

# Experimental study of the thermal conductivity of ammonia + water refrigerant mixtures at temperatures from 278 K to 356 K and at pressures up to 20 MPa

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#### ABSTRACT

The thermal conductivity of binary ammonia + water mixtures was measured over the temperature range from 278 K to 356 K and at pressures to 20 MPa using the steady-state hot-wire method. Measurements were made for ten compositions over the entire concentration range from 0 to 1 mole fraction of ammonia, namely, 0.0, 0.1905, 0.2683, 0.3002, 0.4990, 0.5030, 0.6704, 0.7832, 0.9178, and 1.0 mole fraction of ammonia. In total, 316 experimental data points were obtained. The expanded uncertainty, with a coverage factor of k = 2, of the thermal conductivity, pressure, temperature, and concentration measurements is estimated to be 3%, 0.05%, 0.02 K, and 0.0014%, respectively. The average absolute deviation (AAD) between the measured and calculated reference values for pure water and ammonia is 1.3% and 1.4%, respectively. Correlation models for the thermal conductivity of liquid ammonia + water mixtures were also developed.

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# Etude expérimentale sur la conductivité thermique des mélanges ammoniac/eau à des températures entre 278 et 356 K et des pressions allant jusqu'à 20 MPa

Mots clés : ammoniac ; ammoniac-eau ; modèles de corrélation ; conductivité thermique ; eau

### 1. Introduction

The ammonia + water mixture is the subject of increased attention due to the potential use of this system as a working

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fluid in refrigeration and power cycles. The binary ammonia + water mixture is technically significant in the fields of absorption refrigeration machines, absorption heat pumps, and heat transformers. To reduce negative

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Nomenclature $\lambda$ thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> ) $\Delta\lambda$ thermal conductivity difference (W m <sup>-1</sup> K <sup>-1</sup> ) $\lambda_{mix}^{linear}$ linear mixture thermal conductivity $p$ pressure (MPa)Ttemperature (K) $\rho$ density (kg m <sup>-3</sup> )xconcentration (mole fraction of ammonia)Ameasuring cell constant (m <sup>-1</sup> )Qamount of heat released by the heater (kJ) $\alpha$ temperature coefficient of resistanceT_wirehot-wire temperature (K)	$\begin{array}{lll} T_{wall} & \mbox{measuring-tube wall temperature (K)} \\ \Delta T_W & \mbox{temperature difference in the sample layer (K)} \\ d_1 & \mbox{diameter of wire of the inner platinum resistance} \\ & \mbox{thermometer (PRT) (mm)} \\ d_2 & \mbox{inner diameter of the capillary (mm)} \\ l & \mbox{length of the hot-wire (mm)} \\ Q_e & \mbox{end effects corrections (kJ)} \\ Q_r & \mbox{radiation heat losses (kJ)} \\ A_2 & \mbox{eccentricity of the wire} \\ R & \mbox{electrical resistance } (\Omega) \\ p & \mbox{pressure (MPa)} \\ p_0 & \mbox{reference pressure (MPa)} \\ U & \mbox{voltage (V)} \end{array}$
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environmental impact, natural working fluids such as ammonia and water are being considered as alternative refrigerants to replace chlorofluorocarbons (CFC) in some refrigeration applications. The ammonia + water mixture does neither affect the atmospheric ozone layer, nor contribute to the greenhouse effect and is therefore of significant interest. A refrigeration cycle with ammonia + water mixtures as working fluids, proposed by Amano et al. (2000), has been shown to attain a higher coefficient of performance than traditional working fluids. Thermophysical modeling of technological processes requires information on the transport properties (thermal conductivity, viscosity), phase equilibrium, and thermodynamic properties. The thermal conductivity is the most important property required for absorption cycle analysis, and will be addressed here.

Power cycles with ammonia + water mixtures as working fluids also have been shown to reach higher thermal efficiencies than the traditional steam turbine (Rankine) cycle with water as the working fluid (Amano, 1999; Dejfors et al., 1998; Gawlik and Hassani, 1998; Hassani et al., 2001; Jonsson, 2003; Jonsson et al., 1994; Kalina and Leibowitz, 1989; Olsson et al., 1994; Park and Sonntag, 1990; Thorin, 1998, 2000; Thorin et al., 1998; Wall et al., 2000). The best ammonia + water cycle produced approximately 40-70% more power than a single-pressure steam cycle, and 20-25% more power than a dual-pressure steam cycle. In calculating the performance of the power cycles, accurate thermophysical properties data play an important role. The goal of decreasing the consumption of primary energy has led to the optimization of technological processes. To improve the ammonia + water cycle efficiency, and to operate apparatus at high temperatures and pressures, the need for pertinent data in regions beyond those covered by the available data becomes more urgent. For this reason, engineering design of absorption air-conditioning equipment utilizing the ammonia + water cycle requires accurate thermophysical properties data of ammonia + water mixtures over a wide range of T, p, x. However, existing thermophysical properties data, particularly thermal conductivity data, cover only a very limited range of T, p, x, and contain large uncertainties and inconsistencies.

Water and ammonia are strongly polar fluids. The gas phase dipole moment at the normal boiling point is 1.855 D for water and 1.470 D for ammonia (Poling et al., 2001). The acentric factor is 0.3443 for water and 0.2561 for ammonia (Poling et al., 2001). Thus, the specific chemical nature (H-bonding, for example) of the intermolecular interactions between the water and ammonia molecules are considerable, and have an effect on the temperature, pressure, and concentration dependencies of the thermal conductivity of the mixture. As IAPWS Certified Research Need ICRN #6 (September 2000) stated, the transport properties data for ammonia + water mixture are very limited. A survey of the literature reveals that there are only four data sources (Baranov, 1997; Braune, 1937; Lees, 1898; Riedel, 1951); one of them was published in 1898 (Lees, 1898) and one in 1937 (Braune, 1937). Only a few data points (in total 6) was reported by these authors. The measurements in works (Braune, 1937; Lees, 1898) were performed at atmospheric pressure and over very limited temperatures and concentrations (only at 291.15 K and at x = 0.28 mole fraction (Braune, 1937) and at 302.15 K and x = 0.1 mole fraction (Lees, 1898)). Riedel (1951) measured the thermal conductivity of ammonia + water mixtures at room temperature (293.15 K) and 0.1 MPa in the concentration range from 0 to 0.32 mole fraction. As was mentioned in the report by M. Conde Engineering (Conde-Petit, 2006) the reported thermal conductivity data show large inconsistencies. Baranov (1997) measured thermal conductivity of ammonia + water mixtures in the liquid phase using a method based on a heat flow calorimeter. Measurements were made at temperatures up to 460 K for the concentrations of 10, 40-45, 58, and 80 wt.%. The measurements were performed at five isotherms (303 K, 352 K, 375 K, 423 K, and 460 K) as a function of concentration at 0.1 MPa. Unfortunately, the authors did not provide numerical thermal conductivity data (these data never were published); only graphical results are available. There are no reported thermal conductivity data under pressure. Thus, the main objective of the paper is to provide new accurate experimental thermal conductivity data, using a steady-state hot-wire method, over the temperature range from 278 K to 356 K and at pressures up to 20 MPa for the entire concentration range of liquid ammonia + water mixtures.

### 2. Experimental

Measurements of the thermal conductivity of ammonia + water binary mixtures were performed using a

well-known steady-state hot-wire technique. Previously, this technique was successfully applied to measure the thermal conductivity of organic compounds (Brykov et al., 1970; Mukhamedzyanov and Usmanov, 1971; Mukhamedzyanov et al., 1968; Zaripov and Mukhamedzyanov, 2008) at high temperatures and high pressures. This method also provides highly accurate thermal conductivity measurements and was used previously to measure thermal conductivity in various liquids over wide temperature and pressure ranges. The details and theory of the method were described in several review papers and book chapters by various authors (Abdulagatov and Assael, 2008; Assael et al., 1991).

### 2.1. Steady-state hot-wire thermal conductivity apparatus. Working equation

In this method, the wire of finite length *l* is mounted vertically along the axis of the outer cylinder. The heat flux in the wire was generated by the passage of a direct electrical current through the wire. With this method, the heat generated by the hot-wire is conducted radially through the narrow samplefilled annulus to a measuring-tube wall. The thermal conductivity  $\lambda$  of the sample was deduced from measurements of heat *Q* transmitted across the fluid layer, the temperature difference  $\Delta T_W$  between the tube wall and hot-wire, the thickness of the fluid layer ( $d_1$ ,  $d_2$ ) and effective length *l* of measuring part of the hot-wire (effective length of the wire). The working equation for thermal conductivity in this method at any experimental *T* and *p* is

$$\lambda = A_1 \frac{Q}{\Delta T_W},\tag{1}$$

where  $A_1 = (1/2\pi l) \ln d_2/d_1$  is a geometric parameter (cell constant) of the measuring tube which can be determined from the geometric characteristics of the experimental thermal conductivity cell or by a calibration procedure (m<sup>-1</sup>); Q = IU is the amount of heat (electrical energy) released by the heater (W) that can be determined by measuring the voltage U and

the thermal conductivity measurements the following corrections of the measured values of Q and  $\Delta T_W$  were taken into account: 1. end effects corrections,  $Q_e$ ; 2. temperature difference across the liquid layer (temperature-jump effect); 3. eccentricity of the wire, (*a*); 4. radiation effect,  $Q_r$ . Taking into account these corrections, the final working equation for the steady-state hot-wire method can be expressed as (Tsederberg, 1963):

$$\lambda = A_1 \frac{Q - Q_{\ell} - Q_r}{\Delta T_{\text{wire}}^{\text{cor}}}.$$
(2)

