Thermal conductivity calculation model of refrigerant mixtures on the dew line

E P Raschektaeva, O I Verba and S V Stankus
Institute of Thermophysics SB RAS, Novosibirsk, Russia
E-mail: raschektaevaep@gmail.com

Abstract. The results of the thermal conductivity measurements of ten mixture refrigerants in the gas phase are analysed. An equation for calculating the thermal conductivity is given for each mixture as a function of temperature and pressure. Basing on experimental information and the theory of of corresponding states a model for predicting thermal conductivity on dew line is proposed.

1. Introduction
The conditions of international protocols and global climate change prevention impose restrictions on the refrigerants used in domestic and industrial sphere. The way out of this situation was the creation of a large number of new mixed refrigerants that meet modern requirements for environmental safety. The exact thermophysical properties of such solutions should be known for the active introduction of the new mixtures.

Obviously it is impossible to experimentally investigate the thermophysical properties of all refrigerant compositions not only because of their large number, but also because of the laboriousness and long time required for carrying out the measurements. Therefore methods for calculating and predicting the refrigerants properties have been developed. The model of properties calculation must meet a number of criteria, among them are a minimal set of initial data, high accuracy of results, simple and fast computational operations. One of the ways to develop effective models for predicting thermophysical properties that meet the requirements listed above is to apply the similarity theory methods to generalize the data of a wide class of refrigerants.

2. Experimental data and their generalization
The thermal conductivity was measured by the stationary method of coaxial cylinders in the temperature ranges from 300 to 430 K and pressures from 0.1 MPa to 2.1 MPa. A detailed description of the measurement procedure and the experiment is done in [1, 2]. The error of the experimental data on the thermal conductivity was equal to 1.5–2.5%, while that on the temperature was 0.05 K and that on the pressure was within 4 kPa. Objects of research (solutions of refrigerants and intervals of thermal conductivity measurements) are given in Table 1. All refrigerants consist of such components as: R-22 (CHClF₂), R-32 (CH₂F₂), R-124 (C₂HClF₄), R-125 (C₂HF₅), R-134a (C₂H₂F₄), R-142b (C₂H₃ClF₂), R-143a (C₂H₃F₃), R-152a (C₃H₂F₂), R-227ea (C₃F₇), R-600a (C₄H₁₀). It should be noted that 10 mixture refrigerants were analysed in the work, the thermal conductivity of which was investigated at one unit, which increases the reliability of the results obtained, since systematic errors due to the use of different methods of measuring thermal conductivity are excluded.
Experimental data were approximated by empirical dependence on temperature and pressure:

\[
\lambda(p,T) = a_0 + a_{10} \frac{T}{100} + a_{20} \frac{100}{T} + p \left( a_{11} \frac{T}{100} + a_{21} \frac{100}{T} \right) + p^2 \left( a_{12} \frac{T}{100} + a_{22} \frac{100}{T} \right),
\]

where \(T\) is the temperature in K, \(p\) is the pressure in MPa, and \(\lambda\) is in mW/(m K). For example figure 1 shows experimental data and results smoothed by the equation (1) on isotherms for one of the mixtures.

**Table 1.** Investigated mixture.

| Mixture | Measurement intervals |
|---------|-----------------------|
| R-404A (R-125/R-134a/R-143a 44/4/52) [3] | 309-422 K, 0.1-1.8 MPa |
| R-406A (R-22/R-142b/R-600a 55/41/4) [4] | 308-424 K, 0.1-1.5 MPa |
| R-407C (R-134a/R-125/R-32 52/25/23) [2] | 303-425 K, 0.1-2.1 MPa |
| R409A (R-22/R-124/R-142b 60/25/15) [5] | 306-425 K, 0.1-1.3 MPa |
| R-410A (R-32/R-125 50/50) [6] | 314-430 K, 0.1-2.0 MPa |
| R-415A (R-22/R-152a 50/50) [7] | 308-415 K, 0.1-1.7 MPa |
| R-507A (R-125/R-143a 50/50) [8] | 312-425 K, 0.1-1.9 MPa |
| R-227ea/R-134a (61.5/38.5) [9] | 308-419 K, 0.1-1.2 MPa |
| R-227ea/R-134a (88.8/11.2) [10] | 307-426 K, 0.1-2.1 MPa |
| R-227ea/R-134a (45/55) [10] | 306-426 K, 0.1-1.6 MPa |
Thermal conductivity on the condensation line ($\lambda_d$) of the studied refrigerants was determined on the basis of the results of measurements. Values of $\lambda_d$ were obtained by two methods: by the extrapolation of the mixture vapor thermal conductivity isotherms to the dew line and by calculation according to the generalizing equation (1). Within the measurement errors both methods showed similar results. In order to maintain the uniformity of the description of the properties within the whole parameter range, a second calculation method was selected. The calculated $\lambda_d$ values are approximated by the dependence

$$\lambda_d = b_1 + b_2 T + b_3 T^2. \quad (2)$$

The coefficients of the equation are presented in table 2.

