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# ALTERNATIVE REFRIGERANTS IN THE LIQUID PHASE: THERMAL CONDUCTIVITY OF BYNARY AND TERNARY MIXTURES

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## ABSTRACT

Refrigerant mixtures seem the most promising candidates as replacement fluids in refrigeration devices and heat pumps. In this paper two prediction methods are proposed for the evaluation of the thermal conductivity of refrigerant mixtures in their saturated liquid state and in the subcooled region. The first method is based on the use of mixing rules applied to pure refrigerant data evaluated by means of a prediction method originally developed by present authors. The second method approaches azeotropic refrigerant mixtures as pure refrigerants. It requires the knowledge of the molar mass and the critical temperature only showing very good accuracy and conformity with experimental data. The methods were tested against experimental data and show typical average absolute deviations which are less than 4%, with maximum absolute deviations usually less than 9% in the reduced temperature range 0.30 to 0.95.

## INTRODUCTION

Refrigerant mixtures are becoming the most promising candidates for the replacement of many working fluids in refrigeration devices and heat pumps. In fact, the necessity to replace many, widely used, compounds, combined with the usual requirements for effectiveness and safety, compelled scientific and engineering communities to study and develop new products at a constantly increasing rate. As a result, the number of binary and ternary mixtures introduced as new refrigerants by major industrial companies greatly increased during past years.

While many new effective alternatives have been proposed to replace most of working fluids already banned or becoming illegal in few years, the new bottle neck is represented by the testing of these compounds. In most of cases, the mixtures proposed by industrial companies are composed of refrigerants whose characteristics are well known. Thus the central problem becomes the evaluation of the properties of mixtures by means of reliable and effective mixing rules. However, a general equation, able to evaluate transport properties of mixtures as a sole function of their thermophysical properties, would be exceptionally useful. In principle this new approach would be possible but no proposal seems to have been published.

According to these concepts we stated to approach the evaluation of transport properties of refrigerant mixtures both by testing and refining the usual techniques based on the use of mixing rules and by introducing a new general equation as a sole function of mixture thermophysical properties. For what concerns the first issue, in this paper various alternatives for the evaluation of liquid thermal conductivity of mixtures composed of organic compounds are presented. The latter study, based on the new approach, was, at the moment, performed on azeotropic mixtures only. This is mainly due to the fact that their composition is fixed and their equilibrium properties are well known.

In both cases the mean and maximum deviations between evaluated and experimental liquid thermal conductivity data are usually less than 4% and 9% respectively, in temperature ranges which go from the normal melting point near to the critical point.

## THE PREDICTION METHOD FOR PURE REFRIGERANTS

Both our prediction methods for the liquid thermal conductivity of refrigerant mixtures are based on the semi-empirical equation already proposed by present authors for pure refrigerants [Latini, 96] and for other organic compounds [Latini, 95b]:

$$\lambda = B \cdot \left(1 - \frac{3}{4} T_r\right) \tag{1}$$

where $T_r$ was the reduced temperature $T/T_c$ and the constant $B$ was linked with some thermophysical properties in the form:

$$B = B^* \cdot T_c^{\alpha} \cdot P_c^{\beta} \cdot M^{\gamma} \tag{2}$$

The constant $B^*$ and the exponents $\alpha$, $\beta$, and $\gamma$ assumed different values for the methane series refrigerants and the ethane series refrigerants as listed in Table 1 [Latini, 96].

| Halocarbon refrigerants of the | $B^*$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|
| methane series | 0.4 | 1/4 | 1/3 | -3/4 |
| ethane series | 2.8 | -1/6 | 1/6 | -1/2 |

Table 1 - Coefficients of Eq. (2)

The Eq. (1) with the constant $B$ evaluated by means of Eq. (2) allowed the evaluation of the thermal conductivity of pure refrigerants in their saturated liquid state leading to maximum deviations between predicted values and experimental data usually less than 5% in temperature ranges from the normal melting point near to the critical point.