The value of  $Q_r$  was calculated using the relation

$$Q_{r} = C_{n} F \left[ \left( \frac{T_{1}}{100} \right)^{4} - \left( \frac{T_{2}}{100} \right)^{4} \right],$$
(3)

where  $F = \pi d_1 \ell$  is the area of the measuring part of the internal resistance thermometer;  $C_n$  is the reduced radiation coefficient. The contribution of the radiation correction in our experimental conditions is negligible due to the small thickness of the liquid layer ( $\delta = 0.3-0.5$  mm) (Brykov et al., 1970; Mukhamedzyanov and Usmanov, 1971; Mukhamedzyanov et al., 1968, 1971). The temperature drop in the liquid layer was estimated using the equation

$$\Delta T_{L} = (T_{wire} - T_{wall}) - \Delta T_{wall} \pm \Delta T_{calib}, \qquad (4)$$

where  $\Delta T_{\rm wall}$  is the temperature drop at the capillary wall;  $\Delta T_{\rm calib}$  is the calibration of internal resistance thermometer relative to the outer one. The temperature drop at capillary wall was calculated from the equation

$$\Delta T_{\text{wall}} = Q \frac{\ln(d_3/d_2)}{2\pi \ell \lambda_{\text{mol}}} = A_2 \frac{Q}{\lambda_{\text{mol}}},$$
(5)

where  $\lambda_{mol}$  is the molybdenum glass thermal conductivity;  $A_2 = (\ln(d_3/d_2))/2\pi \varrho$ . The heat losses from the ends of the hotwire (end effect) and from the potentiometer wires were estimated by calculation and experimentally. In this work we estimated relative heat losses due to ends effect as (Popov, 1958)

$$\frac{Q_{\text{end}}}{Q} = \frac{\lambda_{\text{pt}} \ln(r_2/r_1)}{\ell \lambda} \frac{r_3^3 \sqrt{\omega} \cos h(\ell_3 \sqrt{\omega}) + \frac{\lambda}{\lambda_{\text{pt}}} \frac{4r_4}{\ln(r_2/r_1)} + \frac{r_1^2 \sqrt{U}}{\sin h(\ell_2 \sqrt{U})}}{1 + \cos h(\ell_2 \sqrt{U}) + \sqrt{\frac{\omega}{U}} \left(\frac{r_3}{r_2}\right)^2 \cos h(\ell_3 \sqrt{\omega}) + \frac{\lambda}{\lambda_{\text{pt}}} \frac{4r_4}{\sqrt{U}r_1^2 \ln(r_2/r_4)}},$$
(6)

current *I* in the hot-wire circuit;  $\Delta T_W = T_{wire} - T_{wall}$  is the temperature difference in the sample layer (K);  $T_{wire}$  is the hot-wire temperature;  $T_{wall}$  is the measuring-tube wall temperature;  $d_1$  is the diameter of wire of the inner platinum resistance thermometer (PRT); and  $d_2$  is the inner diameter of the capillary. As one can see from Eq. (1), the thermal conductivity is obtained from measurements of the hot-wire temperature ( $T_{wire}$ ); measuring-tube wall temperature ( $T_{wall}$ ), and electrical energy released by the heater (Q). Therefore, the uncertainty of the measurements depends on the accuracy of the measurements of Q and  $\Delta T_W$ . In order to increase the accuracy of

where  $U \approx 2\lambda/(\lambda_{pt} + r_1^2 \ln(r_2/r_1)); \omega \approx \lambda/2r_3^2 \lambda_{pt}; r_1, r_2$ , and  $r_3$  are the radius of the hot-wire, measuring capillary; and



Fig. 1 – Detailed view of the measuring cell.

Table 1 – Relative und	ertainty in thermal conductivity	measurement.			
Quantity	$\frac{\delta d_1 d_2 + \delta d_2 d_1}{d_1 d_2 {\ln} \frac{d_2}{d_1}}$	$\frac{\delta l}{l}$	$\frac{\delta U_{\rm wire}}{U_{\rm wire}}$	$\frac{\delta(VP)}{VP}$	$\frac{\delta R_{wire}}{R_{wire}}$
Uncertainty, %	0.31	0.12	0.01	0.03	0.01
Quantity	$\frac{T_{wire} - T_{wall}}{\Delta T_L} \frac{\delta(T_{wire} - T_{wall})}{(T_{wire} - T_{wall})}$	$\frac{\Delta T_W}{\Delta T_L}  \frac{\delta(\Delta T_W)}{\Delta T_W}$	$\frac{Q_e}{Q} \frac{\delta Q_e}{Q_e}$	$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_{\rm P} \delta T$	$\frac{\delta\lambda}{\lambda}$
Uncertainty, %	0.75	0.55	0.08	0.08	1.63

potentiometer wires, respectively;  $\lambda_{\text{pt}}$  is the thermal conductivity of platinum;  $\ell_2$ ,  $\ell_3$  are the distances from the junction (soldered joint) to points where hot-wire and potentiometer wire have the same temperature as the capillary wall temperature (see Fig. 1). We considered that the junction has a cylindrical shape with a radius of  $r_4$  and a length of  $\ell_4 = 2r_4$ . The relative heat losses from the ends of the hot-wire calculated from Eq. (6) are within 0.28–0.60% at  $\ell_2 = \ell_3 = 4$  mm,  $r_4 = 0.075$  mm and  $\lambda_{\text{pt}} = 79$  W m<sup>-1</sup> K<sup>-1</sup>. The effect of eccentricity (*a*) of the capillary and hot-wire has been estimated as (Vargaftik, 1951)

$$\lambda = \frac{Q - Q_{\text{end}} - Q_r}{2\pi \ell \Delta T_L} \ln \frac{\sqrt{(r_2 + r_1)^2 - a^2} + \sqrt{(r_2 - r_1)^2 - a^2}}{\sqrt{(r_2 + r_1)^2 - a^2} + \sqrt{(r_2 - r_1)^2 - a^2}}.$$
 (7)

Therefore the correction for eccentricity (a) is

$$A_{3} = \frac{\ln \frac{\sqrt{(r_{2} + r_{1})^{2} - a^{2}} + \sqrt{(r_{2} - r_{1})^{2} - a^{2}}}{\sqrt{(r_{2} - r_{1})^{2} - a^{2}} - \sqrt{(r_{2} - r_{1})^{2} - a^{2}}}{\ln(r_{2}/r_{1})}.$$
(8)

The values of the uncertainties of all correction contributions to the measured thermal conductivity are given in Table 1. The temperature of the hot-wire can be accurately determined from the measured electrical resistance R(T) at the steady temperature in the hot-wire circuit (see below, Eq. (9)). The hot-wire circuit can also be used to determine the amount of heat generated by the measuring section of the hot-wire (heater).

## 2.2. Experimental apparatus for thermal conductivity measurements

A schematic diagram of the experimental apparatus for the thermal conductivity measurements is shown in Fig. 2. The main part of the apparatus is the measuring unit (see Fig. 3), which is located in a high-pressure autoclave. The main body of the measuring cell is made of a thermal-resistive molyb-denum glass capillary with an extended end. The inner diameter of the capillary was 0.92 mm and the outer diameter was 2.12 mm. The thickness of the liquid layer was 0.41 mm. The length of the measuring section (working part) of the wire was 69 mm. The platinum (99.999% purity) hot-wire with 0.1 mm diameter was coaxially fixed at both ends of the measuring capillary to rigid supports on the axis of the capillary. The wire is stretched along the axis of the glass



Fig. 2 – Schematic diagram of the steady-state hot-wire thermal conductivity apparatus for measurement on liquids. 1 – Dead-weight pressure gauge; 2 – separating vessel; 3 – filling system (sample); 4 – nitrogen cylinder; 5 – high-pressure pump; 6 – vacuum pump; 7 – thermostat; 8 – thermostatting system; 9 – measuring unit; 10 – computing unit (data-acquisition and control system).



Fig. 3 – Measuring unit. 1 – Nipple; 2 – upper flange of the electrical lead; 3 – packing ring; 4 – lower flange of electrical lead; 5 – flange; 6 – autoclave; 7 – measuring cell.

capillary between the upper and lower ends of the measuring capillary. The platinum wire was simultaneously used as a heater and a resistance thermometer. The current-carrying wires with diameter of 0.2 mm and 0.3 mm were brazed with gold alloy to the measuring section of the resistance thermometer. A tungsten spring was used to tension the wire so that the wire extension during heating is compensated by contraction of the spring. The inner thermometer (hot-wire) was centered in the measuring capillary by means of quartz bushings with an inner diameter 0.104 mm and an outer diameter 0.800 mm. The average value of deviation from concentricity was less than 0.022 mm. A small gap between the capillary and the bushing is needed to fill the capillary with fluid and transmitting potentiometric wires. The outer surface of the measuring capillary was wound with the second resistance thermometer, made from platinum wire with a diameter of 0.1 mm. The uncertainty in the thermal conductivity depends to a large extent on the geometrical characteristics of the capillary and hot-wire. The outer diameter of the capillary, the rectilinearity, the length of the measuring section, the coaxiality of the hot-wire and the capillary were checked using a microscope with a scale length of  $1 \mu m$ .

The leads for the current and resistance measurements from the measuring tube were insulated from each other using quartz tubes. The PRT were made from pure platinum (99.999%) with a temperature coefficient of resistance

Table 2 — Basic dimensions of the measuring cell.				
Quantity	Denotation	Size		
Wire diameter of the inner PRT (mm)	<i>d</i> <sub>1</sub>	0.1		
Inner diameter of the capillary (mm)	d2	0.92		
Outer diameter of the capillary (mm)	d <sub>3</sub>	2.12		
Thickness of the liquid layer (mm)	δ	0.41		
Length of the measuring section (mm)	1	69		
Average value of eccentricity (mm)	а	0.022		
Value of the geometrical constant	A <sub>1</sub>	5.121		
Inner thermometer resistance at	Ro	0.8893		
$t = 0 \ ^{\circ}C (\Omega)$				
Outer thermometer resistance at	Ro	5.8059		
$t = 0 \ ^{\circ}C (\Omega)$				

 $\alpha=0.003926$  (where  $\alpha=(R_{100}-R_0)/(100\cdot R_0)).$  The resistance ratio  $R_T/R_0$  of the PRT was

$$R_T/R_0 = 1 + 0.0039767t + 5.8751 \times 10^{-7}t^2$$
 at  $t > 0$  °C, (9)

where the values of  $R_0$  for inner and outer resistance thermometer at t = 0 °C and basic characteristics of the measuring cell are given in Table 2.

#### 2.3. Circuit diagram of the experimental apparatus

The schematic diagram of the thermal conductivity measurements (Fig. 4) consists of two measuring parts: measurement of the inner, and outer thermometer resistances. Measurements of the voltage in the hot-wire  $U_{wire}$  and in the wall circuit  $U_{wall}$  were performed with a comparator. To measure  $I_{wire}$  and  $I_{wall}$  the standard resistance with  $R_H = 1 \Omega$ , and  $R_H = 10 \Omega$ , was used.  $I_{wire}$  and  $I_{wall}$  were controlled with milliammeters. To generate various currents (0.15–0.75 A) in the hot-wire circuit, a resistance box was used. The hot-wire and wall circuits were connected with the comparator by a multipoint switch. A direct current switch was used to take into account the effect of parasitic thermo-emf in the circuits. Standard resistances were thermostatted. Thermostatting of the measuring cell was performed with an ultra-thermostat (see below).

