Thermal conductivity prediction of Trans-1-Chloro-3,3,3-Trifluoropropene (R1233zd (E))

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Abstract. R1233zd(E), trans-1-chloro-3,3,3-trifluoropropene, is a fluorinated propene isomer which may be considered as an alternative working fluids in the field of heat pump and organic Rankine cycle. R1233zd(E) has a much lower GWP than hydrochlorofluorocarbons (HCFC) and their mixtures. In this paper an extension of a previously developed predictive methods for thermal conductivity to a new family of organic compounds, namely R1233zd(E) is considered. A study of the correlation of thermal conductivities of polyatomic gases in the limit of zero density of R1233zd(E) is presented. A theoretically correlation scheme based on the formalism Mason-Monchik-Parker theory has been examined and found to be useful for prediction of thermal conductivity data of dilute gas. An attempt is made in this work on the theoretical approach by Predvoditelev, Vargaftik and Filippov proposed for prediction of thermal conductivity for liquid state. The scheme has been tested against the limited amount of experimental data available and shown to be capable of reproducing the thermal conductivities to within few percent. This predicting approach appears promising as an assist in the judgments in the area of this new generation of working fluids data studies.

Keywords: R1233zd(E), thermal conductivity, prediction method, saturated liquid, rarefied gas

1 Introduction
Chlorofluorocarbons (CFC) refrigerants have then phased out under the Montreal Protocol. Conversion from CFCs refrigerants to HFCs have been realized on the condition of no chlorine atoms because of zero ozone depletion potential (ODP). However another global environment issue, which is global warming, becomes more serious concerning working fluids in the refrigeration engineering. An Kigali amendment to the Montreal Protocol adopted in October 2016 requires a significant reduction of global warming potential (GWP) of working fluids used in the low temperature generating systems. Hydrofluorocarbons (HFC) refrigerants were pointed as direct greenhouse gases because of their high Global Warming Potential. There are different options to replace HFC refrigerants. Very recently hydrofluoroolefins (HFOs) were nominated as an alternative to HFCs due to its very Similar thermodynamic properties and extremely low GWP.

Among possible candidate as a working fluid in chiller applications, high temperature heat pump, organic Rankine cycle is a hydrochlorofluoroolefin (HCFO) –trans-1-chloro-3,3,3-trifluoropropene
HCFOs contain on chlorine atom in their molecule and a carbon-carbon double bond. HCFOs might in theory contribute to local stratosphere ozone depletion, but the magnitude of this contribution is ultralow ODP=0.00034 for R-1233zd(E) [1 - 3].

A carbon-carbon double bond makes the HFCOs chemically less stable in the atmosphere. Atmospheric lifetime at R1233zd(E) is 26 days that contributes to reduce environmental impact. The HFOs are flammable, the HCFOs (R-1234zd(E)) are non-flammable refrigerants. Following the ISO 817 there are in the world only 46 refrigerants with GWP<500 and only five refrigerants including R1233zd(E), are non-flammable [4]. Basic thermodynamic properties of R-1233zd(E) are listed in Table 1.[5]

| Parameters                        | Symbol | Value    |
|-----------------------------------|--------|----------|
| Chemical formula                  |        | CF₃CH=CHCl |
| Critical temperature, K           | Tₜₚ   | 439.6    |
| Critical pressure, MPa            | pₜₚ   | 3.6237   |
| Critical density, kgm⁻³           | ρₜₚ   | 480.23   |
| Molecular mass, gmol⁻¹            | M      | 130.5    |
| Normal boiling point, K           | Tₙₜ   | 291.1    |
| Global Warming Potential          | GWP    | 7        |
| Ozone Depletion Potential         | ODP    | 0.00034  |

A great amount of effort has been devoted in the past decades for estimating thermophysical properties for practical application of HFOs as working fluid. Numerous experimental measurements of the thermodynamic properties have been completed. However, research of the transport properties of HFO-s has fallen comparatively behind. This study present an extension of a previous developed predictive methods describing the thermal conductivity as one of the most important properties to a new family of halocarbons, namely, R-1233zd(E) as propene new family refrigerant with extremely low global warming potential (GWP) [6].

2. Thermal conductivity in the liquid state

Knowledge of the thermophysical properties of this kind of fluids has paramount importance and the present study is devoted to the development of procedures for estimating the thermal conductivity along the saturation curve very useful to the refrigeration applications in the development of HFOs as a working fluid and processing. The transport properties are for behind that of equilibrium properties and practically are no satisfactory theory of transport properties of real dense gases and liquids.

A large number of relationships have been proposed for the thermal conductivity of liquids. In 1948 Predvoditelev proposed theoretical arguments assuming heat energy is transferred in liquids by the hyperacoustical waves (phonons) [7,8]. Predvoditelev’s method was modified by Vargaftik to account for the density dependence, which was found to be

\[ \lambda = B \rho^4 \]  

where \( B \) is a substance dependent parameter and independent of temperature and pressure.

