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Summary of Dissertation Thesis

Thermophysical properties of refrigerants:
experiment and simulations

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experiment a simulace

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Název práce:

Termofyzikální vlastnosti chladiv: experiment a simulace

Anotace:

Předkládaná doktorská práce je studií termodynamických vlastností čistých chladiv a směsí chladiv včetně směsí nestejnorodých látek. Podrobně je studována rovnováha kapalina-pára a rychlost zvuku v obou fázích těchto směsí. První část práce se zabývá návrhem zařízení pro velmi přesné měření rychlosti zvuku, které je použito pro získání unikátních termodynamických dat. Druhá část je věnována výpočtům rychlosti zvuku a rovnováhy kapalina-pára čistých látek i směsí pomocí stavových rovnic. Hlavní motivací pro tento výzkum je současný vývoj nových směsí chladiv v komerčním sektoru a potřeby chladicích a monitorovacích systémů částicových detektorů v CERN v Ženevě.

Výpočty vlastností směsí různorodých látek (přírodní chladiva + fluorovaná chladiva) jsou náročný úkol. Složité kontribuční modely jsou v současné době jedinou volbou pro přesné výpočty směsí, ke kterým neexistují experimentální data. V rámci předkládané práce jsou vyvinuty nové korelace pro odhad binárních interakčních koeficientů pro model SAFT-BACK, který pro podobné směsi ještě nikdy nebyl použit. Tři SAFT modely jsou důkladně testovány na experimentálních datech rovnováhy kapalina-pára a rychlosti zvuku v obou fázích přírodních chladiv, fluorovaných chladiv a jejich směsí. Výsledkem spojení modelu SAFT-BACK s nově vyvinutými korelacemi je predikční model pro výpočty nových směsí chladiv, který vyžaduje jen malý počet parametrů.

Title: Thermophysical properties of refrigerants: experiment and simulations

Abstract:

This PhD thesis focuses on thermodynamics of pure refrigerants and refrigerants mixtures including mixtures of unlike fluids. The vapour-liquid equilibrium of these mixtures is studied along with speed of sound in both phases. The thesis consists of two parts: the first part is dedicated to design of a high accuracy speed of sound measurement apparatus which is used to obtain unique thermodynamic data. The second part deals with prediction models in form of equations of state. The research is driven by ongoing development of new refrigerant blends for commercial applications and by future needs of the cooling and monitoring systems for particle detectors at CERN.

The prediction of thermodynamic properties of fluid mixtures, especially mixtures of unlike fluids (natural refrigerants + fluorocarbons) is a challenging task. Currently only complex contribution methods can provide reasonable accuracy for new blends where no experimental data exists. This work presents newly developed correlations for prediction of binary interaction coefficient for SAFT-BACK model which has never been used for such mixtures. Three SAFT models are scrutinized in terms of prediction of vapour liquid equilibrium and speed of sound using extensive data sets for natural refrigerants, fluorocarbons and their mixtures. The combination of the SAFT-BACK model with developed correlations creates prediction model for new refrigerant blends that uses only few fitting parameters.

Contents

1. Introduction	2
Uses of speed of sound in refrigeration applications	2
Refrigerant blends at CERN	3
2. Current status of research	4
Thermodynamic models.....	4
Binary interaction coefficients	6
Speed of sound measurement.....	7
3. Problem statement and goals	8
4. Development of high accuracy speed-of-sound measurement apparatus	9
5. Thermodynamic models	11
Pure fluids	11
Mixtures	12
Developed correlations of binary interaction coefficients	12
6. Summary and conclusions.....	13
Development of high accuracy speed-of-sound measurement apparatus	13
Evaluations of models.....	13
Applications	14
Publications related to the title of Dissertation *	16
References.....	18

1. Introduction

All refrigerants were pure fluids in the past but blends have been slowly introduced along the way. Either to replace phased-out pure refrigerants that were no longer allowed due to their high environmental impact (high Global Warming Potential GWP or Ozone Depletion Potential ODP). Or to provide certain performance characteristics that could not be achieved with pure fluids. Modern refrigerant blends are often mixtures of very different components (natural refrigerant, hydro-fluorocarbons HFCs, hydrofluoroolefins HFOs etc.) in order to provide desired properties, namely the low environmental impact. Unfortunately, modelling of such complex mixtures is a difficult task. Accurate models of the pure fluids coupled with appropriate mixing rules are required along with large and accurate experimental data sets that are needed for model fitting and model evaluations.