## 2.4. Thermostatting and temperature regulating systems

A uniform temperature field in the measuring cell was provided by thermostat and temperature regulating systems. The temperature regulating system (Fig. 5) was turned on when the desired working temperature in the sample was reached. The electrical signal due to the temperature difference between the jacket and block, after amplification, was supplied to the input of the computer. During the heating process, the relay periodically disconnects and all supply power is distributed between the heater and ballast resistance. The required accuracy of the temperature regulation can be achieved by appropriately selecting the current and ballast resistance. The regulating system is turned off after reaching a steady-state temperature field. During the experiment the temperature oscillation was less than 0.01 K due to small heat losses and the large mass of the autoclave and thermostat



Fig. 4 – Schematic diagram of the measuring circuit of apparatus with ADC (analog to digital converter) and PC. 1 – Voltage comparator; 2 – current direction switch; 3 – D.C. power supply; 4 – D.C. voltage stabilizer; 5 – standard resistance (10  $\Omega$ ); 6 – standard resistance (1  $\Omega$ ); 7 – milliammeter; 8 – resistance box; 9 – ammeter; 10 – auto-transformer.

block. The steady-state temperature field control is provided by measuring the temperature at the center of thermostat block and on the side surface using copper-constantan thermocouples.

An ultra-thermostat was used to thermostat the liquid under study. The temperature inside the thermostat was maintained uniform within 0.02 K. Distilled water was used as the thermostat liquid in the temperature range from 298 K to 363 K. Uniformity of the temperature distributions along the autoclave was checked with a thermocouple probe at the experimental temperatures. High thermal stability was maintained due to the small heat losses, a large autoclave mass, and thermostat block.

#### 2.5. Pressure generation and measurement system

The pressure generation and measurement system was built in a conventional experimental way: using a dead-weight



Fig. 5 – Schematic diagram of the thermostatting and temperature regulating system. 1 – Thermostatting unit; 2 – temperature transducer; 3 – differential amplifier; 4 – relay; 5 – rheostat; 6 – feeding system; 7 – voltmeter; 8 – thermostat; 9 – measuring unit.



Fig. 6 – Separating vessel. 1 – Body; 2 – coil; 3 – bellows battery; 4 – steel core.

pressure gauge, separating vessel, and measuring cell. The pressure in the system was generated and measured with a dead-weight pressure gauge with an uncertainty of 0.05%, which is connected to the separating vessel. The atmospheric pressure was measured with standard barometer with an uncertainty of 107 Pa. The separating vessel is connected by valves with the filling system, sample, and vacuum pump. On the upper parts of the vessel, two outlet pipes were mounted for connection with an inert gas cylinder and vacuum pump. The separating vessel (Fig. 6) is a high-pressure vessel made from titanium alloy.

#### 2.6. Procedure for thermal conductivity measurement

Prior to the start of the measurements, the measuring unit was installed in a vertical position. The measuring unit was then connected to the filling and pressure generation systems. The measuring system initially was rigorously cleaned and vacuumed. After filling the measuring cell with the sample, the upper nozzle was cut off. The valves were then opened and the bellows filled. Then the pump was turned off and disconnected from the system, and the pressure generated using the dead-weight pressure gauge. The mixture was prepared gravimetrically in the measuring cell using a separate unit, and then the cell with known sample concentration was transferred into the measurement apparatus. Water was first pumped into the cell and weighed. Then ammonia was cooled to -20 °C in an additional cell of volume (50 cm<sup>3</sup>) before it was pumped to the measurement cell that contains water, and then weighed again. All measurements were performed after reaching steady state (usually after 1-2 h). The measuring process consists of heating and cooling the measuring cell while simultaneously recording the signal from resistance thermometers, and continuously monitoring the electrical signals from the transducers and thermocouples in the measurement circuit.

Each measured data point is the average of 5–10 measurements. During the experiment, the measured data were collected in separate data files. After the measurements were completed, the program evaluated the results (calculating the amount of heat released by the heater, temperatures of the inner and outer resistance thermometers). During the measurements and data evaluation, all information was displayed on the computer screen.

## 2.7. Uncertainty of the thermal conductivity measurements

The experimental thermal conductivity data were evaluated using Eq. (2). All input parameters used for uncertainty analysis are given in Tables 2 and 3. Therefore, the uncertainty of a single thermal conductivity measurement is a function of the input parameters (see Tables 2 and 3) entering the thermal conductivity evaluation procedure. Table 3 provides the uncertainty analyses of the thermal conductivity measurements. Assuming that all of the input parameters  $X_i$  (A, Q,  $Q_e$ ,  $Q_r$ ,  $\Delta T_{wire}$ ,  $d_i$ , l, T, p, x) are independent, the variance of thermal conductivity (Y) is

$$u(\mathbf{Y})^{2} = \sum_{i=1}^{N} \left( \frac{\partial \mathbf{Y}}{\partial X_{i}} u(X_{i}) \right)^{2}, \tag{10}$$

Table 3 – Es	timation	of the un	certainty	of measur	ed quant	ities.					
Quantity	$d_1 \  imes 10^3$ (mm)	$d_2 \  imes 10^3$ (mm)	$d_3 \  imes 10^3$ (mm)	L (mm)	$I_{\rm wire} \  imes 10^3$ (mA)	$U_{\rm wire} \  imes 10^3 \ (V)$	ΔT <sub>L</sub> (°C)	ΔT <sub>wall</sub> (°C)	$(W m^{-1} K^{-1})$	Q (kJ)	T (°C)
Uncertainty	0.5	2.0	10	0.1	0.15	0.15	0.12	0.02	0.05	0.1	0.1

Table 4a – The results of test measurements of thermal conductivity of toluene with the hot-wire method. Calculated reference values are from Assael et al. (2012).

Т (К)	p (MPa)	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )	$\lambda_{calc}$	Deviation (%)
			(w m - K -)	
276.19	0.101	0.1359	0.13683	-0.68
278.42	0.101	0.1339	0.13621	-1.69
281.25	0.101	0.1324	0.13542	-2.23
281.25	0.101	0.1325	0.13542	-2.15
302.05	0.101	0.1290	0.12951	-0.39
304.59	0.101	0.1268	0.12878	-1.54
329.65	0.101	0.1235	0.12156	1.59
329.65	0.101	0.1253	0.12156	3.07
331.24	0.101	0.1237	0.12111	2.13
337.63	0.101	0.1242	0.11516	3.95
339.65	0.101	0.1220	0.11929	2.69
339.85	0.101	0.1226	0.11871	3.21
340.17	0.101	0.1200	0.11866	1.19
351.33	0.101	0.1166	0.11522	1.01
351.55	0.101	0.1200	0.11536	3.87
352.25	0.101	0.1179	0.11542	2.32

where N is the number of input parameters (see Tables 2 and 3) in the working equation (2) and the combined standard uncertainty is the square root of the variance (ISO, 1993). Tables 2 and 3 provide the values of each of the input parameters X<sub>i</sub> and their estimated standard uncertainties. Based on the data from Tables 2 and 3 the total expanded uncertainty of the thermal conductivity measurements at the 95% confidence level (coverage factor of k = 2) is estimated to be 1.7%. This value of the uncertainty does not include the uncertainty related to the concentration. The uncertainty analyses (see Table 3) for the present method were performed for pure fluids. Therefore, the uncertainty in the present thermal conductivity data will be slightly larger than 1.7% (approximately 2.0-2.5%) due to concentration measurement uncertainty. As one can see from Table 5, our apparatus reproduces reference data for standard fluids within 3% (approximately 2 standard deviation). This is acceptable for this method because all available reported data for toluene (for example) deviate from the values calculated with reference correlation within 5-6% (discrepancy all of the reported data is within 10%).

Table 4b — The results of test measurements of thermal conductivity of air with the hot-wire method. Calculated reference values are from Lemmon and Jacobsen (2004).					
Т (К)	p (MPa)	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )	$\lambda_{\text{calc}}$ (W m <sup>-1</sup> K <sup>-1</sup> )	Deviation (%)	
97.150	0.101	0.0090	0.0090	-0.28	
105.75	0.101	0.0097	0.0098	-1.50	
117.37	0.101	0.0110	0.0109	0.545	
165.49	0.101	0.0152	0.0153	-0.56	
171.53	0.101	0.0158	0.0158	-0.06	
184.72	0.101	0.0168	0.0169	-0.81	
205.44	0.101	0.0186	0.0187	-0.35	
218.14	0.101	0.0197	0.0197	-0.01	
287.46	0.101	0.0254	0.0251	1.31	
307.05	0.101	0.0269	0.0265	1.47	
363.32	0.101	0.0308	0.0305	1.07	
378.59	0.101	0.0314	0.0315	-0.35	

#### 2.8. Test measurements

To check the accuracy of the method, correct operation of the apparatus, and confirm the reliability of thermal conductivity data, test measurements were made on pure water, toluene, air, and ammonia at selected isobars from 0.101 MPa to 20 MPa and a range of temperatures for which reliable reference values are available. The results are presented in Table 4a–d, and summarized in Table 5. The average absolute deviation (AAD) for all four pure fluids is 2% or less, demonstrating good agreement with the literature reference correlations for water (Huber et al., 2012), toluene (Assael et al., 2012), air (Lemmon and Jacobsen, 2004), and ammonia (Tufeu et al., 1984). Fig. 7 presents the deviations graphically as a function of temperature.

# 2.9. Effect of electrical conductivity on the thermal conductivity measurements of weak electrolytes

The ammonia + water mixture is a weak electrolyte, therefore the effect of electrical conductivity on the measured values of thermal conductivity should be taken into account. In order to examine the effect of electrical conductivity of the ammonia + water mixture on the measured values of thermal conductivity, the measurements were made for two mixtures (0.0527, and 0.1052 mole fraction) at atmospheric pressure with a hot-wire method using a measuring cell with an insulated outer thermometer (see Figs. 8 and 9). The measuring cell is a capillary with an expansion (widened ends), welded inside the capillary with diameter of 8 mm. The capillary is made from high thermal resistance molybdenum glass. A schematic diagram of the measuring capillary is presented in Fig. 9. Current-carrying wires with diameters of 0.2 mm and 0.30 mm were brazed with gold alloy to the measuring part of the resistance thermometer. To determine the voltage drop in the measuring section, the potentiometric wires with 0.05 mm diameter were welded. In order to avoid the effect of electrical conductivity of the ammonia + water mixture on the measured thermal conductivities, electrical insulation of the inner and outer resistance thermometer circuits was used. The inner capillary is filled with a 2 ml layer of the sample under study. The outer resistance thermometer is located in the ring gap between the outer and inner capillary. The ring gap was filled with electrically non-conducting liquid. The very narrow ring gap between the capillary impedes convection development in the liquid layer, and thereby helps maintain isothermal conditions of the outer surface of the capillary. Also in order to avoid the possible convection the measurements were performed at small ( $\Delta T = 3-6$  K) temperature differences. In the range of the present experiments, the values of Rayleigh number Ra were always less than the critical value  $Ra_c = 1000$  for this method, and convective heat transfer,  $Q_{\text{convection}}$ , was estimated to be negligible. The absence of convection was verified experimentally by measuring the thermal conductivity with various temperature differences  $\Delta T$  (3–6 K) across the fluid gap, and with different heating powers, Q, transferred from the hot-wire to the outer cylinder. The measured thermal conductivities were independent of the applied temperature differences  $\Delta T$ , and power Q. The results of the measured values of the thermal Table 4c – The results of test measurements of thermal conductivity of water with the hot-wire method. Calculated reference values are from Huber et al. (2012).