### Table 2. Coefficients of equation (2).

| Equation (2) | $b_1$  | $b_2$  | $b_3$       |
|--------------|--------|--------|-------------|
| R-404A       | 34.023 | -0.2503| 6.297×10^{-4}|
| R-406A       | 15.115 | -0.1049| 3.151×10^{-4}|
| R-407C       | 93.995 | -0.6297| 1.220×10^{-3}|
| R-409A       | 42.221 | -0.2662| 5.525×10^{-4}|
| R-410A       | 85.690 | -0.6282| 13.18×10^{-4}|
| R-415A       | 78.305 | -0.5073| 9.750×10^{-4}|
| R-507A       | 95.567 | -0.6901| 1.400×10^{-3}|
| R-227ea/ R-134a (61.5/38.5) | 45.8203 | -0.3090| 6.715×10^{-4}|
| R-227ea/ R-134a (88.8/11.2) | 69.6968 | -0.4597| 9.064×10^{-4}|
| R-227ea/R-134a (45/55)     | 54.2724 | -0.3696| 7.833×10^{-4}|

![Figure 2. Reduced thermal conductivity on dew line. Line is the equation (3).](image)
Following the general approaches of the corresponding state theory one can obtain an equation for $\lambda_d$ as a function of temperature in reduced units. As the normalizing temperature, $T_m = 0.9T_c$ was chosen, where $T_c$ is the critical temperature. $T_c$ of the refrigerant mixtures was calculated from data for pure components using the Li-Kessler mixing rules [11].

As it can be seen from figure 2, data for $\lambda_d$ for all 10 refrigerants is described by a quadratic dependence (3) with a standard deviation of 1.45%, which is less than the estimated errors in thermal conductivity measurements.

$$\lambda_d(T) = 3.188 - 7.033T + 4.846T^2,$$

where $T_r = T/T_m$, $\lambda_{dr} = \lambda_d(T)/\lambda_d(T_m)$.

Equation (3) makes it possible to calculate $\lambda_d$ of a wide class of refrigerant mixtures in a technically important temperature range from a single measurement of the vapor thermal conductivity at 0.9 $T_c$ and the critical parameters and the acentric factor of the pure components. Comparison of experimental data with the equation (3) has shown that the standard deviation for all refrigerants lies in the range 0.4-2.1%, which does not exceed the estimated measurement errors.

The suggested approach makes it possible to calculate the thermal conductivity of mixed refrigerants in a wide temperature range using experimentally determined values of $\lambda_d(T_m)$. Also the possibility of its determination through data for pure components is of interest. For this reason the dependence of the complex $\lambda_d(T_m)/C_p^0(T_m)$ on molecular weight $M$ was considered (figure 3). $C_p^0(T_m)$ is the ideal-gas heat capacity [12-14]. The heat capacity $C_p^0$ is strictly additive so it is easy to calculate through the ideal-gas heat capacity of the components.

It can be seen from figure 3 that this complex is well approximated by the equations

$$\lambda_d(T_m)/C_p^0(T_m) = 0.48 + 1.73 \cdot 10^{-3} M - 1.199 \cdot 10^{-5} M^2.$$

The standard deviation was 2.5%. In the equations (4) the dimensions are $\lambda_d(T_m)$ mW/(mK), $C_p^0(T_m)$ J/(mol K), $M$ g/mol. From the generalization, the mixture R-409A was excluded, the deviations from the approximation dependences for it were 11.8% for $\lambda_d$. The reason for such deviations seems to be that this mixture is the only one consisting of components, each of which contains chlorine.

![Figure 3](image-url)  
*Figure 3. Dependence $\lambda_d(T_m)/C_p^0(T_m)$ on molecular weight $M$. 1 – dew line based on experimental data; 2 – equation (4).*
3. Conclusions
The two methods for predicting the thermal conductivity of refrigerants mixtures on dew line have been developed. In the first method, the density and critical parameters of the mixtures are calculated from the equation of state and the Li-Kessler mixing rules using data for pure components. Further using single experimental value of the thermal conductivity at $0.9T_c$, the thermal conductivity of the refrigerant mixture on the condensation line is estimated.

In the second method, in contrast to the first, instead of the experimental value $\lambda_d(T_m)$, the value obtained from the equation (4) is used. Thus the calculation is performed without involving experimental information for the mixture. Comparison of the experimental data with the calculated methods showed that the standard deviation was 0.4-2.5%, which is within the estimated measurement errors.

References
[1] Verba O I and Gruzdev V A 2002 Thermophys. Aeromech. 9 445
[2] Verba O I, Raschektaeva E P and Stankus S V 2012 High Temp. 50 200
[3] Verba O I 2008 Thermophys. Aeromech. 14 165
[4] Verba O I, Raschektaeva E P and Stankus S V 2014 High Temp. 52 135
[5] Verba O I, Raschektaeva E P and Stankus S V 2011 Thermophys. Aeromech. 18 661
[6] Verba O I, Raschektaeva E P and Stankus S V 2017 Thermophys. Aeromech. 24 135
[7] Verba O I, Raschektaeva E P and Stankus S V 2013 Thermophys. Aeromech. 20 477
[8] Verba O I 2011 Thermophys. Aeromech. 18 151
[9] Verba O I, Raschektaeva E P and Stankus S V 2015 High Temp. 53 158
[10] Raschektaeva E P 2016 Thermal conductivity experimental study of refrigerants mixture in the vapor state Dissertation
[11] Lee B I, Kesler M G 1975 AIChE Journal. 21 510
[12] Lemmon E W, McLinden M O and Huber M L 2002 NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties—REFPROP, Version 8.0. Standard Reference Data Program, Gaithersburg, Maryland, United States: National Institute of Standards and Technology
[13] He M G, Liu Z G, Yin J M 2002 Int. J. Thermophys. 23 1599
[14] Gruzdev V A, Khairulin R A, Komarov S G and Stankus S V 2002 Int. J. Thermophys. 23 809