Apart from the fact that the speed of sound is needed to obtain the ideal gas heat capacity of the refrigerants and that it plays important role during the development of the thermodynamic models, it can be also used for fluid analysis of the blends. Relatively simple and inexpensive yet accurate instruments for speed of sound measurement coupled with appropriate model can be used for online monitoring of blend composition during blend development or during operation.

Uses of speed of sound in refrigeration applications

Analysis of air contaminants such as flammable gases based on the speed of sound has a long history. The speed of sound is tightly related with the molecular weight and density, very light or very heavy gases exhibit large differences in speed of sound when compared to air.

Possible uses for acoustic analysis in a typical refrigeration circuit are outlined in Figure 1. The speed of sound can be measured either in liquid or gas phase. The analyser number 1 in Figure 1 monitors the ambient air inside the cooling plant housing or in the room where the plant is installed to detect leak of a refrigerant from the system. The refrigerant sometimes leaks out of the system and sometimes the air gets inside the system. This can happen during maintenance, through pneumatically controlled valves and pressure regulators that are driven by compressed air (dome loaded / piloted valves) or when the low pressure suction side of the system operates below atmospheric pressure. These gases can be detected by the analyser number 2 at the top of the condenser. The refrigerant blend composition monitoring can be provided

by the analysers 3 and 4 that operates in liquid phase and vapour phase respectively. The number 3 can furthermore monitor the oil content in the refrigerant.

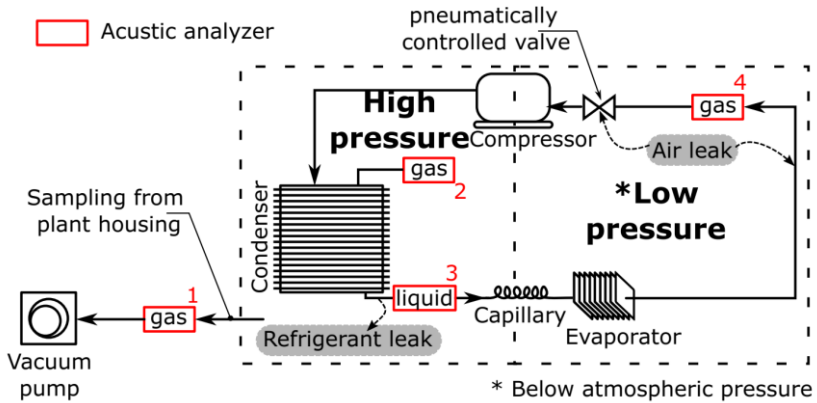


Figure 1 Internal and external leak detection

Refrigerant blends at CERN

The zeotropic mixtures of R-218 and R-116 are proposed as a replacement for pure R-218 that is currently in use for cooling of the inner detector that is part of the ATLAS experiment in the Large Hadron Collider at CERN [Bitadze, 2014]. Addition of up to 30% of R-116 into the currently used R-218 refrigerant would allow to keep the silicon particle detectors at lower temperature providing increased safety margins from thermal runaways. The R-116+R-218 blends are strongly zeotropic and therefore thermodynamic models have to be used to predict the composition of the saturated phases. The online composition analysis provided by the speed-of-sound analyser proved to be invaluable help for the blend development and testing [Bitadze, 2014].

