

Review of the doctoral thesis (PhD)

**“Thermophysical properties of refrigerants: experiment and simulations”**

written and submitted by Ing. Martin Doubek

Doctoral Study Program: Mechanical Engineering

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Dissertation thesis for obtaining the academic title of "Doctor" abbreviated to "Ph.D."

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Study Field: Mathematical and Physical Engineering

The thesis can be divided in two basic lines. The first one, experimental, is focused to development of the experimental apparatus designed for precise measurements of speed of sound in gases at various temperatures and pressures using the time-of-flight concept. Two gaseous binary technologically important mixtures R-116 ( $C_2F_6$ ) + R-218 ( $C_3F_8$ ) and R-218 ( $C_3F_8$ ) + R-728 ( $N_2$ ) at fixed compositions (one for each mixture) were selected for the study and the speed of sound in pure fluorocarbons (R-116, R-218) and in the mixtures was measured in the ranges from  $(-22$  to  $52)^\circ C$  and from  $(0.06$  to  $0.3)$  MPa. The second line of the study is focused on the thermodynamic modelling vapour-liquid equilibria (VLE) and speed of sound in pure and mixed refrigerants using selected equations of state (EoS). VLE and speed of sound data collected from the literature were used for the selections of the best performing EoS (SAFT-BACK, SB). An attempt to generalize the interaction parameters obtained for SB EoS is presented. Both above lines meet at the point where the values of speed of sound in two experimentally investigated gaseous mixtures calculated using the SB EoS with the generalized interaction parameters are compared with the experimental ones.

The topics of the thesis is closely related to the development of cooling systems and sound-speed analyzers applied at CERN. Thus the results of the thesis are of the direct and significant practical impact.

The goals of the thesis as summarized in Section 4.2 were fully reached. The state-of-art of both parts of the thesis is thoroughly and in detail presented in Sections 2 (Prior art) and 3 (Speed of sound measurement). Selected experimental and modelling methods and methodology issue clearly from the presented analysis, the reasons for the selections are clearly given. Construction of the apparatus for measurements of speed of sound in gases is described in detail (Section 5). It should be noted that the apparatus is the top result of the author's activity which dates back to his bachelor thesis (2012). Methodology selected for the thermodynamic modelling of the mixtures investigated and related refrigerant systems is based on the application of equations of state (to both the liquid and gas phases). Several equations of state (incl. “classical” Peng-Robinson one and modern SAFT models) are examined and their abilities concerning the description of VLE (incl. densities of liquid and vapour phases) and speed of sound are analyzed.

Ing. Doubek proved high level of his abilities in both the experimental and the theoretical aspects. This is evident not only from his doctoral thesis but also from his contributions in scientific literature and conferences (Ing. Doubek is a co-author of 11 published contributions (among them 5 papers in scientific journals, 3 conference proceedings) related to the topics of the

thesis). His multi-tasking skills (construction of mechanical parts, electronics, application of thermodynamics, computer programming) are clearly obvious.

The thesis is well structured, easily understandable. It is written in good English, evidently the author has an experience with the international scientific community. Unfortunately, some obvious misprints and errors which could be removed by a thorough reading of the thesis before submitting can be detected (some of them are summarized below). This, on the other hand, does not affect high standard of the content and extent of the thesis.