Т (К)	p (MPa)	$\lambda (W m^{-1} K^{-1})$	(W $m^{-1}$ K <sup>-1</sup> )	Deviation (%)
276.41	0.101	0.5538	0.56727	-2.37
277.85	0.101	0.5500	0.57000	-3.51
300.61	0.101	0.6257	0.61134	2.35
300.70	0.101	0.6201	0.61149	1.41
300.70	0.101	0.6198	0.61149	1.36
301.09	0.101	0.6005	0.61214	-1.9
301 20	0 101	0.6078	0.61232	-0.73
301.20	0 101	0.6165	0.61321	0.53
303 32	0 101	0.6103	0.6158	-0.89
303.52	0.101	0.6109	0.6164	_0.90
303.71	0.101	0.6098	0.6165	_1.09
306 14	0.101	0.6095	0.6202	_1.05
307 17	0.101	0.6055	0.6202	_0.94
325 57	0.101	0.6581	0.6210	1 91
325.57	0.101	0.6474	0.64697	0.07
226.67	0.101	0.6405	0.04057	1.09
220.02	0.101	0.0403	0.04738	-1.09
220.45	0.101	0.0422	0.6517	-1.52
221 27	0.101	0.0431	0.0517	-1.55
331.37 221 72	0.101	0.6508	0.6526	-0.28
222.72	0.101	0.0550	0.65297	0.004
332.27	0.101	0.6454	0.65352	-1.24
332.40	0.101	0.6493	0.0537	-0.08
332.83	0.101	0.6392	0.65407	-2.2/
333.39	0.101	0.6498	0.6546	-0.74
350.97	0.101	0.6877	0.66866	2.85
352.08	0.101	0.6642	0.66936	-0.77
352.69	0.101	0.6622	0.66974	-1.12
355.05	0.101	0.6720	0.6/113	0.13
355.56	0.101	0.6606	0.6/142	-1.6
356.00	0.101	0.6781	0.6/16/	0.95
356.22	0.101	0.6716	0.6/1/9	-0.015
356.54	0.101	0.6823	0.67197	1.53
356.63	0.101	0.6536	0.67202	-2.74
356.76	0.101	0.6589	0.67209	-1.96
356.90	0.101	0.6827	0.67216	1.57
360.47	0.101	0.6765	0.6740	0.37
361.52	0.101	0.6756	0.6745	0.16
2/8.9/	10.133	0.5561	0.57723	-3.66
300.48	10.133	0.6142	0.61567	-0.24
301.00	10.133	0.6101	0.61653	-1.04
301.59	10.133	0.6032	0.61750	-2.31
302.20	10.133	0.6023	0.61850	-2.62
325.44	10.133	0.6555	0.65094	0.70
326.00	10.133	0.6653	0.65158	2.10
326.54	10.133	0.6528	0.65219	0.09
327.14	10.133	0.6521	0.65286	-0.12
354.98	10.133	0.6857	0.67622	1.40
355.48	10.133	0.6761	0.67652	-0.06
356.05	10.133	0.6/11	0.6/685	-0.85
356.61	10.133	0.668/	0.6//1/	-1.24
300.42	15.199	0.6204	0.61787	0.41
300.96	15.199	0.6132	0.61876	-0.89
301.55	15.199	0.6100	0.61973	-1.56
300.40	20.265	0.6254	0.62014	0.85
300.40	20.265	0.6254	0.62014	0.84
300.92	20.265	0.6204	0.62100	-0.09
301.50	20.265	0.6118	0.62196	-1.63
302.11	20.265	0.6103	0.62295	-2.03
325.90	20.265	0.6585	0.65621	0.35
326.43	20.265	0.6543	0.65682	-0.38

Tabl	e 4c (con	tinued)		
T (K)	p (MPa)	$\lambda (W m^{-1} K^{-1})$	(W $m^{-1}$ K <sup>-1</sup> )	Deviation (%)
327.01	20.265	0.6425	0.65748	-2.28
355.45	20.265	0.6895	0.68167	1.15
356.00	20.265	0.6924	0.68200	1.52
356.60	20.265	0.6887	0.68235	0.93

conductivity of the ammonia + water mixtures for two compositions at atmospheric pressure with hot-wire method using an insulated outer thermometer are presented in Table 6. Fig. 10 provides the comparison between the thermal conductivity values of the ammonia + water mixtures measured using the hot-wire methods with insulated and not-insulated outer thermometers; the results of the two methods are consistent with each other.

#### 2.10. Materials and their purity

The sample of ammonia was obtained commercially and had a stated purity of  $\geq$ 99.95 wt.%. The values of density and refractive index of the pure water and a selected mixture at 0.1 MPa are given in Table 7 together with reference values.

#### 3. Results and discussion

In addition to the pure fluid measurements on water and ammonia presented in Tables 4c and 4d, measurements of the thermal conductivity were performed for eight mixture compositions (0.1905, 0.2683, 0.3002, 0.4990, 0.5030, 0.6704, 0.7832, and 0.9178 mole fraction of ammonia) along five isobars (0.101, 5.066, 10.133, 15.199, and 20.265 MPa) at temperatures from 278 K to 356 K in the liquid phase. The measured values of thermal conductivity of the ammonia + water mixtures are given in Table 8 and shown in Figs. 11–15 in various projections ( $\lambda$ –T,  $\lambda$ –x,  $\lambda$ – $\rho$ ). The values of density at experimental *p* and *T* conditions were calculated using reference equation of state model by Tillner-Roth and Friend (1998).

Fig. 11 shows the temperature dependence of the measured thermal conductivities for the mixture along the two selected isobars (5.066 and 20.265 MPa) together with pure-component values calculated from reference correlations (Huber et al., 2012; Tufeu et al., 1984). As this figure shows, the behavior of the measured thermal conductivities is almost a linear function of temperature. The slope changes of the  $\lambda_{mix}^{exp}$ -T dependence of the mixture are complicated, however, because the temperature behavior of the pure components is in the opposite direction (for water  $\lambda$  increases with temperature in our experimental range, while for ammonia it decreases with temperature). At some of our experimental conditions, pure water and pure ammonia are in different phases (water in liquid, while ammonia in gas phase). It is obvious that behavior of the temperature dependence of  $\lambda_{mix}^{exp}(T,p,x)$  (slope of  $\lambda_{mix}^{exp}{-}T$  curves) strongly depends on composition. In Fig. 11, at concentrations above about 0.8 mole fraction of ammonia, the slope of  $\lambda_{mix}^{exp}$ -T at fixed x and p is negative (similar to ammonia), while at low concentrations

Table 4d — The results of test measurements of thermal conductivity of ammonia with the hot-wire method. Calculated reference values are from Tufeu et al. (1984).

T (K)	p (MPa)	$\lambda (W m^{-1} K^{-1})$	(W $m^{-1}$ K <sup>-1</sup> )	Deviation (%)
285.08	0.101	0.0244	0.02382	-2.36
286.66	0.101	0.0247	0.02395	-3.03
302.70	0.101	0.0254	0.02535	-0.19
302.96	0.101	0.0255	0.02537	-0.49
302.97	0.101	0.0253	0.02537	0.29
304.33	0.101	0.0255	0.02550	0.01
307.07	0.101	0.0267	0.02576	-3.51
327.09	0.101	0.0275	0.02781	1.14
327.13	0.101	0.0276	0.02782	0.79
327.17	0.101	0.0274	0.02782	1.54
328.37	0.101	0.0270	0.02795	3.52
328.82	0.101	0.0278	0.02800	0.73
332.11	0.101	0.0291	0.02837	-2.51
352.15	0.101	0.0311	0.03073	-1.18
352.17	0.101	0.0312	0.03073	-1.49
352.77	0.101	0.0317	0.03081	-2.81
351.07	5.066	0.350	0.34608	-1.12
351.27	5.066	0.347	0.34551	-0.42
351.67	5.066	0.352	0.34438	-2.16
353.00	5.066	0.338	0.34060	0.76
353.62	5.066	0.339	0.33883	-0.05
354.31	5.066	0.340	0.33686	-0.92
289.06	10.133	0.5088	0.52768	3.71
289.49	10.133	0.5185	0.52644	1.53
289.56	10.133	0.5183	0.52624	1.53
290.37	10.133	0.5118	0.52392	2.37
303.21	10.133	0.4919	0.48/82	-0.83
303./1	10.133	0.4977	0.48643	-2.26
304.22	10.133	0.5034	0.48503	-3.65
328.50	10.133	0.4181	0.41953	0.34
250.05	10.133	0.4230	0.41408	-2.57
200.00	15 100	0.5000	0.50215	0.59
289.48	15 199	0.5215	0.53469	2.50
290.20	15 199	0.5268	0.53266	1 11
291.03	15 199	0.5391	0.53032	-1.63
302 19	15 199	0.5003	0 49943	-0.17
302.82	15.199	0.5050	0.49772	-1.44
303.02	15.199	0.5010	0.49718	-0.76
303.25	15.199	0.5004	0.49655	-4.58
328.65	15.199	0.4210	0.42978	2.08
330.07	15.199	0.4257	0.42616	0.11
331.78	15.199	0.4128	0.42182	2.18
350.50	15.199	0.3810	0.37516	-1.53
351.00	15.199	0.3790	0.37393	-1.34
351.20	15.199	0.3740	0.37344	-0.15
289.11	20.265	0.5323	0.54369	2.14
289.40	20.265	0.5321	0.54288	2.02
289.42	20.265	0.5328	0.54283	1.88
291.03	20.265	0.5391	0.53835	-0.14
328.61	20.265	0.4313	0.43975	1.96
330.94	20.265	0.4297	0.43398	0.99
331.75	20.265	0.4302	0.43198	0.41
352.76	20.265	0.3800	0.38154	0.40
353.46	20.265	0.3820	0.37991	-0.55

is positive (similar to pure water). The contribution of water to the total thermal conductivity of the mixture is more than that of pure ammonia, therefore, the slope of the  $\lambda_{mix}^{exp}$ -T curve changes at high concentrations of ammonia. At

Table 5 – Deviation statistics for test measurements for
pure fluids.