The new inner detector cooling system called Thermosiphon, Figure 2, was designed to accommodate either pure R-218 or the blends, [Battistin et al., 2015]. The speed-of-sound based analysers are integral part of the system since they would be essential to control R-116+R-218 blend composition during operation and maintenance. Half of the Thermosiphon circuit will operate below the atmospheric pressure to allow for even lower evaporation temperature and therefore the air and humidity can contaminate the refrigerant and deteriorate the cooling performance or even cause damage.

For this reason, a unique purging system based on the speed of sound analyser was designed to detect and purge the air from the Thermosiphon condenser, Figure 3. The air is lighter than the refrigerant and it will accumulate on the top of the condenser. As the air displaces the R-218 in the provided accumulation volume, the speed of sound changes and when a threshold is reached the volume is released.

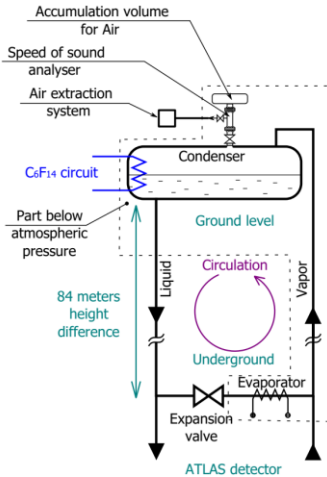


Figure 2 Thermosiphon cooling circuit



Figure 3 Degassing system for Thermosiphon condenser

2. Current status of research

Thermodynamic models

Primary interest of this work is in models, mostly equation of states, for prediction of vapour-liquid equilibrium and the speed of sound that require only few fluid-specific parameters and that can be applied to refrigerants and their blends including mixtures of unlike fluids. In addition, the models must work well in both vapour and liquid phases.

The equation used to obtain speed of sound from equation of state has following form:

$$w^2 = \frac{c_p}{c_v} \left(\frac{\partial p}{\partial \rho} \right)_T \quad (1)$$

The partial derivative of pressure with respect to the density at constant temperature and the heat capacities are evaluated from pressure or Helmholtz energy form of selected equation of state.

Empirical equations of state

Typical example of an empirical equation of state is the BWR (Benedict–Webb–Rubin) and mBWR (modified Benedict–Webb–Rubin) equation. The BWR equation of state uses eight fitting parameters while the modified version employs up to 32 fitting parameters. The resulting reference equation provide very good accuracy below 1%. The saturated pressure is often represented by an ancillary equation and not by the mBWR equation of state itself.

Virial equations of state

The acoustic virial equations of state, can be used to predict the speed of sound with high accuracy and it is used to correlate experimental speed of sound data. Unfortunately, this equation of state does not model the phase change and it is therefore usable only for gases.

Cubic equations

There is a vast list of various cubic equations of state, they provide good accuracy (often better than 1%) in terms of saturated pressure and vapour phase density but they fall short in predicting the PVT properties near critical region and the liquid density.

Volume-translated cubic equation of state

The volume translation has been proposed in order to improve the accuracy of the cubic equation in predicting the saturated liquid phase density. The translation is in fact a correction factor that shifts the predicted volumes. It is usually not recommended to use the volume translated cubic equations above the critical point or in the dense fluid region.

Helmholtz-energy equations of state

Modern equations of state are formulated in Helmholtz energy form as explicit functions of temperature and density. Such equations are replacing the mBWR equation of state as the reference high-accuracy equation of state for pure fluids. Models with up to 50 fitting parameters can represent the experimental density measurement with accuracy of 0.1% over wide range of temperature and pressures. So called Multi-fluid models can combine equations of state in the Helmholtz energy form for different pure fluids into

a model that describes a mixture. The resulting model is very accurate; the uncertainty of the speed-of-sound prediction can be below 0.5%.

