Thermal Conductivity and Viscosity of a New Stratospherically Safe Refrigerant- 1, 1, 1, 2-Tetrafluoroethane (R-134A)

I. R. Shankland
Genetron R Products Laboratory

R. S. Basu
Genetron R Products Laboratory

D. P. Wilson
Genetron R Products Laboratory

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Abstract

Recent hypothesis on stratospheric ozone depletion by chlorofluorocarbons has prompted industry to look for environmentally safe alternates to refrigerants such as dichlorodifluoromethane (R-134a). In order to help design compressor and refrigeration equipment a number of basic thermophysical property data is needed. There is a real lack of such data on R-134a in the open literature.

Measurements on thermal conductivity and viscosity of R-134a are discussed in this paper. No data on these properties have been found in the literature. Thermal conductivity is measured by a transient hot wire method in our research laboratory over a temperature range of 5° to 54°C. Viscosity is measured by Ostwald Viscometer in a temperature range of -25° to 70°C. Correlation equations have been developed for these properties over the range of measured data.

Keywords: Refrigeration, R-134a, Thermal conductivity, viscosity

RESUME : Une hypothèse récente sur l'épuisement de l'ozone stratosphérique par les CFC a incité l'industrie à rechercher des frigorigènes de remplacement, sans danger pour l'environnement, tels que le dichlorodifluorométhane (R134a). Pour aider à concevoir les compresseurs et le matériel frigorifique, il faut disposer d'un certain nombre de propriétés thermophysiques de base. Pour le R134a, ces propriétés manquent réellement dans la littérature.

Les mesures de la conductivité thermique et de la viscosité du R134a sont examinées dans ce rapport. On n'a pas trouvé de renseignements sur ces propriétés dans les publications. La conductivité thermique est mesurée par la méthode en régime transitoire du fil chaud au laboratoire des auteurs à des températures de 5 à 45°C. La viscosité est mesurée à l'aide du viscomètre d'Ostwald à des températures de -25 à 70°C. Des équations de corrélation ont été établies pour ces propriétés dans le domaine des valeurs mesurées.

Mots-clés : froid, R134a, conductivité thermique, viscosité.
THERMAL CONDUCTIVITY AND VISCOSITY OF A NEW STRATOSPHERICALLY SAFE REFRIGERANT - 1,1,1,2-TETRAFLUOROETHANE (R-134a)

By

I. R. Shankland, R. S. Basu and D. P. Wilson
Allied-Signal Inc.
GENETRON® Products Laboratory
20 Peabody St, Buffalo, N.Y. 14210

1. INTRODUCTION

A large body of scientific experiments and theoretical calculations have been published relating to the depletion of earth’s stratospheric ozone layer by chlorofluorocarbons since Rowland and Molina [1] first published their work on this subject. A summary of the present status of knowledge in this subject can be found in reference [2]. As a result a recent convention of the United Nations Environment Programme (UNEP) (held in Montreal, October 1987) [3] reached an international agreement and a protocol has been established to limit production and emission of fully halogenated CFCs. The protocol calls for a freeze in the production levels of these substances at the 1986 levels for the next three years and then gradual decrease of production and emission in subsequent years.

One of the CFCs which will face production cutbacks under this protocol is R-12, which finds application in a wide variety of refrigeration and air-conditioning areas. The reasons for its wide application is that it is a very stable, non-toxic, non-flammable, safe to use material which also possesses the appropriate thermophysical properties. Developing an environmentally acceptable replacement which will have this unique combination of properties is a very challenging task. To date, the most promising candidate is 1,1,1,2-tetrafluoroethane (R-134a). R-134a does not contain any chlorine and has zero ozone depletion potential. Its physical properties such as boiling point, heat of vaporization, vapor pressure matches very well with that of R-12 [4,5].

At the present time there is a dearth of data in open literature on physical properties of R-134a. In order for the refrigeration engineers to use this as a working fluid a large amount of thermophysical properties data will be required. In this paper we have presented recent measurements of low density vapor thermal conductivity and liquid viscosity of R-134a and the respective correlating equations to aid the design engineers.
2. EXPERIMENTAL METHODS

2.1 Vapor Thermal Conductivity

Low density vapor thermal conductivity of R-134a is measured using a transient hot wire method. The details of the method can be found in reference [6]. We are going to present only a brief description of the underlying principles and experimental method in this section.

