$	(23)	Superheated vapor	0,9997752451	0,9995505406
24	$T = f(p,h)$	(24)	Superheated vapor	0,9998518145	0,9997036509
25	$h = f(p,t)$	(25)	Supercooled liquid	0,9999980335	0,9999960670
26	$s = f(p,t)$	(26)	Supercooled liquid	0,9999989569	0,9999979138
27	$T = f(p,h)$	(27)	Supercooled liquid	0,9999980990	0,9999961980

In all cases, both correlation coefficients and coefficients of determination exceed 99%, which suggests that the models explain almost the entire variability of the explanatory variable. The lowest values of correlation coefficients and coefficients of determination occur for the relationship describing the specific enthalpy of superheated vapor as a function of pressure and specific entropy (formula 22), and they are 0.9993992312 and 0.9987988233, respectively.

The maximum mean relative deviation equals to 0.381464% (formula 14). However, only for 6 out of 27 relationships, the mean relative deviations exceed 0.1%. For 13 of them, the maximum relative deviation exceeds 1%, but only in 3 cases it is greater than 2% (formulas 9, 14 and 23). Narrowing the pressure range results in a decrease in the maximum relative deviations to less than 1% for 11 relationships. Only for the formula for the Prandtl number of the saturated liquid and the specific heat of dry saturated vapor, the maximum deviations slightly exceed 1% and are 1,023 and 1,248%, respectively (Table 16).

TABLE 15

Absolute and relative deviations between the given values and the calculated ones

No.	Formula		Region	Absolute deviation			Relative deviation [%]	
1	2	3	4	5	6	7	8	9
1	$T' = f(p)$	(1)	Saturated liquid	mean	[K]	0,005136	mean	0,001715
				maximum		0,027540	maximum	0,012916
2	$h' = f(p)$	(2)	Saturated liquid	mean	[kJ/kg]	0,082525	mean	0,033553
				maximum		0,635970	maximum	0,285866
3	$s' = f(p)$	(3)	Saturated liquid	mean	[kJ/(kg·K)]	0,000235	mean	0,020356
				maximum		0,001844	maximum	0,146016
4	$c_p' = f(p)$	(4)	Saturated liquid	mean	[kJ/(kg·K)]	0,007629	mean	0,360568
				maximum		0,110998	maximum	1,732418
5	$\rho' = f(p)$	(5)	Saturated liquid	mean	[kg/m^3]	0,499398	mean	0,048945
				maximum		7,821968	maximum	0,580390
6	$v' = f(p)$	(6)	Saturated liquid	mean	[m^3/kg]	$3,32 \cdot 10^{-7}$	mean	0,033861
				maximum		$4,23 \cdot 10^{-6}$	maximum	0,568096
7	$\lambda' = f(p)$	(7)	Saturated liquid	mean	[W/(m·K)]	0,000060	mean	0,088842
				maximum		0,001014	maximum	1,018024
8	$\mu' = f(p)$	(8)	Saturated liquid	mean	[kg/(m·s)]	$5,29 \cdot 10^{-8}$	mean	0,057589
				maximum		$4,34 \cdot 10^{-7}$	maximum	0,779155
9	$\mathrm{Pr}' = f(p)$	(9)	Saturated liquid	mean	[-]	0,007240	mean	0,197897
				maximum		0,140540	maximum	2,511703
10	$\sigma' = f(p)$	(10)	Saturated liquid	mean	[N/m]	$3,82 \cdot 10^{-7}$	mean	0,048540
				maximum		$2,67 \cdot 10^{-6}$	maximum	1,898087
11	$T'' = f(p)$	(11)	Dry saturated vapor	mean	[K]	0,006405	mean	0,002124
				maximum		0,037968	maximum	0,017735
12	$h'' = f(p)$	(12)	Dry saturated vapor	mean	[kJ/kg]	0,131472	mean	0,035387
				maximum		0,980858	maximum	0,266893
13	$s'' = f(p)$	(13)	Dry saturated vapor	mean	[kJ/(kg·K)]	0,000372	mean	0,023646
				maximum		0,002817	maximum	0,185800
14	$c_p'' = f(p)$	(14)	Dry saturated vapor	mean	[kJ/(kg·K)]	0,006895	mean	0,381464
				maximum		0,100269	maximum	3,274770
15	$\rho'' = f(p)$	(15)	Dry saturated vapor	mean	[kg/m^3]	0,018776	mean	0,036023
				maximum		0,234722	maximum	1,291476
16	$v'' = f(p)$	(16)	Dry saturated vapor	mean	[m^3/kg]	$3,06 \cdot 10^{-6}$	mean	0,043398
				maximum		0,000025	maximum	0,746406
17	$\lambda'' = f(p)$	(17)	Dry saturated vapor	mean	[W/(m·K)]	0,000014	mean	0,085361
				maximum		0,000098	maximum	0,898104
18	$\mu'' = f(p)$	(18)	Dry saturated vapor	mean	[kg/(m·s)]	$5,72 \cdot 10^{-9}$	mean	0,044076
				maximum		$6,82 \cdot 10^{-8}$	maximum	0,712399
19	$\mathrm{Pr}'' = f(p)$	(19)	Dry saturated vapor	mean	[-]	0,003285	mean	0,238728
				maximum		0,044918	maximum	1,159188
20	$\sigma'' = f(p)$	(20)	Dry saturated vapor	mean	[N/m]	$3,80 \cdot 10^{-7}$	mean	0,047686
				maximum		$2,64 \cdot 10^{-6}$	maximum	1,847727