## MIXING RULES FOR REFRIGERANT MIXTURES

This part of our study was carried out in three steps. In a preliminary phase we exhaustively checked the mixing rules based on weight fractions $w$ and mole fractions $x$ which do not consider at all the interactions between the mixture components [Reid, 87]:

$$\lambda_m = \sum \lambda_i \cdot x_i \tag{3}$$

$$\lambda_m^{1/2} = \sum \lambda_i^{1/2} \cdot x_i \tag{4}$$

$$\lambda_m^{1/3} = \sum \lambda_i^{1/3} \cdot x_i \tag{5}$$

$$\lambda_m = \sum \lambda_i \cdot w_i \tag{6}$$

$$\lambda_m^{1/2} = \sum \lambda_i^{1/2} \cdot w_i \tag{7}$$

$$\lambda_m^{1/3} = \sum \lambda_i^{1/3} \cdot w_i \tag{8}$$

The result of this test let to conclude that all the mixing rules based on weight fractions lead to better results and that all these mixing rules over-estimate the thermal conductivity. The latter topic could be expected since there is an experimental evidence that the thermal conductivity of a mixture is usually less than the mere average of the component ones due to the interaction between the different molecules but we found that errors were unacceptable. Both the conclusions are apparently in contrast with those we determined while studying the liquid dynamic viscosity of refrigerant mixtures [Latini, 95a].

As a second step we checked two mixing rules originally conceived to evaluate the liquid thermal conductivity of binary mixtures of organic compounds.

The first rule is based on an extension of Eq.(2), developed by one of the present authors and successfully applied to refrigerant mixtures [Latini, 96]:

$$B = B_1 \cdot x_1^2 + B_2 \cdot x_2^2 + 2.20\sqrt{B_1^3/B_2} \cdot x_1 \cdot x_2 \tag{9}$$

where $B_1$ and $B_2$ are the constants of Eq. (1), evaluated by means of Eq. (2) and related to the two components of the mixture with $B_1 \geq B_2$. The constant $B$ evaluated by means of Eq. (9) could be introduced in Eq. (1) provided that the reduced temperature was calculated using a critical temperature evaluated by means of the Kay's rule [Reid, 87].

The second test regarded a mixing rule conceived by Filippov and Novoselova [Filippov, 55a] [Filippov, 55b] [Filippov, 55c]:

$$\lambda_m = \lambda_1 \cdot w_1 + \lambda_2 \cdot w_2 - C \cdot w_1 \cdot w_2 (\lambda_1 - \lambda_2) \tag{10}$$

where $\lambda_1 \geq \lambda_2$ and the factor $C$ was usually set to the value 0.72. We found the Filippov rule to be a good choice since it is based on the use of weight fraction and it contains a cross-term which is function of the difference between the thermal conductivity of the mixture compounds. This kind of correction seems to be the best one and leads to results coherent with experimental evidence. After such knowledge, Eq. (10) has been adapted by evaluating a new optimum value for the factor which was found to be $C$=0.5.

The third step regarded the extension of the latter binary mixing rules to ternary mixtures. We found that this was possible simply introducing new cross-term factors in the same form of the ones already present inside original formulas:

$$B = B_1 \cdot x_1^2 + B_2 \cdot x_2^2 + B_3 \cdot x_3^2 + 2.20\left(\sqrt{B_1^3/B_2} \cdot x_1 \cdot x_2 + \sqrt{B_1^3/B_3} \cdot x_1 \cdot x_3 + \sqrt{B_2^3/B_3} \cdot x_2 \cdot x_3\right) \quad (11)$$

where $B_1 \geq B_2 \geq B_3$;

$$\lambda_m = \lambda_1 \cdot w_1 + \lambda_2 \cdot w_2 + \lambda_3 \cdot w_3 - C \cdot \left(|\lambda_1 - \lambda_2| w_1 \cdot w_2 + |\lambda_1 - \lambda_3| w_1 \cdot w_3 + |\lambda_2 - \lambda_3| w_2 \cdot w_3\right) \quad (12)$$

where the absolute values were introduced according to the condition $\lambda_1 \geq \lambda_2 \geq \lambda_3$.