2.1.1 Theoretical Remarks

In the transient hot wire apparatus the thermal conductivity of a gas is measured by observing the rate at which the temperature of a very thin platinum wire (0.5 mil diam.) increases with time after a voltage is applied to it. The thin wire acts as a line source of constant heat flux $Q$. This has the effect of producing throughout the gas a temperature field which increases with time. The temperature increase $\Delta T(a, t)$ at the platinum wire of radius $a$ after a time $t$ can be described by the formula [6],

$$\Delta T(a, t) = \frac{Q}{4\pi \kappa} \ln \left( \frac{4\kappa t}{a^2 C} \right)$$

where $\kappa = \lambda/\rho C_p$, is the thermal diffusivity of the gas, $\lambda$ is the thermal conductivity, $\rho$ is the density and $C_p$ is the specific heat of the gas, $C = \exp(\gamma)$ where $\gamma = 0.5772$ is the Euler’s constant.

The increase in temperature described by the equation (1) implies that the plot of $\Delta T$ vs. $\ln t$ will be a straight line with slope inversely proportional to $\lambda$, the thermal conductivity of the gas surrounding it. In the experiment, however, a straight-line relation will be observed only between times $t_1$ and $t_2$ say 200 to 1000 ms with systematic deviations occurring both for short and long times.

In order to determine the thermal conductivity $\lambda$, with great precision, thermal conductivity is determined at a number of points $(\Delta T, t)$ on the line than one such pair, and the slope is calculated by least squares. The heat flux $Q$ is determined by measuring the resistance $R$ of the wire and its length $l$ and the current flowing through it.

2.1.2 Experimental Methodology

The details of the experimental methodology will be found in reference [7]. Briefly the resistance measurement is done using a standard bridge and measuring the out-of-balance signal. Two of the wires of different lengths are used in the two arms of the bridge and both are kept inside the chamber containing the gas whose thermal conductivity is being determined. This set-up reduces errors due to the end effects. Figure 1 shows the schematic diagram of the bridge used in the resistance measurements. Here $R_1$ and $R_2$ are the resistance of the short
and long wires used in the apparatus. \( R_3 \) and \( R_4 \) are fixed standard resistances and \( R_5 \) is a precision variable resistor. \( V \) is the constant voltage power supply and \( E \) is the out-of-balance signal measured by a digital voltmeter. The heat flux can be related to the resistances used in the bridges and the measured voltages using the \( I^2R \) formula.

Accurate measurements of the resistance improves the accuracy of the determination of the heat flux and thereby improves the measurement accuracy of the thermal conductivity. It can be shown further that using \( R_5 \) to equal to the sum of \( R_1 \) and \( R_2 \) will ensure constancy of heat flux. The details of the derivation will be presented elsewhere [8].

2.2 Liquid Viscosity

Viscosity of liquid R-134a is determined using an Ostwald Viscometer[9]. The details of the method can be found in reference [10]. The method utilizes the flow of a liquid in a capillary to determine the viscosities of liquids.

2.2.1 Theoretical Remarks

In this method a definite volume \( V \) of a liquid flows through a capillary of length \( L \) and radius \( R \) and the time of flow is measured. Assuming the flow is laminar the flow is directly proportional to the head pressure \( P \), which in turn is directly proportional to the density \( \rho \) of the liquid provided the pressure is kept constant. The liquid viscosity \( \eta \) is given by,

\[
\eta = \frac{\pi PR^4t}{8VL} = k\rho t
\] (2)

Here \( t \) stands for the time of flow of the fluid and \( k \) stands for the constant of proportionality which is determined by using a liquid of known density and viscosity. The accuracy of the measurement in this method depends on the uniformity of the radius of the capillary.

2.2.2 Experimental Method

A modified (heavy walled glass) Ostwald Viscometer (Fig. 2) is used to measure the liquid viscosity of R-134a. The calibration of the equipment was done using diethyl ether. The sample of R-134a used in the experiment had purity of 99.9% by mole or better.

R-134a was distilled into the viscometer over \( P_2O_5 \) to ensure dryness and the glass tube is sealed. Following distillation into the viscometer, degassing was done at liquid nitrogen temperatures using usual freeze-thaw techniques.

Temperature determination was done by platinum resistance thermometer coupled with a Leeds and Northrup "Speedomax" Type G bridge. The thermometer was calibrated by NBS and its accuracy was periodically checked
against the ice point of water. Accuracy of temperature measurement is ±0.03°C.

Measurement of time of flow of the liquid was done with an electronic stop watch whose accuracy has been checked against time signals from NBS station WWV. The flow times were generally reproducible to ± 0.1 seconds and they varied from approximately 90 to 400 seconds.

3. RESULTS

3.1 Vapor Thermal Conductivity

Measurements of low density vapor thermal conductivity \( \lambda_0(T) \) were done over a temperature range of 25° to about 55°C. A total of six(6) data points were taken over this range. The overall accuracy of the method is expected to be ±1%.