1	22	3	4	5	6	7	8	9
21	$h = f(p,t)$	(21)	Superheated vapor	mean	[kJ/kg]	0,158482	mean	0,039215
				maximum		5,344301	maximum	1,454311
22	$h = f(p,s)$	(22)	Superheated vapor	mean	[kJ/kg]	0,710363	mean	0,177020
				maximum		4,774271	maximum	1,299192
23	$s = f(p,t)$	(23)	Superheated vapor	mean	[kJ/(kg·K)]	0,001372	mean	0,080406
				maximum		0,036341	maximum	2,397484
24	$T = f(p,h)$	(24)	Superheated vapor	mean	[K]	0,383385	mean	0,114696
				maximum		5,655104	maximum	1,652046
25	$h = f(p,t)$	(25)	Supercooled liquid	mean	[kJ/kg]	0,059675	mean	0,037309
				maximum		3,750973	maximum	1,170972
26	$s = f(p,t)$	(26)	Supercooled liquid	mean	[kJ/(kg·K)]	0,000184	mean	0,022495
				maximum		0,010883	maximum	0,789730
27	$T = f(p,h)$	(27)	Supercooled liquid	mean	[K]	0,057474	mean	0,023855
				maximum		1,812201	maximum	0,529602

TABLE 16

Maximum relative deviations for various pressure ranges

No.	Formula		Region	Maximum relative deviation [%]			
				0,5÷35 bar	1,0÷35 bar	0,5÷30 bar	1,0÷30 bar
1	$c_p{}' = f(p)$	(4)	Saturated liquid	1,732418	1,727272	1,732418	0,760168
2	$\lambda' = f(p)$	(7)	Saturated liquid	1,018024	0,408520	1,018024	0,364734
3	$\mathrm{Pr}' = f(p)$	(9)	Saturated liquid	2,511703	1,023024	2,511703	1,023024
4	$\sigma' = f(p)$	(10)	Saturated liquid	1,898087	1,898087	0,056059	0,056059
5	$c_p{}'' = f(p)$	(14)	Dry saturated vapor	3,274770	1,247633	3,274770	1,247633
6	$\rho'' = f(p)$	(15)	Dry saturated vapor	1,291476	0,237256	1,291476	0,237256
7	$\mathrm{Pr}'' = f(p)$	(19)	Dry saturated vapor	1,159188	0,874937	1,159188	0,529235
8	$\sigma'' = f(p)$	(20)	Dry saturated vapor	1,847727	1,847727	0,056640	0,056640
9	$h = f(p,t)$	(21)	Superheated vapor	1,454311	1,454311	0,406696	0,406696
10	$h = f(p,s)$	(22)	Superheated vapor	1,299192	1,299192	0,814614	0,699748
11	$s = f(p,t)$	(23)	Superheated vapor	2,397484	2,397484	0,955014	0,701793
12	$T = f(p,h)$	(24)	Superheated vapor	1,652046	1,652046	0,765522	0,765522
13	$h = f(p,t)$	(25)	Supercooled liquid	1,170972	1,170972	0,252675	0,251144

5. Summary

Knowledge of thermodynamic and thermokinetic parameters of the refrigerant R404A is essential not only to analyze the performance of refrigeration equipment but, most importantly, in comparative analyses with new replacements with low GWP values. For this purpose, 27 formulas developed by the authors, occurring in the supercooled liquid region, saturated liquid region, dry saturated vapor region and superheated vapor region, can be used. The relationships for the regions where two variables (supercooled liquid, superheated vapor) are required to unambiguously determine the thermodynamic parameters are especially useful. Thanks to a simple formula, a wide range of application (0.5÷35.0 bar) and, above all, very high values of correlation coefficients and coefficients of determination, the developed formulas can be used not only in all calculations of refrigeration and air conditioning in mines, but also in other areas where air compression refrigerators are used.

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