Acoustic models

The speed-of-sound predictive model by Scalabrin, Marchi and Grigante [Scalabrin et al., 2007] is an interesting alternative to the models mentioned above. Although it is an acoustic model which cannot itself predict the vapour liquid equilibrium, it could be used alongside a cubic equation of state. The prediction accuracy of the model was tested on refrigerants R-11, R-22, R-123, R-134a, R-143a and R-152a. The average deviation of the model was 0.32% in the vapour region and 1.5% in the liquid region.

SAFT models

The SAFT (Statistical Associating Fluid Theory) models were developed by applying the perturbation theory to the equations of state of a monomer fluid. The perturbations accounts for chain formation (monomer chains), and additional terms can be added to account for association (hydrogen bonding) or polar molecules. The equations of state are in the Helmholtz energy form. The SAFT approach has become quite popular in the last two decades since it offers good accuracy for a broad range of fluids; from simple organic or inorganic molecules to complex polymers. A great advantage of these models is the small number of fitting parameters.

Binary interaction coefficients

One or more additional model parameters are introduced in order to provide better accuracy when the equations of state are used for mixtures. These parameters are called binary interaction parameters and their values are obtained by fitting experimental data of binary mixtures. For instance, the simplest combination rules for the parameters a corresponding to pure fluid i of a cubic equation of state can be following:

$$\bar{a}_{ij} = \sqrt{\bar{a}_i \bar{a}_j} k_{ij} \quad (2)$$

Where a_i are parameters corresponding to each pure fluid i . The interaction parameter k_{ij} is used to adjust value of a_{ij} which is assigned to each fluid pair ij in the mixture.

The two main approaches for estimation of interaction parameters are:

- group contribution methods
- correlations

Speed of sound measurement

The great advantage of the speed of sound is that it can be measured with astounding accuracy relatively easily. Following are the main speed of sound measurement principles:

- Resonance, Interferometry - methods based on resonance
- Time-of-flight, Sing-around, Pulse-echo - methods based on sound propagation over a distance

The resonators offer the highest accuracy from all known measurement methods. The resonator cavity is usually spherical although cylindrical or annular cavities are sometimes used as well, Figure 4. The cavity must be precisely manufactured and it is therefore expensive. A resonator model based solely on the unperturbed resonance frequency would provide measurement accuracy in the order of 0.01% [Hess, 1989]. A resonance model that employs the perturbations correcting for Thermal boundary layer, Bulk absorption and molecular relaxation and other effects can increase the accuracy up to 0.0001% [Hess, 1989].

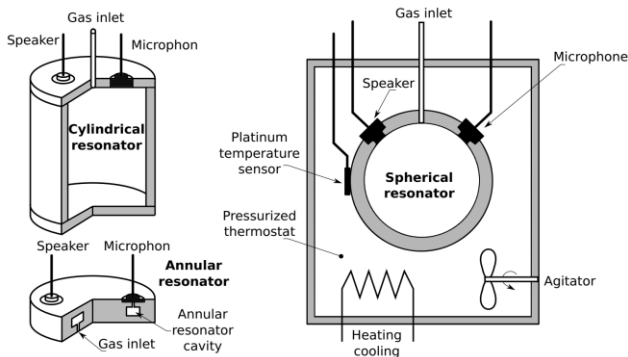


Figure 4 Cylindrical, spherical and annular resonator.

The time-of-flight method is very suitable for liquids and somewhat less for gases. The method has four significant advantages:

1. The measurement principle is robust, no delicate components are required.
2. Required instrumentation is simple and cheap.
3. The speed of sound is measured in a real time.
4. It can be combined with flow measurement.

The advantages of the time-of-flight method are exploited in industrial applications where it is widely used. The pulse-echo technique is used for thickness measurements of solid materials, level measurement and distance measurement.