**I recommend the thesis for the defense.**

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### Comments and questions

1. Terminology (Nomenclature). “Molar density” is an inadequate term. Molar quantities are defined as  $\langle \text{extensive quantity} \rangle / \langle \text{amount of substance (number of moles)} \rangle$ ; for example molar volume  $v$  ( $\text{m}^3 \cdot \text{mol}^{-1}$ ) =  $V/n$ . Thus density cannot be molar since there is no extensive density. For the reciprocal molar volume  $n/V$  ( $\text{mol} \cdot \text{m}^{-3}$ ) IUPAC recommends the term “amount density” (in Czech “hustota látkového množství”).
2. Typography. Symbols (incl. those in super/subscripts) derived from the text should be written in normal fonts (see Nomenclature: LJ, RA, calc, exp, HC, id, perturbation, residual, etc.). Symbols for functions, quantities, and variables should be written in italics fonts. Thus, for example, the symbol for molar isobaric heat capacity of ideal gas should be as  $c_{p,m}^{\text{id}}$ .
3. Page 12, text below eqn (2.1.). Entropy during the adiabatic process is constant only if the adiabatic process is reversible.
4. Chap. 5. (Experimental) The accurate composition of the measured mixtures is one of crucial input information. It is not clearly described (page 78) how the composition was calculated from the pressures measured during the filling the sound-speed cell (pressure after filling one component, then total pressure after filling the second one). The calculation procedure would be simple in case of ideal gases (just from partial pressures), but how the real behavior of the gases was described (it is stated that compressibility factors of pure components from Lemmon and Span EoS were available with uncertainty of 0.5 – of what?), incl. the state behavior of the resulting mixture. What the statement “This is due to the compressibility being different from unity” means? I would guess that “compressibility factor” is the correct term in the sentence.
5. Section 5.7. (Measured data). I could not find any table with the experimental speeds of sound  $w(T,p)$  in two binary gaseous mixtures (R-218 + R-116, R-218 + N<sub>2</sub>) measured at  $T,p$  pairs shown in upper plots of Figs. 5.15 and 5.16. Since these values are main outputs of the experimental part of the thesis the measured data should be presented also in a tabular form, not only as plots (lower plots in Figs. 5.15 and 5.16; by the way, they are

- presented as functions of non-experimental vapour phase density calculated using the PR EoS).
6. Figures 7.2 through 7.4 show obvious correlation between correlated interaction coefficients  $k_{ij}$  and the fitted ones. Would it be possible to examine the effect of the use of correlated  $k_{ij}$  interaction coefficients (Table 7.16) on compositions calculated for VLE, i.e., how the deviations in  $x_1, y_1$  would change compared to values in Table 7.14 (fitted  $k_{ij}$ ) if the correlated  $k_{ij}$  would be used? The use of correlated (generalized) interaction coefficients would be true prediction of VLE compared to the results presented in Table 7.14 which are not the predictions but fitting the experimental data (minimization of the objective function (7.4) to find the optimum value of the interaction coefficient).
  7. Prediction of speed of sound in mixtures (Section 7.8). According to Table 7.15, R-218 and R-116 belong to Group 1 (G1), while R-728 (nitrogen) to Group 3 (G3). I understand that, according to Table 7.16, in the correlation Group1 + Group3 (selected for the predictions) the first group is G1 and the second group is G3. But for  $k(\text{R116+R218})$  (eqn (7.16)) the values of  $a_1 = a_2$  and  $b_1 = b_2$  presented for G3 (Table 7.16 and Fig. 7.3) are used while for  $k(\text{R-218+R-728})$  (eqn (7.17))  $a_1$  and  $b_1$  (R-218) presented for G3 and  $a_2$  and  $b_2$  (R-728) presented for G1 are used. This should be clarified.
  8. Page 125. According to Figs. 7.5 and 7.6 the deviations of the predicted speeds of sound from the experimental ones are below 1% (R-116 + R-218, positive – if the differences are (predicted – experimental)) and 1.5% (R-218 + R-728, negative). Would it be possible to estimate what would be the “error” in concentration of a sound analyzer which would employ the predicted values of speed of sound? In other words, what is the slope ( $dw/dx_1$ ) (or better ( $dx_1/dw$ )) in the vicinity of compositions of the mixtures investigated? This information would enable us to estimate the “error” in concentration  $\delta x_1 = (dx_1/dw)\delta w$  where  $\delta w$  is the “error” in predicted speed of sound. It is likely that there is no experimental information concerning ( $dx_1/dw$ ) but would it be possible to estimate it from the applied models?
  9. Are there any experimental data available in the literature for speed of sound in gaseous mixtures of refrigerants included in Table 7.15 which could be employed for more extensive examination of the performance of the designed generalization of interaction coefficients?