The test of all the previous mixing rules was performed against experimental data related to mixtures showed in Table 2.

| Refrigerant Mixture | ASHRAE code | References | Mole Fract. of 1st compound | Mole Fract. of 2nd compound | Weight Fract. of 1st compound | Weight Fract. of 2nd compound |
|---|---|---|---|---|---|---|
| R141b/123 | | Kim, 93a | 0.287-0.799 | | 0.2354-0.7528 | |
| R22/152a | | Kim, 93b - Tsvetkov, 96 | 0.2019-0.6967 | | 0.2488-0.7505 | |
| R22/142b | | Kim, 93b - Tsvetkov, 96 | 0.3108-0.7909 | | 0.2796-0.7650 | |
| R32/134a | | Bivens, 94 | 0.395 | | 0.250 | |
| R22/134a | | Kim, 93a | 0.2939-0.7823 | | 0.2608-0.7528 | |
| R32/125 | | Bivens, 94 | 0.776 | | 0.600 | |
| R22/125/290 | R402A | Bivens, 94 | 0.446 | 0.508 | 0.380 | 0.600 |
| R22/125/290 | R402B | Bivens, 94 | 0.657 | 0.300 | 0.600 | 0.380 |
| R125/143A/R134a | R404A | Bivens, 94 | 0.358 | 0.604 | 0.440 | 0.520 |
| R32/R125/R134A | R407D | Bivens, 94 | 0.462 | 0.067 | 0.300 | 0.100 |

Table 2 - Refrigerant mixtures used for the check of mixing rules.

## NEW ESTIMATION METHOD FOR AZEOTROPIC REFRIGERANT MIXTURES

The aim of this part of our work was the introduction of a formula able to evaluate the liquid thermal conductivity of mixtures by approaching them as pure refrigerants. We firstly modified Eq. (2) in order to reach a single formula both for ethane series and methane series refrigerants. This preliminary step was essential since mixtures are usually composed of refrigerants belonging to different series. Moreover the knowledge that a single equation was able to estimate the thermal conductivity of all the refrigerants with reasonable errors was a good guarantee that our approach was, at least, worth to be developed. We found that the new equation:

$$B = 0.85 \cdot T_c^{1/3} \cdot M^{-3/4} \quad (13)$$

was able to evaluate liquid thermal conductivity of all the refrigerants with errors still acceptable being typical mean deviations with respect to experimental data within 5%. Thus we applied the Eq. (1) with the constant B evaluated by means of Eq. (13) to four azeotropic mixtures listed in Table 5 and we obtained very good results, being deviations of the same order of those we got for pure refrigerants. This seems to prove that a general equation for the prediction of transport properties of refrigerants could be able to evaluate the same properties of azeotropic refrigerant mixtures. This result could be even more significant as soon as it will be demonstrated, as we expect, that the same equation is applicable to quasi-azeotropic mixtures.

## RESULTS

The results of the validation of mixing rules are shown in Table 3 and Table 4 in form of Average Absolute Deviation (AAD) and Maximum Absolute Deviation (MAD) in the reduced temperature range 0.30÷0.95 being AAD(%) = $\{[\Sigma abs(\lambda_{calc}/\lambda_{exp}-1)]/n\}\cdot 100$ and MAX(%) = $\max[\Sigma abs(\lambda_{calc}/\lambda_{exp}-1)]\cdot 100$ with $\lambda_{exp}$ = experimental liquid thermal conductivity value, $\lambda_{calc}$ = estimated liquid thermal conductivity value and n = number of experimental points.

It must be pointed out that these results were obtained by applying Eq. (1) and Eq. (2) to pure refrigerants and then using Eq. (3) to Eq. (13) as mixing rules. Thus, errors derive both from original prediction methods and from mixing rules. However, to test mixing rules we also applied Eq. (1) introducing b constants extracted from experimental data in order to minimise errors not related to the rules. The results of such preliminary test show conformity within 3% with the

ones listed inside tables and cannot be showed due to space limitations. Some thermal conductivity data are not related to the liquid state along the saturation line but to the subcooled region at pressures near the saturation. Our prediction method seems to be still applicable in such conditions being deviations of the same order in both cases.