Fluid	No.	AAD	Bias	St. Dev	RMS	Max. Dev
	Points	(%)	(%)	(%)	(%)	(%)
Water Toluene	63 21	1.30	-0.36	1.57	0.22	3.66 3.95
Air	12	0.69	0.04	0.90	0.26	1.50
Ammonia	60	1.44	-0.01	1.79	0.24	3.71

concentrations between 0.8 and 0.9 mole fraction of ammonia, the measured thermal conductivity of the mixture  $\lambda_{\min}^{exp}(\mathbf{T},p,\mathbf{x})$ is almost independent of temperature, i.e., the slope of the  $\lambda_{mix}^{exp}-T$  isobars at these concentrations is zero. Figs. 12 and 13 demonstrate how the concentration behavior of the measured thermal conductivity of the mixture depends on temperature and  $\lambda_{NH_3}^{ref}(T,p)$  pressure. The concentration dependence (Fig. 12) of the thermal conductivity of the mixture shows a considerably negative deviation from linear mixture behavior (up to temperature of 333 K, see below) along the various isobars. As shown in Fig. 13, at temperatures above 333 K the curvature of the  $\lambda_{mix}^{exp}$ -x curves changes (becomes convex) while at low temperatures (below 333 K)  $\lambda_{mix}^{exp}$ -x curves have a concave shape. At high temperatures, the contribution of the interaction between the molecules of water and ammonia to total thermal conductivity is larger than the linear mixture contribution. At low temperatures (below 323 K),  $\lambda_{mix}^{exp}-x$ curves goes through a concentration minimum. This minimum vanishes at high temperatures. As temperature increases, the minimum of thermal conductivity becomes less pronounced and finally at temperatures above 323 K vanishes. At some isotherm between 333 K and 343 K, the  $\lambda_{mix}^{exp}-x$ dependence curves along the various isobars becomes linear, then changes to convex curvature.

Fig. 14 demonstrates that the pressure dependence of the thermal conductivity,  $\lambda_{mix}^{exp} - p$ , along the various isotherms at fixed concentrations is almost linear. The slope of the  $\lambda_{mix}^{exp} - p$  curves changes with temperature (increasing with T). At low temperatures (below 313 K), the measured thermal conductivity of mixtures changes very slightly with pressure. The density dependence of the measured thermal conductivity of the mixtures,  $\lambda_{mix}^{exp} - \rho$ , is presented in Fig. 15 for two selected concentrations and for various pressures. As one can see from this figure, the density dependence of the  $\lambda_{mix}^{exp}$  is very close to a linear function.

The thermal conductivity difference,  $\Delta \lambda^{\exp}(T,p,x)$ , for ammonia + water mixtures was calculated using the present thermal conductivity data for the mixtures and purecomponent values calculated from reference correlations for pure water (Huber et al., 2012) and ammonia (Tufeu et al., 1984) with the following relation:

$$\Delta \lambda^{\exp}(T, p, x) = \lambda^{\exp}_{\min}(T, p, x) - \lambda^{\text{linear}}_{\min}(T, p, x),$$
(11)

$$\lambda_{\text{mix}}^{\text{linear}}(T, p, x) = x \lambda_{\text{NH}_3}^{\text{ref}}(T, p) + (1 - x) \lambda_{\text{H}_2\text{O}}^{\text{ref}}(T, p), \tag{12}$$

where x is the mole fraction of ammonia,  $\lambda_{\min}^{exp}(T, p, x)$  is the experimentally determined thermal conductivity of the mixture of concentration x, temperature *T*, and pressure *p* (Table 8), and  $\lambda_{H_2O}^{ref}(T, p)$  are the thermal conductivity of the



Fig. 7 – Percentage deviations,  $\delta \lambda = 100[(\lambda^{cal} - \lambda^{exp})/\lambda^{exp}]$ , of the measured thermal conductivities for pure ammonia, water, toluene, and air from the values calculated with the reference correlations (Assael et al., 2012; Huber et al., 2012; Lemmon and Jacobsen, 2004; Tufeu et al., 1984). Ammonia:  $\circ$ , 0.101 MPa;  $\bullet$ , 5.066 MPa;  $\blacktriangle$ , 10.133 MPa;  $\times$ , 15.199 MPa;  $\Box$ , 20.265 MPa; Water:  $\bullet$ , 0.101 MPa;  $\circ$ , 10.133 MPa;  $\times$ , 15.199 MPa;  $\bigstar$ , 20.265 MPa; Toluene:  $\bullet$ , 0.101 MPa; Air:  $\bullet$ , 0.101 MPa.



Fig. 8 – Schematic diagram of the steady-state hot-wire experimental thermal conductivity apparatus with insulated outer thermometer. 1 – Measuring cell; 2 – vacuum pump; 3 – vessel with sample under study; 4 – thermostat; 5 – comparators; 6 – data-acquisition system.



Fig. 9 – Measuring cell with electrically insulated outer thermometer.

pure ammonia and pure water at the same pressure p and temperature T, respectively. The thermal conductivity difference,  $\Delta \lambda^{\exp}(T, p, x)$ , is affected by differences in size and polarity of the constituents of the mixture. Figs. 16 and 17 show the thermal conductivity differences,  $\Delta \lambda^{\exp}(T, p, x)$ , calculated from the present mixture thermal conductivities. Note that the values of  $\Delta \lambda^{\exp}(T,p,x)$  for ammonia + water mixtures are negative for all measured pressures and temperatures over the whole composition range, except for high temperatures above 343 K. This means that thermal conductivity for linear  $\label{eq:mixtures} \text{mixtures}, \lambda_{\text{mix}}^{\text{linear}}(T,p,x) > \lambda_{\text{mix}}^{\text{exp}}(T,p,x) \text{, is larger than the}$ measured thermal conductivity of the mixture at temperatures below 343 K and at any pressure up to 20 MPa. As one can see from Figs. 16 and 17, the curves of thermal conductivity difference  $\Delta \lambda^{\exp}(T,p,x)$  are noticeably symmetric. The thermal conductivity difference minimum is found at a concentration of about 0.5 mole fraction of ammonia. This can be attributed partly to the small differences between the size of the water and ammonia molecules (both fluids have almost the same molecular weights, 17.03 g mol<sup>-1</sup> for ammonia and

Table 6 – Experimental thermal conductivities ( $\lambda$ ,
W $m^{-1}$ K <sup>-1</sup> ), temperatures (K), and compositions (mole
fraction of ammonia) of ammonia + water mixtures at
various concentrations at atmospheric pressure
measured with hot-wire method using an insulated outer
thermometer.

Concentration of ammonia, x mole fraction

x = 0.0527	7	x = 0.1052			
Т (К)	$\lambda (W m^{-1} K^{-1})$	Т (К)	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )		
276.19	0.5361	276.22	0.4962		
276.17	0.5359	277.74	0.4989		
277.64	0.5300	279.52	0.5020		
279.32	0.5250	281.55	0.5056		
301.91	0.5855	300.45	0.5348		
301.86	0.5870	301.33	0.5360		
303.35	0.5659	304.34	0.5401		
305.10	0.5667	306.55	0.5430		
327.97	0.6057	318.67	0.5575		
329.86	0.6004	320.54	0.5595		
-	-	322.70	0.5618		



Fig. 10 – Experimental thermal conductivity of ammonia + water mixtures as a function of concentration along two selected isotherms (277. 99 K and 305.12 K) measured using insulated (open circles) and not-insulated (full circles) outer thermometers.

Table 7 — Physical chemical characteristics (density and refractive index) of the samples at 0.1 MPa and reference temperatures.						
Fluid and fluid mixture	Refractive index, $n_D^{20}$	Density $ ho$ , kg m <sup>-3</sup> at 0.1 MPa and 25 °C				
Water	1.333 (this work) 1.3334 (Schiebener et al., 1990)	997.10 (this work) 997.05 (Wagner and Pruβ, 2002)				
$\begin{array}{l} \mbox{Ammonia} + \mbox{water}, \\ \mbox{$x = 0.2683$ mole} \\ \mbox{fraction} \\ \mbox{of ammonia} \end{array}$	1.3462 (this work)	905.2 (this work) 904.71 (Tillner-Roth and Friend, 1998)				

Table 8 – Experimental thermal conductivities ( $\lambda$  (W m<sup>-1</sup> K<sup>-1</sup>)), temperatures (K), concentration (mole fraction), and pressures (MPa) of ammonia + water mixtures measured with hot-wire method. p = 10.133 (MPa) p = 2.189 (MPa) p = 5.066 (MPa) p = 20.265 (MPa) p = 1.115 (MPa) T (K) λ T (K) λ T (K) λ T (K) λ T (K)

x = 0.1905 mole fraction										
293.56	0.4955	293.58	0.5031	284.34	0.4849	293.22	0.4971	293.35	0.5172	
293.57	0.4967	293.60	0.5020	284.17	0.4813	293.24	0.5040	293.24	0.5031	
293.58	0.4984	293.35	0.4966	284.14	0.4849	293.41	0.5008	293.42	0.5040	
p = 2.077 (	MPa)	293.36	0.4949	284.22	0.4923	293.44	0.5063	327.29	0.5788	
302.56	0.5125	293.40	0.4993	293.49	0.4955	293.45	0.5057	327.29	0.5759	
302.57	0.5120	-	-	293.51	0.5004	293.46	0.5102	_	-	
302.59	0.5154	-	-	293.54	0.5055	293.47	0.5094	-	-	
302.64	0.5175	-	-	293.65	0.5118	293.48	0.5073	_	-	
_	-	-	-	302.56	0.5200	327.40	0.5728	_	-	
-	-	-	-	353.56	0.6272	327.41	0.5741	-	-	
-	-	-	-	353.58	0.6286	327.45	0.5713	-	-	
-	-	-	-	353.61	0.6242	-	-	-	-	
<i>p</i> = 0.101	(MPa)	p = 5.0	66 (MPa)	<i>p</i> = 10.1	33 (MPa)	p = 15.1	p = 15.199 (MPa)		p = 20.265 (MPa)	
Т (К)	λ	T (K)	λ	T (K)	λ	Т (К)	λ	Т (К)	λ	
x = 0.268	3 mole fraction	L								
277.99	0.4192	302.63	0.443	302.39	0.4499	302.39	0.4688	301.92	0.5110	
278.00	0.4247	304.42	0.460	304.20	0.4565	303.97	0.4758	303.76	0.5113	
279.81	0.4320	304.51	0.4680	304.51	0.4750	304.51	0.4870	306.80	0.5118	
281.95	0.4303	307.18	0.475	307.18	0.4754	306.97	0.4905	315.52	0.5120	
281.96	0.4279	307.34	0.469	315.52	0.5010	315.52	0.5080	333.40	0.5914	
281.97	0.4293	333.55	0.5711	333.58	0.5882	333.45	0.5822	333.85	0.5971	
284.14	0.4453	334.00	0.5789	334.07	0.5853	333.86	0.5890	334.07	0.6015	
284.17	0.4467	334.28	0.5858	334.12	0.5836	334.07	0.5921	349.01	0.6402	
286.13	0.4452	345.28	0.6092	349.95	0.6323	349.85	0.6392	349.34	0.6435	
293.18	0.4589	352.88	0.6165	350.63	0.6345	350.82	0.6421	349.56	0.6441	
293.20	0.4579	354.33	0.6223	351.53	0.6363	351.80	0.6432	-	-	
303.14	0.4643	_	_	352.75	0.6398	_	_	-	-	
304.59	0.4615	-	-	-	-	-	—	-	-	
304.51	0.4630	_	_	-		_	_	-	-	
305.12	0.4669	_	_	-	-	_	_	-	-	
307.39	0.4638	_	_	-	-	_	_	-	-	
315.52	0.4720	-	-	-	-	-	-	-	-	
p = 5.066	(MPa)		p = 10.133	(MPa)	MPa) $p=2$		15.199 (MPa)		p = 20.265 (MPa)	
Т (К)	λ	1	Г (К)	λ	Т (К)	λ		Т (К)	λ	
x = 0.300	2 mole fraction									
287.36	0.4070	2	87.39	0.4104	324.08	0.52	21	287.44	0.4166	
287.39	0.4105	2	87.43	0.4108	324.11	0.52	16	287.40	0.4116	
287.38	0.4093	2	87.44	0.4121	324.15	0.53	21	284.41	0.4130	
303.83	0.4319	3	03.93	0.4426	342.95	0.61	61	303.93	0.4529	
303.89	0.4379	3	03.93	0.4482	342.93	0.61	40	303.79	0.4510	
324 13	0 5264	3	03 89	0.4500	342 96	0.61	78	303.88	0 4570	