Utilizing dimensional analysis arguments, consistent with the theorem of corresponding states Filippov proposed the substance-dependent parameter \( \lambda^* \) and suggested the relationship [8] 

\[ \frac{\lambda}{\lambda^*} = \frac{1}{\varphi^2} \cdot f \]  

Table 1. Thermodynamic properties of R-1233zd(E)
where $\lambda^*$ – thermal conductivity parameter, $\varphi$ – reduced density, $f$ – correlation function, $f = 1$ for $\varphi < \varphi_m$, $f > 1$ for $\varphi > \varphi_m$ with $\varphi_m = 0.359 + 0.056\lg A$, $A$ – Riedel parameter.

The validity of Predvoditelev-Vargaftik-Filippov formalism was tested using thermal conductivity measurements obtained for liquid CFC-s, HCFC-s and HFC-s halocarbons [9,10]. The thermal conductivity parameter $\lambda^*$ was presented by

$$\lambda^* = \frac{1}{G_u}$$

(3)

and the temperature dependent relationship for saturated liquid thermal conductivity was proposed in the form [9]

$$\frac{\lambda}{\lambda^*} = a + b\tau$$

(4)

where $\xi = \frac{M^2 \cdot T^{\frac{1}{2}}}{\rho^2}$, $G_u = \frac{T_{\text{cr}}}{T_{\text{ab}}}$, $G_u$ – Gulberg parameter, $a = 2.947 - 0.003M$, $b = 0.00375M - 2.43375$

The predicted data of thermal conductivity for the liquid phase are shown in Table 2. A comparison between the computed and experimental data [11, 12] is represented in Fig.1. at temperatures ranging from 300 to 415 K.

**Tabl. 2. Thermal conductivity data of R1233zd(E) (mWm$^{-1}$K$^{-1}$) at liquid phase**

| $T$,K  | 313.5 | 332.9 | 353.3 | 373.2 | 393.1 | 413.1 |
|--------|-------|-------|-------|-------|-------|-------|
| $\lambda$ | 78.44 | 72.69 | 66.93 | 60.72 | 54.80 | 48.87 |

**Figure 1.** Deviations between experimental and correlated thermal conductivity at liquid state and dilute gas state

3. **Representation for the thermal conductivity in the rarified gas state**

The thermal conductivity of R1233zd(E) in the limit of zero density was presented as the sum of translational $\lambda_t$ and internal $\lambda_{int}$ contributions [13 - 15]
\[ \lambda_0 = \frac{\eta_0}{M} \left( f_{\text{tr}} c_{\text{tr}} + f_{\text{int}} c_{\text{int}} \right) \]  

(5)

Following Maison-Monchick formalism

\[ \lambda_0 = \lambda_{0,G} = \eta_0 M \left\{ \frac{2}{\pi} \left( \frac{5}{2} - \frac{\rho D_{11}}{\eta_0} \right) \left( \frac{c_{\text{tr}}}{z_{\text{rot}}} + \frac{c_{\text{vib}}}{z_{\text{vib}}} \right) \right\} \]

(6)

in which \( c_{\text{tr}}, c_{\text{vib}}, f_{\text{tr}}, f_{\text{int}} \) – molecular isochoric heat capacity and Maxwell factors related to translational and internal contributions; \( D_{11} \) – coefficient of self-diffusion, \( \eta_0 \) - viscosity; \( z_{\text{vib}}, z_{\text{rot}} \) – collision numbers for internal energy relaxations.

The values of \( z_{\text{rot}} \) have been calculated via \( z_{\text{rot}}^0 = 25 \) using Parker relation

\[ z_{\text{rot}} = z_{\text{rot}}^0 \left[ 1 + \frac{\pi^2}{2} \left( \frac{T^*}{T} \right) \left( \frac{3}{4} + \pi \left( \frac{T^*}{T} \right)^{1/2} \right) \right] \]

(7)

For the \( \lambda_{0,G} \) in Eq(6) we accepted

\[ \lambda_{0,G} = \frac{\eta_0}{M} \left[ \frac{15}{4} R + \left( \frac{3}{2} - \frac{\rho D_{11}}{\eta_0} \right) \right] \]

(8)

where \( R \) – universal gas constant. Diffusion coefficient for internal energy have been expressed using

\[ \frac{\rho D_{11}}{\eta_0} = 6 \left[ \frac{\Omega^{(2,2)^*}}{\Omega^{(1,1)^*}} \right] \]

(9)

where \( \Omega^{(2,2)^*}, \Omega^{(1,1)^*} \) are effective collision cross sections, that incorporate all of the information about binary collisions and the intermolecular pair potential , as a function of \( T^* = \frac{T}{e/k} \) using the scaling parameter \( \frac{e/k}{k} = 1.15 T_{nb} \).

A prediction method based on Filippov works have been considered for the viscosity of trans-1-chloro-3,3,3-trifluoropropene:

\[ \frac{\eta_{0,cr} T_{cr}^{1/2}}{M^{1/2} \rho_{cr}^{3/2}} = 15.8 \]

(10)

where \( \eta_{0,cr} \) – viscosity of dilute gas at \( T_{cr} \).