Figures 1 and 2 show the comparison between the thermal conductivity values calculated with the different mixing rules and the experimental data for one binary and one ternary mixture. Figure 4 shows, for each binary mixture, the comparison between thermal conductivities calculated with Eq. (10) and experimental data .

| Refrigerant Mixture | | Equation (3) | | Equation (4) | | Equation (5) | | Equat. (9) (11) | |
|---|---|---|---|---|---|---|---|---|---|
| | | AAD (%) | MAX (%) | AAD (%) | MAX (%) | AAD (%) | MAX (%) | AAD (%) | MAX (%) |
| R141b/123 | | 3.48 | 5.01 | 3.30 | 4.77 | 3.24 | 4.69 | 1.44 | 3.00 |
| R22/134a | | 3.80 | 9.55 | 3.72 | 9.45 | 3.70 | 9.41 | 3.23 | 6.82 |
| R22/152a | | 3.66 | 7.74 | 3.59 | 7.63 | 3.57 | 7.59 | 5.27 | 9.48 |
| R22/142b | | 7.38 | 10.97 | 7.35 | 10.97 | 7.34 | 10.97 | 4.39 | 8.40 |
| R32/134a | | 11.01 | 11.55 | 9.31 | 9.77 | 8.75 | 9.19 | 11.38 | 11.86 |
| R32/125 | | 23.73 | 25.84 | 21.43 | 23.59 | 20.59 | 22.77 | 5.96 | 7.93 |
| R22/125/290 | R402A | 8.85 | 10.16 | 7.85 | 9.31 | 7.51 | 9.03 | 0.96 | 1.90 |
| R125/143A/R134a | R404A | 3.66 | 6.82 | 3.38 | 6.57 | 3.29 | 6.48 | 1.86 | 3.40 |
| R22/125/290 | R402B | 10.57 | 11.59 | 9.77 | 10.84 | 9.49 | 10.58 | 3.51 | 4.53 |
| R32/R125/R134A | R407D | 16.49 | 17.24 | 14.43 | 15.04 | 13.74 | 14.31 | 7.58 | 8.03 |

Table 3 - Results related to the mixing rules based on mole fraction.

| Refrigerant Mixture | | Equation (6) | | Equation (7) | | Equation (8) | | Equat. (10) (12) | |
|---|---|---|---|---|---|---|---|---|---|
| | | AAD (%) | MAX (%) | AAD (%) | MAX (%) | AAD (%) | MAX (%) | AAD (%) | MAX (%) |
| R141b/123 | | 2.43 | 3.90 | 2.25 | 3.73 | 2.19 | 3.67 | 1.00 | 2.13 |
| R22/134a | | 3.51 | 9.09 | 3.45 | 8.98 | 3.43 | 8.94 | 3.07 | 7.64 |
| R22/152a | | 3.05 | 6.92 | 2.99 | 6.82 | 2.97 | 6.79 | 2.01 | 5.49 |
| R22/142b | | 7.16 | 10.98 | 7.13 | 10.98 | 7.12 | 10.98 | 6.42 | 10.96 |
| R32/134a | | 2.70 | 3.07 | 1.36 | 1.76 | 0.94 | 1.37 | 2.67 | 3.51 |
| R32/125 | | 10.92 | 13.03 | 7.74 | 9.92 | 6.65 | 8.85 | 2.37 | 4.28 |
| R22/125/290 | R402A | 5.09 | 6.68 | 4.12 | 5.86 | 3.80 | 5.59 | 1.34 | 2.41 |
| R125/143A/R134a | R404A | 2.50 | 5.05 | 2.36 | 4.78 | 2.32 | 4.69 | 1.98 | 4.14 |
| R22/125/290 | R402B | 7.49 | 8.58 | 6.60 | 7.80 | 6.29 | 7.54 | 2.84 | 4.24 |
| R32/R125/R134A | R407D | 6.35 | 6.86 | 4.54 | 5.08 | 3.96 | 4.50 | 0.67 | 1.01 |

Table 4 - Results related to the mixing rules based on weight fraction.