The thermal conductivity data is correlated using an equation quadratic in absolute temperature \( T \) as shown below,

\[
\lambda_0(T) = k_1 + k_2 T + k_3 T^2
\]  

where

\[
\begin{align*}
\lambda_0(T) &= \text{mW/m·°K} \\
T &= \text{°K} \\
k_1 &= 29.742 \\
k_2 &= -0.17962 \\
k_3 &= 0.42648 \cdot 10^{-3}
\end{align*}
\]

The observed and calculated values using this equation is shown in Table 1 and is plotted in Figure 3. The standard deviation of the fit was found to be ±0.046 mW/m·°K. No systematic deviation of the fit has been observed.

Vapor thermal conductivity has been correlated with a simplified empirical equation. Over the range measured, the data looks nearly linear but the use of a quadratic term has improved the fit. The calculated values agree to the observed values to less than ± 0.5%.

Although the measurement encompasses a smaller range, yet it exhibits a very important feature of the vapor thermal conductivity of R-134a, especially in comparison with the thermal conductivities of R-12 from reference [11]. Thermal conductivity of R-134a has been found to be significantly higher than that of R-12 (Figure 5). This will have significant effect in the design characteristics of the equipments. Fluids with higher thermal conductivity will improve the heat transfer characteristic of the fluid in refrigeration application.
3.2 Liquid Viscosity

Liquid viscosity of R-134a has been measured over a temperature range -22.20 °C to about 70.15°C. The measurement is done in a heavy glass tube which can withstand the required pressure at those temperatures. The viscosity is given in Table 2. The density is obtained from our previous measurement and correlating equations [4,5].

The experimental viscosity data is correlated by the equation (4) given below.

\[ \ln(\eta/mPa \cdot s) = A + \frac{B}{T} + CT \]  

where

- \( \eta = mPa \cdot s \)
- \( A = -3.3528 \)
- \( B = 714.25 \)
- \( C = -0.19969 \cdot 10^{-2} \)

The experimental and calculated values of liquid viscosity has been shown in Table 2 and also in Figure 4. The standard deviation of the fit is ± .003 mPa·s. No systematic deviation has been observed between the experimental and calculated values of the liquid viscosity. Liquid viscosity is also correlated by a somewhat simpler form of the equation and is found to fit the data very well. The density values in Table 2 are obtained from our correlating equations given in reference [4,5].

A comparison with viscosities of R-12 from reference [12] shows that unlike thermal conductivity, the viscosities of the two fluids are reasonably close in value (Figure 6). The plot shows that R-134a has slightly higher viscosity than R-12 below 290°K and slightly lower viscosity than R-12 over 290°K.

4. CONCLUSION

In this paper we have presented the preliminary low density vapor thermal conductivity and liquid viscosity of R-134a over a limited range of temperature. At this point no other data set has been found in the literature of these properties, therefore, comparison can not be made to other data sets. Empirical correlation equation have also been derived and has been found to represent the data adequately. This paper clearly shows the need for further measurement of thermophysical properties of R-134a in developing this fluid as an alternate to R-12 in refrigeration and other applications.

ACKNOWLEDGEMENTS

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8. I.R.Shankland - (To be Published)


Table 1

Vapor Thermal Conductivity of R-134a

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Vapor Thermal Conductivity (mW/m/K)</th>
<th>% Difference</th>
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<tr>
<td>298.15</td>
<td>14.10</td>
<td>0.000</td>
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<tr>
<td>303.15</td>
<td>14.50</td>
<td>0.138</td>
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<tr>
<td>313.15</td>
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<tr>
<td>323.15</td>
<td>16.20</td>
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<tr>
<td>333.15</td>
<td>17.30</td>
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<tr>
<td>343.15</td>
<td>18.30</td>
<td>-0.164</td>
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Table 2
Liquid Viscosity of R-134a

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Density (kg/m³·10⁻³)</th>
<th>Liquid Viscosity (mPa·s)</th>
<th>Experimental</th>
<th>Calculated</th>
<th>% Difference</th>
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<td>0.153</td>
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<td>0.9964</td>
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<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

Fig 1: Schematic of bridge circuit used in Transient Hot Wire apparatus, $R_1$ and $R_2$ are the short and long cell resistance.

Fig 2: Modified Ostwald Viscometer.
Fig 3: Experimental and calculated values of vapor thermal conductivity of R-134a.

Fig 5: Comparison of vapor thermal conductivity of R-12 and R-134a.

Fig 4: Experimental and calculated values of liquid viscosity of R-134a.

Fig 6: Comparison of liquid viscosity of R-12 and R-134a.