Maxwell factors for gaseous 
2.3.3.3-tetrafluoropropene and 
cis-1.3.3.3-tetrafluoropropene at zero density

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Abstract. In this study we focused on the Maxwell factor of fluorinated propene isomers 2.3.3.3-tetrafluoropropene and cis-1.3.3.3-tetrafluoropropene last years receiving considerable attention as the next generation of refrigerants. Fluorinated propene isomers contain carbon-carbon double bound. The advantage of both refrigerants is a low global warming potential value of 4 and 6 respectively. This paper deals with the temperature dependence of thermal conductivity in the limit of zero density for dilute gases. A theoretically based correlation formalism has been examined according to the kinetic theory of Mason–Monchik–Parker using a set of trial functions and related to the translational and integral effective collisions that incorporate the information concerning intermolecular pair potential and binary collisions. The results have correlated using the Maxwell factor. The analysis of quantities for practical purposes which are related to the thermal conductivity and viscosity has been made.

1. Introduction
Refrigerants are playing an important role in many of the social, demographic and technological changes and advancement that have occurred in developing and developed countries. The 2.3.3.3-tetrafluoropropene (R1234yf) and the isomer cis-1.3.3.3-tetrafluoropropene (R1234ze(Z)) are potential refrigerants nominated as an alternative to hydrofluorocarbons (HFC) and recently used as a working fluids with extremely low warming potentials in refrigeration, organic Rankine cycles and industrial heat pumps. Available thermodynamic data for R1234yf and R1234ze(Z) are summarized in table 1 [1–3].

Table 1. Fundamental constants and characteristic properties of R1234yf and R1234ze(Z).

| Refrigerant       | $M$, kg·mol$^{-1}$ | $T_{cr}$, K   | $p_{cr}$, MPa | $\rho_{cr}$, kg·m$^{-3}$ |
|-------------------|-------------------|--------------|--------------|-----------------|
| R1234yf           | 114.04            | 367.85       | 3.435        | 473             |
| R1234ze(Z)        | 114.04            | 423.27       | 3.533        | 470             |
This paper deals with the Maxwell factors for R1234yf and R1234ze(Z) for gaseous state in the limit of zero density. Conclusions for related properties are also shown.

2. Theoretical background

The temperature dependence of thermal conductivities can be represented by the so-called Maxwell factor

\[ f = \frac{\lambda_0}{C_v \eta_0}. \]

(1)

Here \( f \) – Maxwell factor, \( \lambda_0, \eta_0 \) – thermal conductivity and viscosity of a polyatomic gas in the limit of zero density; \( C_v \) – heat capacity of the gas. According to the kinetic theory the thermal conductivity \( \lambda_0 \) may be written as the sum of translational contribution \( (\lambda_{tr}) \) and the internal energy contribution \( \lambda_{int} \) [4]

\[ \lambda_0 = \lambda_{tr} + \lambda_{int} = (C_{v, tr} f_{tr} + C_{v, int} f_{int}) \eta_0. \]

(2)

Here \( f_{tr}, f_{int} \) are translational and internal Maxwell factors; \( C_{v, tr}, C_{v, int} \) are the translational and the internal heat capacity of the gas. In is important to note that the inelastic collisions have a tendency to decrease the translational contribution and to increase the contribution from the internal energy leaving the total heat flux nearly unchanged [5]. The effective values \( f_{tr} \) and \( f_{int} \) can be deduced from the two collision numbers for internal energy relaxation \( Z_{rot}, Z_{vib} \)

\[ f_{tr} = \frac{5}{2} \left( 1 - \frac{5N}{\pi} \left( \frac{C_{v, rot}}{R Z_{rot}} + \frac{C_{v, vib}}{R Z_{vib}} \right) \right), \]

(3)

\[ f_{int} = L \left( 1 - \frac{5N}{\pi} \left( \frac{C_{v, rot}}{C_{v, int} Z_{rot}} + \frac{C_{v, vib}}{C_{v, int} Z_{vib}} \right) \right), \]