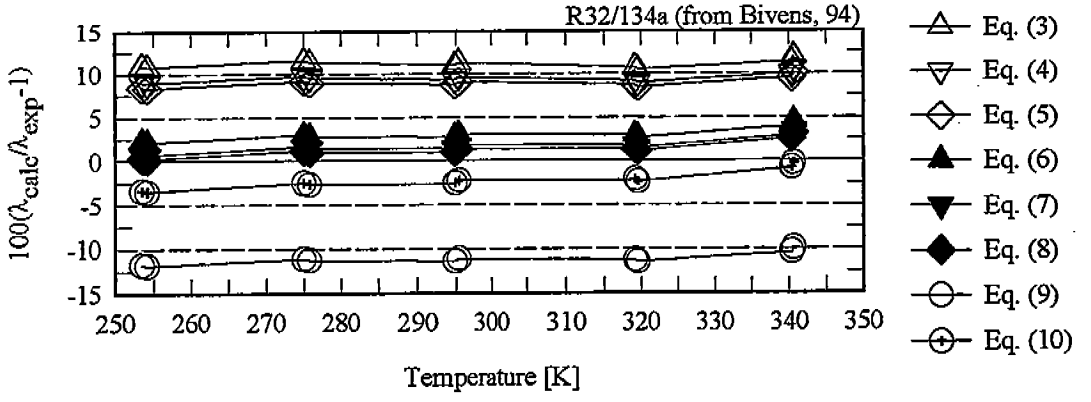


Figure 1 - Comparison between thermal conductivity values calculated with the different mixing rules and experimental data

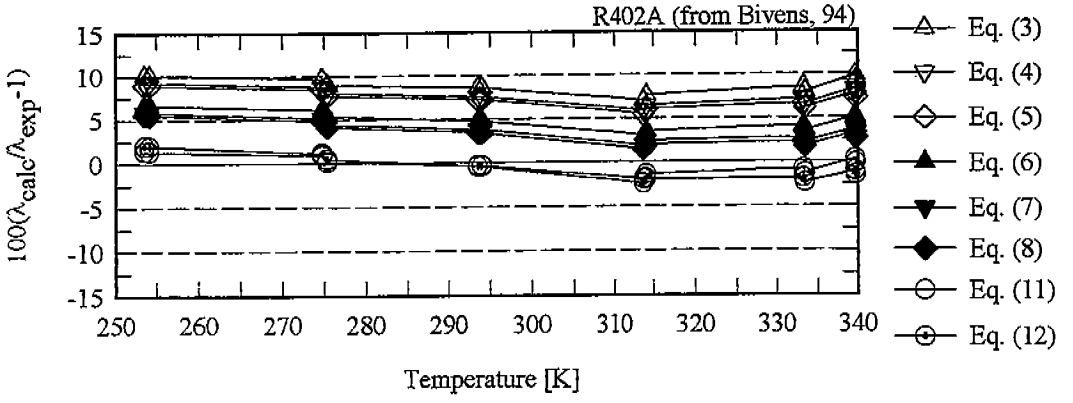


Figure 2 - Comparison between thermal conductivity values calculated with the different mixing rules and experimental data