324.08 0.5298 324.04 0.5053 303.87 0.4582 343.18 0.5856 0.5091 303.86 0.4559 324.06 — \_ 343.17 324.05 0.5083 324.11 0.5356 0.5864 \_ \_ 0.5391 343.21 0.5822 343.13 0.5948 \_ \_ 324.15 343.17 0.5864 343.09 0.5994 324.14 0.5378 \_ \_ \_ \_ \_ 343.18 0.5985 \_ 342.99 0.6362 \_ \_ \_ 342.93 0.6342 \_ \_ \_ \_ \_ \_ \_ \_ 343.03 0.6314

(continued on next page)

λ

Table 8 – (	(continued)						
p = 5.066 (MPa)		p = 10.133 (MPa)		p = 15.199 (MPa)		p = 20.265 (MPa)	
T (K)	λ	T (K)	λ	T (K)	λ	T (K)	λ
x = 0.4990	mole fraction						
294 95	0 3937	294 95	0 3951	294.84	0 3865	294 72	0 3887
296.36	0.4013	296.35	0.4020	296.33	0.4053	296.22	0.4078
297.22	0.4068	297.19	0.4081	297.18	0.4098	297.11	0.4116
353.35	0.5768	353.65	0.5713	353.58	0.5735	354.07	0.5929
353.95	0.5692	353.88	0.5724	353.85	0.5794	353.79	0.5815
353.70	0.5670	354.13	0.5750	354.09	0.5828	353.54	0.5789
p = 5.066 (1	MPa)	p = 10.133 (MPa)		p = 15.199 (MPa)		p = 20.2	65 (MPa)
T (K)	λ	T (K)	λ	T (K)	λ	T (K)	λ
x = 0.5030	mole fraction						
302.92	0.3935	295.28	0.3873	295.27	0.3885	295.25	0.3905
304.39	0.4048	296.79	0.3999	296.77	0.4022	297.27	0.4030
305.21	0.4131	297.59	0.4031	297.59	0.4060	297.43	0.4082
295.23	0.3827	302.93	0.4024	305.82	0.4140	306.28	0.4155
296.71	0.3956	304.39	0.4126	307.20	0.4158	307.95	0.4212
297.54	0.4015	305.21	0.4163	308.08	0.4198	308.96	0.4232
328.49	0.4720	328.37	0.4787	328.36	0.4939	328.38	0.5023
329.94	0.4730	329.89	0.4854	329.90	0.4975	329.86	0.5056
330.71	0.4740	330.76	0.4918	330.74	0.4998	330.71	0.5083
p = 5.066 (I	MPa)	p = 10.133 (MPa)		p = 15.199 (MPa)		р = 20.265 (МРа)	
T (K)	λ	T (K)	λ	T (K)	λ	T (K)	λ
x = 0.6704	mole fraction						
201.65	0 2020	202 72	0.4052	200.40	0.2759	201 56	0.2052
291.05	0.3858	204.07	0.4055	290.49	0.3738	291.30	0.3855
202.55	0.3352	204.91	0.4166	202.01	0.2071	202.69	0.4089
293.09	0.3990	207.01	0.4100	292.91	0.3371	293.08	0.4064
204.02	0.3050	220.26	0.4751	200.70	0.4122	202.02	0.4119
304.81	0.4097	320.11	0.4770	304.03	0.4175	304.69	0.4172
227.90	0.4590	25/ 97	0.5202	204.77	0.4207	220.20	0.4777
220.02	0.4590	255.07	0.5502	207.77	0.4207	229.20	0.4777
220.10	0.4600	252.24	0.5417	220.20	0.4705	229.10	0.401
252.10	0.4040	555.54	0.5018	220.02	0.4706	254.09	0.4652
25/ 01	0.5155		_	252.20	0.4790	252.24	0.5024
255 00	0.5165	_	_	255.29	0.5702	254.00	0.5929
-	0.3199	_	_	355.95	0.5775	355.34	0.6013
n = 5.066.01	MDo)	n – 10 1	22 (MDa)	n _ 15 1	$OO(MP_{0})$	n - 20.2	65 (MDa)
$\frac{p}{T(k)} = 3.000 (l)$		p = 10.1		$\frac{p-15.1}{T(K)}$		$\frac{p-20.2}{T(k)}$	
$\frac{1}{N} = 0.7922$	n mole fraction	I (K)	λ	1 (K)	λ	1 (K)	Λ
x = 0.7632		004.14	0.2000	204.07	0 4007	204.04	0 4057
294.11	0.3942	294.11	0.3996	294.07	0.4027	294.01	0.4057
295.3/	0.404	295.35	0.4053	295.32	0.4130	295.29	0.41/3
296.15	0.4125	296.10	0.4141	296.07	0.4176	295.99	0.4221
328.30	0.4292	328.11	0.4361	327.98	0.4404	327.99	0.4428
329.14	0.43/2	329.49	0.4414	329.43	0.4435	329.39	0.4482
330.33	0.4380	330.33	0.4436	330.24	0.4489	330.22	0.4510
349.81	0.4492	349.74	0.4540	349.67	0.4591	349.69	0.4693
350.90	0.4600	350.62	0.4613	350.68	0.4638	350.66	0.4/4/
351.95	0.4634	351.82	0.4644	351.66	0.4629	351./0	0.4/92
-	—	354.58	0.4698	352.73	0.4783	-	-
_	-	355.14	0.4659	354.08	0.4519	-	-
-	-	355.98	0.4561	354.13	0.4585	-	-
_	-	-	-	354.93	0.4510	-	-
—	_	_	_	354.97	0.4541	—	_

Table 8 (continued)							
p = 5.066 (MPa)		p = 10.133 (MPa)		p = 15.199 (MPa)		p = 20.265 (MPa)	
Т (К)	λ	T (K)	λ	Τ (Κ) λ		Т (К)	λ
x = 0.9178 n	nole fraction						
293.84	0.4160	295.04	0.4340	293.74	0.4220	327.86	0.4590
295.07	0.4330	295.70	0.4400	294.94	0.4370	329.20	0.4605
295.77	0.4360	327.92	0.4430	295.63	0.4410	328.87	0.4621
318.63	0.4133	329.28	0.4434	327.89	0.4489	349.29	0.4176
327.87	0.4167	348.57	0.4231	329.23	0.4495	350.04	0.4098
329.14	0.4151	-	-	329.96	0.4562	349.68	0.4052
329.17	0.4124	_	-	349.34	0.4069	-	-
347.06	0.3975	-	-	350.20	0.4147	-	-
349.28	0.4080	-	_	_	_	_	-

18.015 g mol<sup>-1</sup> for water). At high temperatures (above 343 K) there may be very significant changes in the chemical interactions between water and ammonia molecules in this mixture, since the thermal conductivity difference changes sign at high temperatures. The maximum value of difference between the mixture thermal conductivity,  $\lambda_{mix}^{exp}(T, p, x)$  and the linear mixture,  $\lambda_{mix}^{innear}(T, p, x)$ , is about -0.16 W m<sup>-1</sup> K<sup>-1</sup>.

Fig. 18 shows the concentration dependence of the thermal conductivity of a series of water-containing binary mixtures with the same first component (water) and various second components (alcohols) at a selected temperature of 310 K and at two isobars of 0.101 and 5 MPa. This figure demonstrates the effect of the nature of the second component on the values and concentration dependence behavior of the thermal conductivity of water-containing mixtures. As one can see from Fig. 18, the introduction of alcohols (methanol, ethanol, and 1-propanol) in water results in considerable decreases in the thermal conductivity. As Fig. 18 shows, no concentration minimum was found for alcohol + water mixtures, while for ammonia + water the minimum was found at concentration

of about 0.75 mole fraction at pressure of 5 MPa. Among these binary mixtures, ammonia + water shows the highest values of thermal conductivity, while 1-propanol + water shows the lowest values.

In Fig. 19, we present the present thermal conductivity data for ammonia + water mixture at 0.101 MPa and 5.00 MPa for various temperatures together with available literature data. As one can see the agreement is reasonable (differences are within 1-2%).

### 4. Correlation equation

Since a theory for the thermal conductivity of liquid mixtures of polar mixtures is unavailable, its evaluation is empirical and based solely on experimental data. Therefore, the present measured thermal conductivity data were fitted to simple correlation equation

$$\lambda_{\min}(T, p, x) = x \lambda_{\mathrm{NH}_3}^{\mathrm{ref}}(T, p) + (1 - x) \lambda_{\mathrm{H}_2\mathrm{O}}^{\mathrm{ref}}(T, p) + \Delta \lambda(T, p, x)$$
(13)



Fig. 11 – Measured thermal conductivities of ammonia + water mixtures as a function of temperature at two selected isobars of 5.066 MPa (left) and 20.265 MPa (right) for various concentrations (mole fractions). •, x = 0.2683;  $\circ$ , x = 0.5030;  $\blacksquare$ , x = 0.6704;  $\Box$ , x = 0.7832; and  $\blacktriangle$ , x = 0.9178; solid lines are pure water (Huber et al., 2012) and pure ammonia (Tufeu et al., 1984).