(4)

where

\[ N = 1 - \frac{5}{2} L, \]

(5)

\[ L = \frac{\rho D}{\eta}, \]

(6)

\[ C_{v, int} = C_{v, vib} + C_{v, rot}. \]

(7)

Here \( \rho \) – density of rarified gas, \( D \) – coefficient of self–diffusion, \( Z_{rot}, Z_{vib} \) – rotational and vibrational collision numbers for internal energy relaxation. The values for \( Z_{rot} \) have been obtained from [6]

\[ Z_{rot} = Z_{rot}^{\infty} \left( 1 + \frac{\pi^{1/2}}{2} \left( \frac{1}{T^*} \right)^{1/2} + \left( \frac{\pi^2}{4} + 2 \right) \frac{1}{T^*} + \pi^{3/2} \left( \frac{1}{T^*} \right)^{3/2} \right)^{-1}, \]

(8)

where

\[ Z_{rot}^{\infty} = 25, \]

(9)

\[ T^* = \frac{T}{\varepsilon/k}. \]

(10)

Here \( \varepsilon/k \) – scaling parameter for a Lennard–Jones 6–12 potential, \( T^* \) – reduced temperature. It is necessary to mention that the results for \( \lambda_0 \) naturally depend on the \( Z_{vib} \) data. In agreement with theoretical results for linear molecules this corresponds to setting \( Z_{vib} \gg Z_{rot} \) in equations (3), (4). The values for \( D \) have been calculated in terms of the collision integrals \( \Omega^{(2,2)*} \) and \( \Omega^{(1,1)*} \) ratio

\[ \frac{\rho D}{\eta} = \frac{6}{5} \left( \frac{\Omega^{(2,2)*}}{\Omega^{(1,1)*}} \right). \]

(11)
For R1234yf and R1234ze(Z) we used based on the formalism of the Mason–Monchick–Parker theory the constant value of $\rho D/\eta = 1.328$ [5]. The values for viscosity of refrigerants have been calculated using Kamerling–Ones parameter

\[ \eta^* = \frac{M^{1/3}p_{cr}^{2/3}}{T_{cr}^{1/3}} \]  

(12)

and Filippov recommendations [7] for

\[ \frac{\eta_0}{\eta_{0,cr}} = f(\tau), \]  

(13)

\[ \frac{\eta_{0,cr}}{\eta^*_cr} = 15.8. \]  

(14)

Here $p_{cr}, T_{cr}$ represents the temperature and pressure in the critical point, $M$ – is the molecular mass, $\tau = T/T_{cr}$ is reduced temperature.

3. Application

Values of $\lambda$ and $\eta$ obtained for R1234ze(Z) are given in table 2 and for R1234yf – in table 3.

**Table 2.** Zero–Density R1234ze(Z) thermal conductivity and viscosity data.

| Properties          | Reduced temperature, $\tau$ |
|---------------------|-----------------------------|
|                     | 0.6615 | 0.7560 | 0.8505 | 0.9450 | 1.0000 |
| $\lambda_0 \cdot 10^3$, W(m-K)$^{-1}$ | 10.34  | 12.65  | 15.15  | 17.79 | 19.39 |
| $\eta_0 \cdot 10^6$, Pa-s            | 9.59   | 10.90  | 12.22  | 13.53 | 14.28 |

**Table 3.** Zero–Density R1234yf thermal conductivity and viscosity data.

| Properties          | Reduced temperature, $\tau$ |
|---------------------|-----------------------------|
|                     | 0.6882 | 0.7426 | 0.8241 | 0.9329 | 0.9872 | 1.0000 |
| $\lambda_0 \cdot 10^3$, W(m-K)$^{-1}$ | 10.56  | 11.91  | 14.05  | 17.16 | 18.81 | 19.21 |
| $\eta_0 \cdot 10^6$, Pa-s            | 9.90   | 10.66  | 11.78  | 13.28 | 14.03 | 14.20 |

4. Maxwell factors

It’s widely assumed that the Maxwell factor may a good representation for the thermal conductivity of dilute gases. The results of calculations are given in Table 4 for 2.3.3.3–tetrafluoropropene. The Maxwell factors of cis–1.3.3.3–tetrafluoropropene calculated from equation (1) lists table 5.