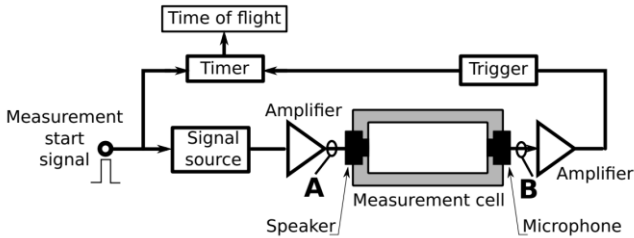


Figure 5 Time-of-flight measurement principle

A typical measurement set-up consist of a cylindrical measurement cell with ultrasonic transducer at the ends, Figure 5. The time it takes for the sound to propagate from the speaker to the microphone is precisely measured. The speed of sound is obtained immediately by dividing the travelled distance between the transducers by the measured time of flight.

3. Problem statement and goals

A universal model that would combine accurate prediction of the speed of sound and saturation properties of mixtures does not exist. It takes a significant effort to fit high accuracy equations to new or less-common fluids while the accuracy of the universal models with few fluid-specific parameters (fitting parameters) varied widely. Parameters called binary interaction coefficients are needed to accurately predict saturation properties of mixtures. There are many combinations for which these parameters are not known.

Goals

The thesis consists of the experimental and theoretical parts.

The goals of the experimental part are:

- to design an apparatus for high accuracy speed of sound measurement that can provide high at low complexity;
- to carry out speed of sound measurements in binary mixtures of R-116, R-218 and nitrogen since no such data exist in available literature and the mentioned binary mixtures have direct applications in the cooling systems of particle detectors.

The goals of the experimental part are:

- to benchmark various thermodynamic models on representative sets of pure fluids and mixtures in order to find the applicability range of the saturated properties and speed of sound predictions;
- to develop new correlations for the prediction of binary interaction coefficients for mixtures of unlike fluids with emphasis on fluorocarbons that will allow to work more accurately with blends and models for which no experimental data exist.

4. Development of high accuracy speed-of-sound measurement apparatus

The time-of-flight measurement method was selected for the measurement apparatus due to its relative simplicity and low cost. The developed setup, Figure 6, includes control system that allows for semi-automated measurement of the speed of sound. The setup provides data archivation in SQL-like database, data visualization through various charts and graphical panels and temperature regulation of the chiller. The fine-tuned PI regulation of the chiller enabled to repeatedly achieve measurement temperature precisely equal to the provided set point. The key component is the custom electronic I have developed and which employs a new triggering mechanism which the unique key element that ensures the high accuracy.

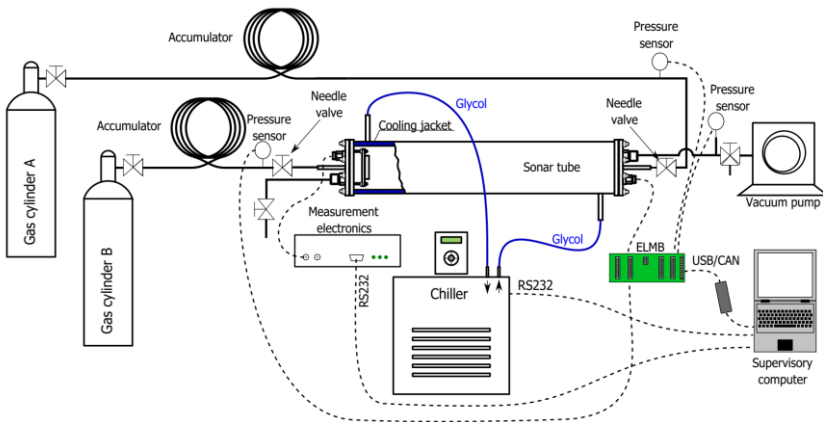


Figure 6 Constructed measurement setup for mixtures

The type A uncertainties u_A of the measured pressure, temperature and speed of sound are listed in Table 1. This uncertainty is a standard deviation of

samples recorded by the used data acquisition system. The type B uncertainties u_B of the temperature and pressure measurements correspond to the sensor calibration.