Fig. 12 – Measured thermal conductivities of ammonia + water mixtures as a function of concentration at selected isotherm-isobars.  $\blacksquare$ , p = 5.066 MPa;  $\circ$ , p = 10.133 MPa;  $\bullet$ , p = 15.199 MPa;  $\Box$ , p = 20.265 MPa. Solid lines are calculated from the correlation (Eqs. (17) and (18)).

where  $\lambda_{\text{NH}_3}^{\text{ref}}(T, p)$  and  $\lambda_{\text{H}_2\text{O}}^{\text{ref}}(T, p)$  are the reference correlation equations for pure components, ammonia (Tufeu et al., 1984) and water (Huber et al., 2012), respectively;  $\Delta\lambda(T,p,x)$  is the thermal conductivity difference between the real and linear mixtures. In general the functional form of the  $\Delta\lambda(T,p,x)$  should satisfy end concentration points (x = 0 and x = 1) conditions. Thus, the functional structure of the concentration dependence of  $\Delta\lambda(T,p,x)$  should be selected as



Fig. 13 – Measured thermal conductivities of ammonia + water mixtures as a function of concentration at selected isotherm-isobars.  $\Box$ , T = 303.15 K;  $\bullet$ , T = 313.15 K;  $\blacksquare$ , T = 333.15 K;  $\circ$ , T = 343.15 K. Solid lines are calculated from correlation (Eqs. (17) and (18)).



Fig. 14 – Measured thermal conductivities of ammonia + water mixtures as a function of pressure at selected isothermisopleths.  $\Delta$ , T = 333.15 K;  $\Box$ , T = 343.15 K;  $\blacklozenge$ , T = 313.15 K;  $\circlearrowright$ , T = 323.15 K;  $\blacklozenge$ , T = 303.15 K.

$$\begin{split} \Delta\lambda(T,p,x) &= x(1-x) \left[ F_0(p,T) + F_1(p,T)(1-2x) \right. \\ &+ F_2(p,T)(1-2x)^2 + \cdots \right], \end{split} \tag{14}$$

where  $F_i(p,T)$  (i = 1,N) are the functions of temperature and pressure only. These functions are responsible for the change of the shape of concentration dependence of  $\Delta\lambda(T,p,x)$  with Tand p (see Figs. 17 and 18). Equation (14) is the general form of the Redlich–Kister type expansion for excess thermodynamic properties of a binary mixture. In practice, usually the first two terms of the expansion (14) are enough to accurately represent any experimental excess thermodynamic property (excess molar volume, enthalpy, heat capacity) of mixtures. In this work, we used relation (14) for thermal conductivity differences.

We applied Eqs. (13) and (14) to the present measured thermal conductivity data. Various functional forms of  $F_i(p,T)$  in Eq. (14) were examined. We first explored Tait-type expression for the function of  $F_i(p,T)$ ; Tait-type equations were successfully used previously to fit the experimental



Fig. 15 – Measured thermal conductivities of ammonia + water mixtures as a function of density at selected isobarisopleths. •, p = 5.066 MPa;  $\Box$ , p = 10.133 MPa;  $\circ$ , p = 15.199 MPa;  $\blacksquare$ , p = 20.265 MPa. Dashed lines are smoothed data.



Fig. 16 – Thermal conductivity difference for ammonia + water mixture at selected isotherm-isobars as a function of concentration.  $\bullet$ , p = 5.066 MPa;  $\Box$ , p = 10.133 MPa;  $\circ$ , p = 15.199 MPa;  $\blacksquare$ , p = 20.265 MPa. Solid lines are calculated from correlation (Eqs. (17) and (18)).



Fig. 17 – Thermal conductivity difference for ammonia + water mixtures at selected isobar-isotherm as a function of concentration.  $\blacksquare$ , T = 303.15 K;  $\circ$ , T = 313.15 K;  $\bullet$ , T = 323.15 K;  $\Box$ , T = 343.15 K;  $\times$ , T = 353.15 K. Solid lines are calculated from correlation (Eqs. (17) and (18)).



Fig. 18 – Thermal conductivity of a series of aqueous alcohol solutions as a function of composition at a selected temperature of 300 K and at two isobars of 0.101 MPa (left) and 5.0 MPa (right) reported by Stephan and Heckenberger (1988) together with the present results for ammonia + water mixture.  $\blacksquare$ , 1-propanol + water;  $\circ$ , methanol + water;  $\bullet$ , ethanol + water;  $\Box$ , ammonia + water (this work).

thermodynamic properties (*p*VT, speed of sound) (Assael et al., 1994; Dymond and Malhotra, 1988; Gardas et al., 2007; Ihmels and Gmehling, 2001) and transport properties (viscosity and thermal conductivity, see for example (Ganiev et al., 1989)) of pure fluids and fluid mixtures. These equations are of the general form

$$\Delta\lambda(\mathbf{T}, \mathbf{p}, \mathbf{x}) = \Delta\lambda(\mathbf{T}, \mathbf{p}_0, \mathbf{x}) \left[ 1 - A \ln \left| \frac{\mathbf{B} + \mathbf{p}}{\mathbf{B} + \mathbf{p}_0} \right| \right], \tag{15}$$

$$\Delta\lambda_0(T, p_0, x) = x(1 - x)[A_0 + A_1(1 - 2x)], \tag{16}$$



Fig. 19 – Comparison of the present experimental thermal conductivity data for ammonia + water mixtures with reported literature data at atmospheric pressure and various temperatures. •, Riedel (1951) (T = 293.15 K);  $\Box$ , this work (T = 293.15 K);  $\circ$ , this work (T = 302.15 K);  $\blacksquare$ , Lees (1898) (T = 302.15 K);  $\times$ , Braune (1937) (T = 291.15 K). Dashed line is smoothed data of Riedel.

where  $p_0$  is a reference pressure. Typically a reference pressure of 0.1 MPa is used, however at this pressure and some of our experimental temperatures, water is liquid while ammonia is in the gas phase. For this reason we selected a reference pressure of 5.066 MPa since at this pressure and our experimental conditions both ammonia and water are in the liquid phase. In Eqs. (15) and (16) A, B, A<sub>0</sub> and A<sub>1</sub> are parameters that may be constants, or functions of temperature and composition. We investigated different cases where the A parameters were functions of temperature and B was a constant, and also a related form used by Kawamata et al. (1988) to represent the experimental thermal conductivity data for aqueous LiBr solutions over wide T, p, and concentration ranges. The results for the best Tait-type model we found are given in Table 9. The Tait-type model represents the present thermal conductivity data to 6.6% at a 95% confidence level, with an AAD = 2.6% and a bias of -0.1%.

We then explored a totally different approach, using symbolic regression (Schmidt and Lipson, 2009). In this approach, the functional form is not known ahead of time; the symbolic regression algorithm is used to find the functional form by using a set of operators  $\{+,-,*,/,Exp,\}$  and operands {constant, T,  $\rho$ }. This method has been used to obtain functional forms for viscosity correlations (Muzny et al., submitted for publication; Shokir and Dmour, 2009) but we are unaware of its use for thermal conductivity formulations. The symbolic regression process gives a series of results, where there is a trade-off between complexity of the function and the error metric for the fit. We selected a form that is reasonably simple yet still provides good agreement with the experimental data. The resulting correlation is

$$\Delta\lambda(T, p, x) = x(1 - x) \left[ 108T_r p_r + 48.64T_r^2 - 16.54T_r - 35.36p_r + F_1 \right]$$
(17)

Table 9 — Summary of two models used for correlation of the temperature, pressure, and concentration dependencies of liquid ammonia + water mixtures.						
Functional form of the correlation model <sup>a</sup>	AAD, %	BIAS, %	RMS, %			
Tait-type model	2.6	-0.1	3.3			
$\Delta\lambda(\mathbf{T}, \mathbf{p}, \mathbf{x}) = \Delta\lambda(\mathbf{T}, \mathbf{p}_0, \mathbf{x}) \left[ 1 - \mathrm{Aln}  \frac{\mathbf{B} + \mathbf{p}}{\mathbf{B} + \mathbf{p}_0}  \right]$						
$\Delta\lambda(T,p_0,x) = x(1-x)[A_0 + A_1(1-2x)]$						
$A_0 = 2.28244 - 0.03134725T + 7.251 \times 10^{-5} T^2$						
$A_1 = 1.333165 - 0.00412631T$						
$A = -0.11753737 + 0.00137045 x T^{0.8}$						
B = -0.10101664						
Model obtained from symbolic regression	2.5	-0.5	3.3			
$\Delta\lambda(T,p,x) = x(1-x)[108T_rp_r + 48.64T_r^2 - 16.54T_r - 35.36p_r + F_1]$						
$F_1 = (1-2x)(85.13p_r^2 + 230.3exp(-16.88T_r - 1216p_r))$						
a Where $T_{x} = T/1000$ ; $n_{x} = n/1000$ ; $n_{0} = 5.066$ MPa is the reference press	sure.					

 $F_1 = (1 - 2x)(85.13p_r^2 + 230.3\exp(-16.88T_r - 1216p_r))$ (18)

where the reduced temperature is  $T_r = T/1000$  and the reduced pressure is  $p_r = p/1000$  with T in K, p in MPa, and the thermal conductivity difference  $\Delta\lambda$  is in W m<sup>-1</sup> K<sup>-1</sup>. As indicated in Table 9, this model represents the present thermal conductivity data to 6.6% at a 95% confidence level, with an AAD = 2.5% and a bias of -0.5%. Fig. 20 presents the deviation plot between the present experimental data and the values calculated from the model obtained from symbolic regression Eqs. (17) and (18) and the Tait-type model given in Table 9. Both models represent the data equally well. Both are valid for the calculation of



Fig. 20 – Percentage deviations,  $\delta \lambda = 100[(\lambda^{cal} - \lambda^{exp})/\lambda^{exp}]$ , of the measured thermal conductivities for ammonia + water mixture from the values calculated with the two models in Table 9.

the liquid-phase thermal conductivity of ammonia + water mixtures over the entire concentration range for temperatures from 278 K to 356 K and at pressures up to 20 MPa.

Finally, for the special case of atmospheric pressure, we obtained the correlation

$$\begin{split} \lambda(T,x,p=0.1) &= 0.0922 + 1.717 T_r + 1.237 x^2 - x^3 - 0.33 x \\ &- 1.631 x T_r, \end{split} \label{eq:lambda}$$

where the reduced temperature  $T_r = T/1000$ . This equation reproduces the present thermal conductivity data for ammonia + water mixtures with an AAD = 0.7% over the entire concentration range and at temperatures from 283 K to 323 K.