**Comments of minor importance** (concern mostly to misprints)

- a. Page 6, Fig. 1.4. Methanol is mentioned in the figure caption but ethanol on the horizontal axis of the lower plot.
- b. Page 13, top. “Translational “ constant volume molar heat capacity is  $(3/2)R$ , not  $(2/3)R$ , thus translational + rotational  $c_{V,m}^{\text{id0}} = (3/2)R$  (monoatomic),  $(5/2)R$  (diatomic and polyatomic linear), and  $(6/2)R$  (polyatomic nonlinear).
- c. Page 13, eqns (2.5), (2.6). According to Nomenclature,  $\rho$  is “molar density” (see also the comment 1 above), but in the equations it stands for “number density” which is not defined in the text (number of particles per unit volume?).
- d. Page 14, top. Superscript <sup>r</sup> stands for residual parts of quantities, I would guess that  $c_V^{\text{res}}$  in eqn (2.7) should be  $c_V^r$ .
- e. Van der “Waalse” is mentioned several times, the correct name is van der Waals.
- f. Page 17, eqn (2.21). Original Redlich-Kwong EoS is formulated with  $(v+b)$  in the denominator of the 2<sup>nd</sup> term on the right-hand side, not with  $(v-b)$ . Soave modification is based on the replacement of  $a_{\text{RK}}/T^{0.5}$  with  $a = a_{\text{SRK}}(T)$ , not  $a_{\text{RK}} = a_{\text{SRK}}(T)$ .

- g. Page 17. It should be, probably, noted that the original PR EoS is the “two-constant” equation with  $b = c$  in eqn (2.25).
- h. Pages 79, 80. The text and Figure 5.15: “mixture of R-218 and 5.6% R-116” (probably correct), while the 4<sup>th</sup> column of Table 5.4 is for 5.6% R-218 + 94.4% R-116.
- i. Page 79, lower part of the text. “The calculated vapour-phase density should be within 1 from a true value...”. How to understand this?
- j. Page 87, eqn (6.25). The quantity  $\rho^*$  is reduced density rather than reduced pressure as stated in the text.
- k. Page 88, Table 6.2. What is  $\gamma$ , heat capacity ratio?
- l. Page 89, Figs. 6.1. and 6.2.  $T/T_c$  is the reduced temperature and thus its dimension cannot be [K] (Kelvin). The unit of specific heat capacity should be either [J/(kg·K)] or [J·kg<sup>-1</sup>·K<sup>-1</sup>], not [J/kg·K] (see also Fig. 6.3).
- m. Pages 108, 120. Saturated hydrocarbons of the general formula  $C_nH_{2n+2}$  are alkanes, not alkenes ( $C_nH_{2n}$  if the molecule comprises one double >C=C< bond).
- n. Page 110, Table 7.2. Reduced temperatures max  $T_r$ , min  $T_r$  are dimensionless (not in Kelvins).
- o. Page 110, Table 7.3. If  $\varepsilon$  is energy per particle ([J/particle]) and  $k_b$  is the Boltzmann constant ([J/(K·particle)]) then the dimension of the ratio  $\varepsilon/k_b$  should be [K] (as  $u^0/k_b$ ), not [J].
- p. Page 114, Table 7.8 and page 115, Table 7.9. Reduced temperatures max  $T_r$ , min  $T_r$  and reduced pressures max  $p_r$ , min  $p_r$  are dimensionless (not in Kelvins and MPa, resp.).
- q. Some symbols are not used consistently throughout the thesis. For example Boltzmann constant is  $k$  (eqn (6.22)),  $k_B$  (eqn 6.24)),  $k_b$  (Table 7.3). Another example: speed of sound as  $w$  or SoS (Tables 2.1, 2.2, 2.3, 2.5, Figs. 7.5, 7.6).
- r. Page 124. According to eqns (7.16) and (7.17) it should be stated that critical pressures in Pascals should be used in calculations of  $Y_i$  (eqn (7.15)). And what about eqns (7.13), (7.14)?
- s. Page 124, the text line above eqn (7.16). “... from Table table 7.16 was used ...”.
- t. Figs. 9.1. through 9.13, 9.14 through 9.37. The symbols on the horizontal axes should be reduced quantities (temperature  $T_r$ , density  $\rho_r$ ), not the critical ones ( $T_c$ ,  $\rho_c$ ,  $Rho_c$ ). Similarly in lower plots of Figs. 7.5 and 7.6 reduced density  $\rho_r$  should stand in place of  $Rho_c$ .
- u. Language. The thesis is written in good English. There are, however, some misprints, both in grammar and spelling (few examples: p. 56, text below eqn (3.20): “... impedance is an intensive material properties ...”); p.86, 2<sup>nd</sup> text line: “... larger data-set then the previous two.” ; p. 97, text line above eqn (6.65): “... which is focused es on easy-to-use ...”; p. 120, bottom: “Thus not it is not possible ...”; p. 124, text below eqn (7.17): “... since the fluid are very similar.”; p.135, top: “... indicate accurcies of the models ...”; p. 154, middle: “The accuracy of the modes .... is show in common ...”).