Table 1 Measurement uncertainties

		u_A	u_B	u_C	U
Temperature	K	0.013	0.03	0.03	0.1
Pressure	Pa	19	300	301	
Speed of sound	m/s	0.008	0.04	0.05	0.09
Composition	%		0.15	0.15	

The constructed setup was used to obtain unique speed of sound data of pure R-116, R-218 and mixtures of R-116+R-218 and R-218+N₂. The R-116 data were compared to several data sets from literature obtained with cylindrical resonator [Hurly, 1999] and [Hurly et al., 2003] with uncertainty of 0.01%, and data from annular resonator [Jarvis et al., 1996] with uncertainty of 0.05% and finally with data obtained with previous version of the time-of-flight instrument [Vacek et al., 2013].

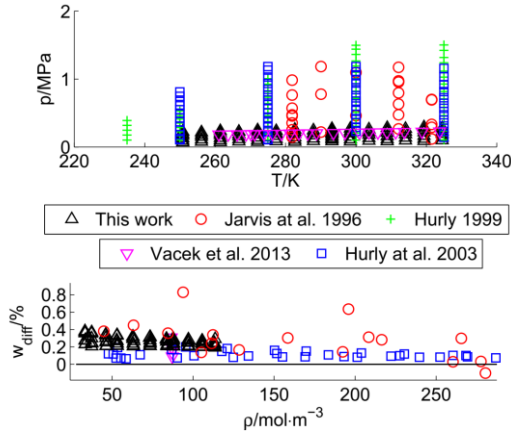


Figure 7 Comparison of the measured speed of sound in R-116 with data from literature

The comparison shown in the Figure 7 reveals that the difference w_{diff} between the speed of sound data obtained with the cylindrical and annular resonator is very high considering the claimed uncertainties of 0.04% and 0.05% respectively. The average deviation of the speed of sound data from

the cylindrical resonator is 0.33% while the average deviation of the data from this work with the data from the cylindrical resonator is only 0.25%.

5. Thermodynamic models

I have benchmarked following thermodynamic models in terms of prediction accuracy of saturated properties and speed of sound:

- Peng-Robinson equation of state (PR)
- Volume-translated Peng-Robinson equation of state
- Soft-SAFT (SS), sPC-SAFT (sPC) and SAFT-BACK (SB)

The volume translated models were later excluded from the comparison as they proved to be very unreliable.

Pure fluids

The models were evaluated using experimental data gathered from available literature, the data included following fluids: R-14, R-116, R-218, C₄F₁₀, C₅F₁₂, C₆F₁₄, R-50, R-170, R-290, R-600, R-728, R-744, Novec 649. The average results are show in in Table 2. The Peng-Robinson equation of state clearly fails in the liquid phase while the SAFT-BACK model performs overall the best.

Table 2 Results from model evaluations with pure fluids

AAD [%]	PR	sPC	SS	SB
Saturated pressure				
AAD [%]	1.59	1.19	2.02	0.94
Saturated vapour density				
AAD [%]	2.46	2.65	7.34	2.36
Saturated liquid density				
AAD [%]	6.2	1.9	3.32	1.93
Speed of sound in vapour				
AAD [%]	0.60	0.39	0.70	0.26
Speed of sound in liquid				
Average	19.03	12.55	9.89	2.84

Mixtures

The models were further evaluated in terms of prediction accuracy of the phase composition of binary mixtures. Experimental data gathered from available literature included following binary mixtures: R-744+R-728, R-50+R-728, R-728+R-170, R-728+R-290, R-728+R-600, R-744+R-50, R-744+R-170, R-744+R-290, R-744+R-600, R-728+ C₄F₁₀, R-744+R-116, R-744+ C₆F₁₄, R-170+R-50, R-50+R-290, R-50+R-600, R-170+R-600, R-600+R-290, R-50+ C₄F₁₀, R-50+ C₆F₁₄, R-170+R-116, R-170+R-218, R-116+R-290, R-600+R-116, R-116+ C₆F₁₄. The pressure and temperature were used as input parameters and the liquid phase composition x_i and vapour phase composition y_i were the calculated values. It can be seen from the results in Table 3 that all the models provides acceptable accuracy and the differences are relatively small.