The results for \( \lambda_0 \) listed in Table 3.

| Table 3. Thermal conductivity values of R1233zd(E) (mW·m⁻¹·K⁻¹) at rarefied gas state |
|---|---|---|---|---|
| \( T, \text{K} \) | 300.15 | 330.15 | 380.15 | 430.15 |
| \( \lambda_0 \) | 11.46 | 13.19 | 16.24 | 19.47 |
Since the Maxwell factor \( f = \frac{\lambda_0}{\eta_0 c_0} \) is often used to represent the temperature dependence of thermal conductivity it is also possible to deduce values for the ratio \( \frac{f}{f_{cr}} \) that has been used in the literature. The values for reduced Maxwell factor \( f^* = \frac{f}{f_{cr}} \), reduced viscosity, heat capacity and thermal conductivity \( \eta^*_0 = \frac{\eta_0}{\eta_{bczr}}, \lambda^*_0 = \frac{\lambda_0}{\lambda_{bczr}}, c^*_v = \frac{c_v}{c_{vr}} \), have been calculated using results of our analyses \( c_{vr}=127.56 (\text{J} \cdot \text{mol} \cdot \text{K}^{-1}), \eta_{bczr} = 15.44 \cdot 10^{-6} \text{ (Pa} \cdot \text{s)}, \lambda_{bczr} = 21.41 \text{ (mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}) \)

Table 4. display the results obtained for R1233zd(E).

| \( T, \text{K} \) | 300.15 | 330.15 | 380.15 | 430.15 |
|-----------------|--------|--------|--------|--------|
| \( \tau \)      | 0.68   | 0.75   | 0.86   | 0.98   |
| \( c^*_v \)     | 0.77   | 0.81   | 0.87   | 0.92   |
| \( \eta^*_0 \)  | 0.69   | 0.76   | 0.87   | 0.98   |
| \( \lambda^*_0 \)| 0.54   | 0.62   | 0.76   | 0.91   |
| \( f^* \)       | 1.02   | 1.01   | 1.00   | 1.01   |

4. Conclusions
Thermal conductivity data of R1233zd(E) have been reported for liquid near saturation state and zero density gaseous state. Predicted results have been shown to be consistent with experimental measurements and to give realistic values of deviations between predicted and experimental data, by up to 5%, [16] indicating the need for increased data and improved correlations to these regions.

References
[1] ANSI/ASHRAE Standard 34-2013 2015 Designation and safety classification of refrigerants NE, Atlanta GA 30329-2305
[2] Mondejar M, McLinden M and Lemmon E 2015 Thermodynamic properties of trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E)). Vapor pressure, (p,v,T) behavior and sound measurements, and equation state J. Chem. Eng. Data 60(8) 2477–89
[3] Orkin V L, Marrynova L E , Kurylo M J 2014 Photochemical properties of trans-1-chloro-3,3,3-trifluoropropene (trans-CHCl=CHCF3): OH reaction, rate constant, VV and IR absorption spectra, global warming potential, and ozone depletion potential J. Phys. Chem., A113(28), 5263–71
[4] Perkins R , Hubert M and Assael M 2017 Measurement and correlation of the thermal conductivity of trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E)) J. Chem. Eng. Data 62 (9) p 2659-65
[5] Alam Md, Islam M, Kariya K and Miyara A 2018 Measurement of thermal conductivity and correlation at saturated state of refrigerant trans-1-chloro-3,3,3-trifluoropropene(R-1233zd(E)) Int.J. of Refrigeration 90 p 174-180
[6] Tsederberg N 1963 Thermal conductivity of gases and liquids (Gosenergoizdat) p 408
[7] Filippov L 1988 Calculation and prognostic of thermophysical properties of substances (Moscow: State University) p 252.

[8] Tsvetkov O 2003 Refrigerants (St.P. State University of Refrigeration Technologies) p 216

[9] Bobbo S, Di Nicola G, Zilio C, Brown J S and Fedele L 2018 Low GWP halocarbons refrigerants: A review of thermophysical properties Int. J. Refrigeration. 90 p 181-201

[10] Domanski P, Brignoli R and Brown J 2017, Low – GWP refrigerants for medium and high-pressure applications Int. J. Refrig. 84 p 198-209

[11] Coulomb D 2014 The refrigerant future: the phase down of HFCs and its consequences Vestnik IAR 1 p 3-6

[12] Tsvetkov O 1984 Thermal conductivity of refrigerants (University of Leningrad) p 247

[13] Tsvetkov O, Laptev Yu and Asambaev A 1994 Thermal conductivity of Refrigerants R123, R134a, and R125 at low temperatures Int. J. of Thermophysics 15 N2 p 203-214

[14] Mason E, Monchik L 1962 Heat conductivity of polyatomic and polar gases J. Chem. Phys 35 p 1622-39

[15] Ferziger J H, Kaper H G 1972 Mathematical theory of transport processes in gases (North-Holland Publ. Company –Amsterdam – London)

[16] Altunin V 1975 Thermophysical properties of carbon dioxide – (Moscow) p 546

[17] Latini G, Sotte M 2012 Thermal conductivity of refrigerants in the liquid state: A comparison of estimation methods Int. J. of Refrig. 35 p 1377–83