## 5. Conclusions

The thermal conductivity of liquid ammonia + water mixtures and their pure components has been measured for the temperature range from 278 K to 356 K at pressures up to 20 MPa using the steady-state hot-wire method for ten compositions in the entire concentration range from 0 to 1.0 mole fraction of ammonia, namely: 0.0, 0.1905, 0.2683, 0.3002, 0.4990, 0.5030, 0.6704, 0.7832, 0.9178, and 1.0 mole fraction of ammonia. Measured values of thermal conductivity for the mixtures were used to calculate the thermal conductivity deviations from linear mixture values using reference correlation equations for the pure components (water and ammonia) as a function of T, p, and concentration. Derived values of the thermal conductivity difference  $\Delta \lambda^{\exp}(T,p,x)$  (Eq. (11)), for ammonia + water mixtures are negative at all measured temperatures, pressures, and concentrations, except at temperatures above 343 K. The thermal conductivity difference minimum is found at a concentration of about 0.5 mole fraction of ammonia. The measured values of thermal conductivity were used to develop two different forms of correlation models for the mixture. The models reproduce the thermal conductivity data of the ammonia + water mixture within 6.6% at a 95% confidence level over the entire T, p, and concentrations ranges of the present measurements.

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#### REFERENCES

- Abdulagatov, I.M., Assael, M.J., 2008. In: Valayshko, V.M. (Ed.), Hydrothermal Properties of Materials. John Wiley & Sons, London, pp. 249–271 Chapter 6.
- Amano, Y., 1999. Effectiveness of an ammonia-water mixture turbine system to hot water heat source. In: Proc. 1999 Int. Joint Power Generation Conf.-ICOPE ASME/JSME PWR, vol. 34, pp. 67–73.
- Amano, Y., Suzuki, T., Hashizume, T., Akiba, M., Tanzawa, Y., Usui, A., 2000. A hybrid power generation and refrigeration cycle with ammonia-water mixture, In Proc. 2000 Int. Joint Power Generation Conference, Miami Beach, FL, July 23–26, IJPGC2000-1'5058, pp. 1–6.
- Assael, M.J., Nieto de Castro, C.A., Roder, H.M., Wakeham, W.A., 1991. In: Wakeham, W.A., Nagashima, A., Sengers, J.V. (Eds.), 1991. Measurements of the Transport Properties of Fluids, vol. III. Blackwell Scientific Publ., Oxford, pp. 161–194 Chapter 7.
- Assael, M.J., Dymond, J.H., Exadaktilou, D., 1994. An improved representation for n-alkane liquid densities. Int. J. Thermophys. 15, 155–164.
- Assael, M.J., Mylona, S.K., Huber, M.L., Perkins, R.A., 2012. Reference correlation of the thermal conductivity of toluene from the triple point to 1000 K and up to 1000 MPa. J. Phys. Chem. Ref. Data 41, 023101–023112.
- Baranov, A.N., 1997. The investigation of ammonia + water gas and liquid mixture properties. In: Friend, D.G., Haynes, W.M. (Eds.), Report on the Workshop on Thermophysical Properties of Ammonia/Water Mixtures, NISTIR-5059. Boulder CO.
- Braune, B., 1937. Dissertation Universität Leipzig.
- Brykov, B.P., Mukhamedzyanov, G.K., Usmanov, A.G., 1970. Experimental study of the thermal conductivity of organic liquids at low temperatures. Inzh. Fiz. Zhurnal 18, 82–89.
- Conde-Petit, M., 2006. Thermophysical Properties of NH<sub>3</sub> + H<sub>2</sub>O Mixtures for the Industrial Design of Absorption Refrigeration Equipment. Formulation for Industrial Use. M. Conde Engineering, Zurich, Switzerland.
- Dejfors, A.S., Thorin, E., Svedberg, G., 1998. Ammonia-water power cycles for direct-fired cogeneration applications. Energy Convers. Manage. 39, 1675–1681.
- Dymond, J.H., Malhotra, R., 1988. The Tait equation 100 years on. Int. J. Thermophys. 8, 941–951.
- Ganiev, Y., Musoyan, M.O., Rastorguev, Y.V., Grigor'ev, B.A., 1989.
   In: Pichal, M., Shifner, O. (Eds.), Proc. 11th Int. Conf. Prop.
   Water and Steam. Hemisphere, NY, pp. 132–139.
- Gardas, R.L., Freire, M.G., Carvalho, P.J., Marrucho, I.M., Fonseca, I.M.A., Ferreira, A.G.M., Coutinho, J.A.P., 2007. Highpressure densities and derived thermodynamic properties of imidazolium-based ionic liquids. J. Chem. Eng. Data 52, 80–88.
- Gawlik, K., Hassani, V., 1998. Advanced binary cycles: optimum working fluids. In: Geothermal Resources Council Annual Meeting, San Diego, CA, Sept. 20–23, pp. 1–7.
- Hassani, V., Dickens, J., Parent, Y., 2001. Ammonia/Water Condensation Test: Plate-Fin Heat Exchanger (Absorber/ Cooler). NREL, Golden CO.

- Huber, M.L., Perkins, R.A., Friend, D.G., Sengers, J.V., Assael, M.J., Metaxa, I.N., Miyagawa, K., Hellmann, R., Vogel, E., 2012. New international formulation for the thermal conductivity of H<sub>2</sub>O. J. Phys. Chem. Ref. Data 41 (033102), 1–23.
- Ihmels, E.C., Gmehling, J., 2001. Densities of toluene, carbon dioxide, carbonyl sulfide, and hydrogen sulfide over a wide temperature and pressure range in the sub- and supercritical state. Ind. Eng. Chem. Res. 40, 4470–4477.
- ISO, 1993. Guide to the Expression of Uncertainty in Measurement. ISO, Geneva, Switzerland, ISBN 92-67-10188-9.
- Jonsson, M., 2003. Advanced Power Cycles with Mixtures as the Working Fluids. RIT, Stockholm Sweden.
- Jonsson, M., Thorin, E., Svedberg, G., 1994. Gas engine bottoming cycles with ammonia-water mixtures as working fluid. In: Proc. Florence World Energy Research Symp., Florence, Italy, July 6–8, pp. 1–11.
- Kalina, A.I., Leibowitz, H.M., 1989. Application of the Kalina cycle technology to geothermal power generation. Geotherm. Res. Counc. Trans. 13, 605–611.
- Kawamata, K., Nagasaka, Y., Nagashima, A., 1988. Measurements of the thermal conductivity of aqueous LiBr solutions at pressures up to 40 MPa. Int. J. Thermophys. 9, 317–329.
- Lees, C.E., 1898. On the thermal conductivities of single and mixture solids and liquids and their variation with temperature. Phil. Trans. R. Soc. Lond. A 191, 399–440.
- Lemmon, E.W., Jacobsen, R.T., 2004. Viscosity and thermal conductivity equations for nitrogen, oxygen, argon, and air. Int. J. Thermophys. 25, 21–69.
- Mukhamedzyanov, G.K., Usmanov, A.G., 1971. Thermal Conductivity Liquid Organic Compounds. Chemistry Publ., Leningrad.
- Mukhamedzyanov, I.K., Mukhamedzyanov, G.K., Usmanov, A.G., 1968. Thermal conductivity of organic liquids at high pressures. Trans. Kazan State Tech. Inst. 37, 52–63.
- Mukhamedzyanov, I.K., Mukhamedzyanov, G.K., Usmanov, A.G., 1971. Thermal conductivity of liquid saturated alcohols at pressures up to 2500 bar. Trans. Kazan State Tech. Inst. 44, 57–67.
- Muzny, C.D., Huber, M.L., Kazakov, A.F. Correlation for the viscosity of normal hydrogen obtained from symbolic regression. J. Chem. Eng. Data, submitted for publication.
- Olsson, E.K., Thorin, E., Dejfors, A.S., Svedberg, G., 1994. Kalina cycles for power generation from industrial waste heat. In: Proc. Florence World Energy Research Symp., Florence, Italy, July 6–8, pp. 39–49.
- Park, Y.M., Sonntag, R.E., 1990. A preliminary study of the Kalina power cycle in connection with a combined cycle system. Int. J. Energy Res. 14, 153–162.
- Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001. The Properties of Gases and Liquids, fifth ed. McGraw-Hill, New York.
- Popov, V.N., 1958. Experimental study thermophysical properties of liquid fuels, PhD Thesis. Moscow Power Institute, Moscow.
- Riedel, L., 1951. Die Wärmeleitfähigkeit von wäßrigen Lösungen starker Elektrolyte. Chem. Ing. Tech. 23, 59–64.
- Schiebener, P., Straub, J., Levelt Sengers, J.M.H., Gallagher, J.S., 1990. Refractive index of water and steam as function of wavelength, temperature and density. J. Phys. Chem. Ref. Data 19, 677–717.
- Schmidt, M., Lipson, H., 2009. Distilling free-form natural laws from experimental data. Science 324, 81–85. Eureqa 80.97 Beta. www.nutonian.com.
- Shokir, E.-M.E.M., Dmour, H.N., 2009. Genetic Programming (GP)based model for the viscosity of pure and hydrocarbon gas mixtures. Energy Fuels 23, 3632–3636.
- Stephan, K., Heckenberger, T., 1988. Thermal Conductivity and Viscosity Data of Fluid Mixtures, vol. X. DECHEMA, Germany. Part 1, p. 448.

- Thorin, E., 1998. Ammonia-water Mixtures as Working Fluid in Power Cycles. RIT, Stockholm, Sweden.
- Thorin, E., 2000. Power Cycles with Ammonia-water Mixtures as Working Fluid. Analysis of Different Applications and the Influence of Thermophysical Properties. RIT, Stockholm, Sweden.
- Thorin, E., Dejfors, A.S., Svedberg, G., 1998. Thermodynamic properties of ammonia water mixtures for power cycles. Int. J. Thermophys. 19, 501–510.
- Tillner-Roth, R., Friend, D.G., 1998. Helmholtz free energy formulation of the thermodynamic properties of the mixture {water plus ammonia}. J. Phys. Chem. Ref. Data 27, 63–96.
- Tsederberg, N.V., 1963. Thermal Conductivity of Gases and Liquids. Nauka, Moscow.
- Tufeu, R., Ivanov, D.Y., Garrabos, Y., Le Neindre, B., 1984. Thermal conductivity of ammonia in a large temperature and pressure

range including the critical region. Ber. Bunsenges. Phys. Chem. 88, 422–427.

- Vargaftik, N.B., 1951. Thermal conductivity of compressed gases and liquids, PhD Thesis. All Union Thermotechnical Institute, Moscow.
- Wagner, W., Pruß, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31, 387–535.
- Wall, G., Chuang, C.-C., Ishida, M., 2000. In: Bajura, R.A., von Spakovsky, M.R., Geskin, E.S. (Eds.), 2000. Analysis and Design of Energy Systems: Analysis of Industrial Processes, vol. 10-3. AES, ASME, pp. 73–77.
- Zaripov, Z.I., Mukhamedzyanov, G.K., 2008. Thermophysical Properties of Liquids and Liquid Mixtures. Kazan State Technological Institute, Kazan.