Table 3 Results from model evaluations with mixtures

	AAD [%]							
	PR		sPC		SS		SB	
	x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
Average [%]	2.00	2.72	1.97	2.31	2.49	3.97	3.32	2.44

Developed correlations of binary interaction coefficients

The values from the models evaluation were used to develop correlations for prediction of the values of these coefficient for the SAFT-BACK model. Firstly, I divided the fluids into three groups, Table 4.

Table 4 Fluid groups

Group 1					
R-14	R-116	R-218	C ₄ F ₁₀	C ₅ F ₁₂	C ₆ F ₁₄
Group 2					
R-50	R-170	R-290	R-600		
Group 3					
R-728	R-744				

By studying the existing correlations, I came to a conclusion that the interaction coefficient should be correlated using fluid properties such as the

molecular weight or critical temperature and group-specific constants in order for the correlation to have prediction ability. I have used an optimization algorithm to search for the optimal correlation from number of candidate equations. The developed equations contain group-specific constants a and b and the fluid property Y , Table 5.

Table 5 Developed correlations

Mixture	Group1+Group2	Group1+Group3	Group2+Group2
Correlation	$\left[\frac{(a_1 + Y_1^{b_1})}{(a_2 + Y_2^{b_2})} \right]^{b_1+b_2}$		
Property	$Y_i = \omega_i$	$Y_i = \omega_i P_{ci}^{0.5} / T_{ci}$	$Y_i = \omega_i P_{ci}^{0.5} / T_{ci}$
First group constant a_1	2.8079	1.4008	-0.9836
First group constant b_1	1.7085	0.3141	0.0067
Second group constant a_2	2.1551	1.3729	-1.0592
Second group constant b_2	0.0755	0.8598	0.1560

6. Summary and conclusions

Development of high accuracy speed-of-sound measurement apparatus

The experimental part of this thesis presents the time-of-flight based instrument for speed of sound measurement I have developed. The instrument was adopted for mixtures so that two gases can be mixed directly inside the measurement chamber. A custom electronics I have designed and continuously improved is used for the speed of sound measurement. I have implemented a new triggering technique which eliminates errors in the transit time measurements to achieve the best accuracy. The comparison of the speed of sound I have measured in pure R-116 and R-218 with the most accurate data from literature, which were measured with extremely precise but expensive and difficult to build spherical resonators, indicated mutual deviation smaller than 0.4%. Although only the extremely accurate data from spherical resonators can be used to safely derive other thermodynamic properties such as the heat capacities, the deviation of 0.4% is smaller than deviations between experimental data and the speed of sound calculated by commonly used equations of state for refrigerants.

Evaluations of models

I have compiled numerous experimental data from literature in order to evaluate the selected thermodynamic models for accuracy in terms of prediction of saturation properties and speed of sound in both phases. The

evaluation focused on fluorocarbons and their mixtures with unlike fluids including carbon dioxide (R-744) that will be used in most of the new cooling applications at CERN. The evaluation of thermodynamic models for speed of sound prediction demonstrated that the simple cubic equations such as the Peng-Robinson equation of state can be used for the vapour-phase speed of sound prediction, for prediction of the saturated pressure and phase compositions but not for the liquid phase. The volume translated Peng-Robinson equation of state proved to be very unreliable with large deviations. The well-known sPC-SAFT proved to be a universal model with good accuracy in all the evaluated disciplines. The Soft-SAFT model exhibited large deviation in the vapour density and cannot be recommended for fluorocarbons. The little-known SAFT-BACK model was by far the best model with a small deviation below 2% even in the liquid region and close to the critical point where other models failed.