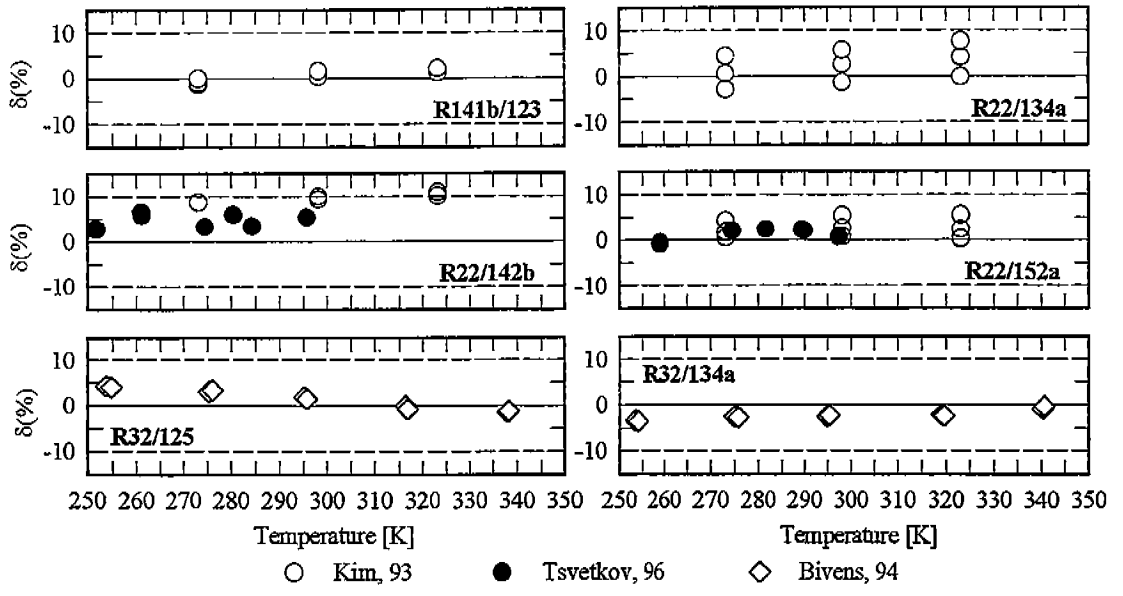


Figure 3 - Comparison between thermal conductivities of binary mixtures calculated with Eq. (10) and experimental data
$\delta(\%)=100(\lambda_{calc}/\lambda_{exp}-1)$

Table 5 shows the results related to our new approach to the evaluation of azeotropic mixtures liquid thermal conductivity. Deviations are far below the ones required for engineering purposes and this makes our equations a powerful candidate method for the preliminary evaluation of liquid thermal conductivity of new refrigerant mixtures as soon as their critical temperature has been assessed. Large Maximum Deviations arise from the fact that we considered, as shown in Fig. 4, a temperature range which almost reaches the critical point while our prediction method does not take into account the critical enhancement.

| Refrigerant Mixture | ASHRAE code | Mole Fract. of 1st compound | Weight Fract. of 1s compound | Source of experimental data | Const. *B* of q.(1) estim.with Eq.(13) | AAD (%) | MAD (%) |
|---|---|---|---|---|---|---|---|
| R12/152a | R500 | 0.606 | 0.738 | ASHRAE, 76 | 0.1954 | 5.8 | 13.6 |
| R22/115 | R502 | 0.630 | 0.488 | ASHRAE, 76 - Shankland, 90 | 0.1753 | 2.8 | 12.9 |
| R13/23 | R503 | 0.500 | 0.599 | ASHRAE, 76 | 0.1976 | 3.8 | 14.5 |
| R32/115 | R504 | 0.734 | 0.482 | ASHRAE, 76 | 0.2233 | 2.6 | 5.2 |

Table 5 - Refrigerant mixtures used to check Eq. (1) and Eq. (13) and related results.