The data tables 4, 5 are of considerable interest. Since the Maxwell factor has often been discussed in the literature we include analysis of this quantity as well, using the reduced values

\[ C_v^* = C_v/C_{v,cr}, \eta^* = \eta_0/\eta_{0,cr}, \lambda^* = \lambda_0/\lambda_{0,cr}, f^* = f/f_{cr}, \]  

where $C_{v,cr}, \eta_{0,cr}, \lambda_{0,cr}, f_{cr}$ are heat capacity, viscosity, thermal conductivity and Maxwell factor for the dilute gas state at
Table 4. Zero–Density R1234yf Maxwell factor data.

| Temperature, K | Maxwell factor | 253.15 | 273.15 | 303.15 | 343.15 | 367.85 |
|----------------|----------------|--------|--------|--------|--------|--------|
| \( f \)        |                | 1.446  | 1.447  | 1.443  | 1.439  | 1.435  |

Table 5. Zero–Density R1234ze(Z) Maxwell factor data.

| Temperature, K | Maxwell factor | 253.15 | 273.15 | 303.15 | 343.15 |
|----------------|----------------|--------|--------|--------|--------|
| \( f \)        |                | 1.4495 | 1.447  | 1.443  | 1.439  |

critical temperature \( T_{cr} \). The following values were used for R1234ze(Z) \( C_{v,cr} = 107.902 \ J/(\text{mol} \cdot \text{K}) \) [8–10], \( \eta_{0,cr} = 14.283 \cdot 10^{-6} \ \text{Pa-s} \), \( \lambda_{0,cr} = 19.390 \cdot 10^{-3} \ \text{W/(m-K)} \) and for R1234yf \( C_{v,cr} = 107.476 \ J/(\text{mol} \cdot \text{K}) \) [11], \( \eta_{0,cr} = 14.203 \cdot 10^{-6} \ \text{Pa-s} \), \( \lambda_{0,cr} = 19.21 \cdot 10^{-3} \ \text{W/(m-K)} \). Tables 6 and 7 lists the results of calculations.

Table 6. Reduced Maxwell factors of R1234ze(Z).

| Parameter | Temperature, K |
|-----------|----------------|
|           | 280 | 320 | 360 | 400 |
| \( C_v^* \) | 0.7893 | 0.8498 | 0.9104 | 0.9678 |
| \( \eta^* \) | 0.6711 | 0.7634 | 0.8554 | 0.9469 |
| \( \lambda^* \) | 0.5334 | 0.6524 | 0.7815 | 0.9176 |
| \( f^* \) | 1.0069 | 1.0055 | 1.0035 | 1.0013 |

Table 7. Temperature dependence of \( f^* = f/f_{cr} \) of R1234yf.

| Parameter | Temperature, K |
|-----------|----------------|
|           | 0.6282 | 0.7426 | 0.8241 | 0.9329 |
| \( C_v^* \) | 0.7811 | 0.8492 | 0.8765 | 0.9529 |
| \( \eta^* \) | 0.6973 | 0.7506 | 0.8297 | 0.9352 |
| \( \lambda^* \) | 0.5497 | 0.6200 | 0.7314 | 0.8933 |
| \( f^* \) | 1.0093 | 1.0083 | 1.0057 | 1.0024 |

The values of \( f^* \) shows a weak function of temperature for both refrigerants. It is worth noting that these conclusions are in agreement whith of Rastorguev results for hydrocarbons [12]. The similar behavior of the Maxwell has been reported previously for tetrafluorocarbon (refrigerant R14) [13].
5. Conclusion
Results of a compressive study about the correlation of thermal conductivity of hydrofluoroolefins in the limit of zero density have been summarized. The results have been correlated using the Maxwell factor.

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