I have used the vapour-equilibrium data of mixtures containing saturated fluorocarbons, hydrocarbons, nitrogen and carbon dioxide to obtain the binary interaction coefficients of the evaluated models. The obtained coefficients of the SAFT-BACK model are especially valuable since they have not been reported in the available literature. I have developed correlations for estimation of the binary interaction coefficients for the SAFT-BACK model since there is no publications dealing with prediction of those coefficients. The correlation was shown to provide significant improvement for the speed of sound prediction for the R-218+R-728 mixture which was measured in the experimental part of the thesis. The correlation also correctly predicts the interaction coefficient very close to unity for R-116+R-218 mixture since it is a mixture of very similar fluids.

As a result, this work provides unique model parameters of 13 refrigerants for the very accurate but little-known SAFT BACK model and binary interaction coefficients of 24 mixtures and 3 correlations that can be used to predict the interaction coefficients for mixtures of saturated fluorocarbons, hydrocarbons, nitrogen and carbon dioxide. Neither the fluid parameters for the saturated fluorocarbons nor any of the binary interaction coefficients have been published in the available literature so far.

Applications

The speed of sound in R-116+R-218 and R-218+R-728 mixtures obtained with the developed instrument were published in Journal of Chemical Engineering Data ([Doubek & Vacek, 2016b]) and in proceedings of the Proceedings of 13th International Conference on Properties and Phase

Equilibria for Products and Process Design ([Doubek & Vacek, 2016a]) and 24th IIR International Congress of Refrigeration ([Doubek & Vacek, 2015]). These mixtures are interesting for the cooling systems currently used at CERN for particle detectors ([Battistin et al., 2015]). The R-116+R-218 blend might be used as a replacement for pure R-218 in the refrigeration systems in order to decrease evaporation temperatures to protect the particle detectors from thermal runaways as they accumulate more and more radiation damage, [Bates et al., 2015] and . The R-218+R-728 mixture is interesting for leak detection and modelling of performance of contaminated refrigerants. The nitrogen (R-728) can represent air mixing with a refrigerant during operation of the cooling plant. In all cases, accurate speed-of-sound measurements and prediction models provide valuable tool for online composition monitoring of refrigerant blends and real-time leak and contamination detection. I have participated in several projects that benefited from the speed-of-sound based analysis of refrigerants as is demonstrated in number of publications: The measurement of R-116+R-218 heat transfer ([Doubek et al., 2017b] and [Doubek et al., 2017a]) benefited from concentration monitoring based on speed of sound which was used to adjust the blend composition in order to evaluate impact of the increasing R-116 level. The Thermosiphon cooling system at CERN is currently using speed-of-sound based analyser I helped to develop to detect refrigerant contamination by air ([Alhroob et al., 2017a], [Alhroob et al., 2015] and [Alhroob et al., 2017b]), the developed simulations models can be used to further increase the detection accuracy. The measurement apparatus and the simulation models presented in this work can also be used for commercial refrigerants, especially for modern ecological blends or for monitoring and leak detection systems in industrial refrigeration plants. I have described several such applications as a co-author of the contribution presented on the IEEE SENSORS 2016 conference ([Doubek et al., 2016]).

Publications related to the title of Dissertation *

[Doubek et al., 2017b] Doubek, M., Haubner, M., Vacek, V., Battistin, M., Hallewell, G., Katunin, S., & Robinson, D. 2017b. Measurement of heat transfer coefficient in two phase flows of radiation-resistant zeotropic C2F6/C3F8 blends. *International Journal of Heat and Mass Transfer*, 113, 246 – 256.

[Alhroob et al., 2015] Alhroob, M., Battistin, M., Berry, S., Doubek, M., et al. 2015. Development of a custom on-line ultrasonic vapour analyzer and flow meter for the ATLAS inner detector, with application to Cherenkov and gaseous charged particle detectors. *Journal of Instrumentation*, 10(03), C03045.

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