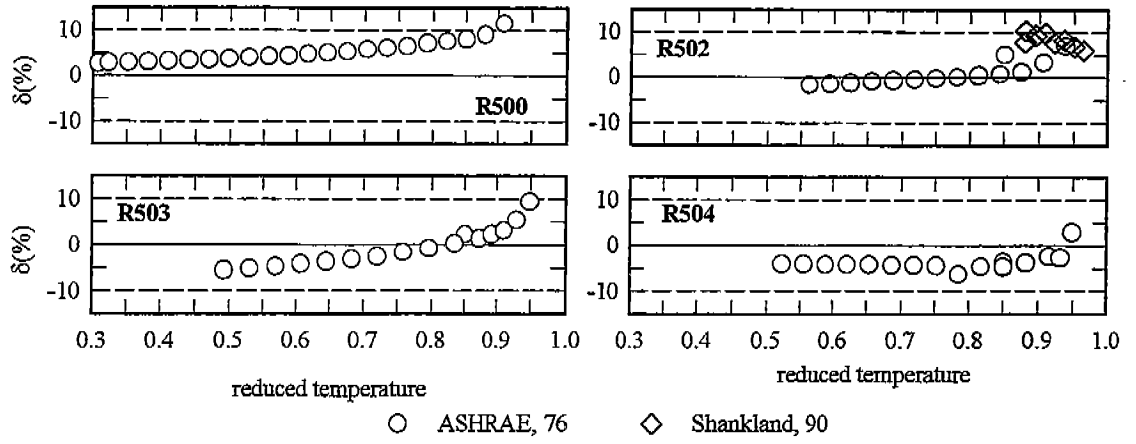


Figure 4. Comparison between calculated thermal conductivities and experimental data for azeotropic mixtures $\delta(\%)=100(\lambda_{calc}/\lambda_{exp}-1)$

## CONCLUSIONS

Two prediction methods are proposed for thermal conductivity of refrigerant mixtures. Both evaluate the thermal conductivity in the liquid state along the saturation line and in the subcooled region at pressures near the saturation and determine thermal conductivity as a function of the reduced temperature.

The first method is based on the use of mixing rules, adapted and enhanced from those already present in literature, and uses pure refrigerant data evaluated by means of a prediction method originally developed by present authors.

The second method was conceived in order to approach azeotropic refrigerant mixtures as pure refrigerants. It requires the knowledge of the molar mass and the critical temperature only, showing very good accuracy and conformity with experimental data.

Both the methods were tested against experimental data and show average absolute deviations which are generally less than 4%, with maximum absolute deviations usually less than 9% in the reduced temperature range 0.30 to 0.95. Hence they can be useful for engineering purposes while the second one could also be used for a preliminary test of candidate replacement fluids.

In the near future we expect to test the new method against experimental data related to quasi-azeotropic mixtures to prove, as we hope, that it is suitable also for such fluids. We also expect to develop the same approach for what concerns liquid dynamic viscosity of the same compounds.

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### References

ASHRAE, 1976. Thermphysical Properties of Refrigerants, New York.

I. R. Shankland,1990. AIChE Spring Nat. Meeting, Orlando, Fl.

G. Latini, G. Passerini, F. Polonara, 1995a. Proc. 4th Asian Thermophysical Conf., Tokyo, Japan, Vol. 3, pp. 631-634.

G. Latini, G. Passerini, F. Polonara, G. Vitali, 1995b. presented at 23rd Int. Thermal Conductivity Conf., Nashville, Tenn.

G. Latini, G. Passerini, F. Polonara, 1996. International Journal of Thermophysics, Vol. 17, No. 1, pp. 85-98, 1996.

Filippov L. P., Novoselova N. S., 1955a. Vestnik Moscov. Gas. Univ., Vol. 10(2), pp. 39-.

Filippov L. P., Novoselova N. S., 1955b. Vestnik Moscov. Gas. Univ., Vol. 10(3), pp. 37-.

Filippov L. P., 1955c. Vestnik Moscov. Gas. Univ., Vol. 10(5), pp. 67-.

D. S. Kim, J. Y. Kim, S. T. Ro, 1993a. Thermal Conductivity 22, pp. 177-178.

S. H. Kim, D. S. Kim, M. S. Kim, S. T. Ro, 1993b. International Journal of Thermophysics, Vol. 14, No. 4, pp. 937-950.

O. B. Tsvetkov, Y. A. Laptev, A. G. Asambaev, 1996. International Journal of Thermophysics, Vol. 17, No. 3, pp. 597-606.

D. B. Bivens, A. Yokozeki, V. Z. Geller, M. E. Paulaitis, 1994. Transport Properties and Heat Transfer of Alternatives for R502 and R22, E. I. du Pont de Nemours & Company, Wilmington, DE.

R. C. Reid, J. M. Prausnitz, B. E. Poling, 1987. The Properties of Gases & Liquids. 4th Edition, McGraw-Hill, New York.