



Universidade de Aveiro Departamento de Química
Ano 2009

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Gonçalves Pinto
Varanda**

**Condutividade Térmica de Misturas de Gases para
Espumas Rígidas de Poliuretano**

**Thermal Conductivity of Gas Mixtures for
Polyurethane Rigid Foams**



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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química realizada sob a orientação científica do Prof. Dr. Ralf Dohrn, Director da Divisão de Propriedades Termofísicas da Bayer AG e da Prof.^a Dr.^a Isabel Marrucho, Professora auxiliar do Departamento de Química da Universidade de Aveiro

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palavras-chave

Agente Expansor; Condutividade Térmica; Método Transiente do Fio Aquecido, Mistura de Gases; Modelo Generalizado de Wassiljewa.

resumo

A temática do presente trabalho insere-se na procura de agentes expansores mais eficientes para espumas de poliuretano. Nesta perspectiva, são apresentadas medições da condutividade térmica de misturas binárias de gases contendo X3 e um alceno, utilizando o Método Transiente do fio Aquecido.

A calibração do aparelho foi efectuada através da medição da condutividade térmica de azoto, por comparação com valores da literatura (NIST). Foram estudados dois sistemas binários para possível aplicação como agentes expansores: X1 + X3 e X2 + X3. Foram realizadas medidas de condutividade térmica em três misturas de composições diferentes de cada um dos referidos sistemas na gama de pressão entre 1 e 5 bar e temperaturas entre 300 e 400K.

Para a correlação dos resultados experimentais foi utilizado o Modelo Generalizado de Wassiljewa, tendo sido também estudada a dependência do parâmetro ϵ com a pressão e temperatura. Concluiu-se que o Modelo Generalizado de Wassiljewa apresenta um bom ajuste aos valores experimentais da condutividade térmica de ambos os sistemas estudados, tendo-se verificado que o parâmetro ϵ apresenta sempre um valor próximo da unidade.

O sistema X2 + X3 é aquele que apresenta valores condutividade térmica mais promissores para aplicação como agente expansor de espumas de poliuretano.

keywords

Blowing Agent; Extended Wassiljewa Model; GasMixture; Thermal Conductivity; Transient-Hot Wire Method.

abstract

The present work aims at finding a suitable, highly efficient blowing agent for polyurethane rigid foams. In this framework, measurements of the thermal conductivity of binary gas mixtures using the Transient Hot-wire Method are presented.

The calibration of the apparatus was performed using nitrogen and the results were compared with values from the literature (NIST). Two binary systems were studied as possible blowing agents: X1 + X3 and X2 + X3. Three different compositions were measured within a pressure range 1 to 5 bar and temperatures between 300 and 400K. The obtained thermal conductivity data was correlated using the Extended Wassiljewa Model and the dependence of the ϵ parameter with pressure and temperature was addressed. The Extended Wassiljewa model performs very well in the description of thermal conductivity of both systems and the ϵ parameter presents always a value close to unity.

In conclusion, the X2+ X3 system is the one that seem to be more promising for the proposed application.

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1. Introduction

Polyurethanes were an invention of Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany [1]. However, commercial production of flexible polyurethane foam, initially called *imitation swiss cheese* by the inventors, only began in 1954. The invention of these (flexible and rigid) foams was thanks to water accidentally introduced in the reaction mix. As soon realized, polyurethane foams are extremely versatile in terms of chemistry, processability and properties that are reflected in the large range of products with a wide variety of applications in many countries around the world. Flexible foams are the major market for PU's, followed by rigid PU foams [2].

Rigid polyurethane foam (PURF) is recognized as an outstanding material for different applications. It has a unique set of properties such as low thermal conductivity, low density, excellent dimensional stability, high strength-to-weight ratio, low moisture permeability and low water absorption that enables its application in household refrigerators, construction and industrial insulation, flotation in boats, life preservers, buoys, and other marine equipment [3]. The most important environmental characteristic of this foam is that it represents a large energy saving. In addition, the foam is robust and keeps up its performance in energy terms over many years. Taking into account the long lifetime of the foam, this property is the major contribution of these insulating foams to society.

Rigid Polyurethane foams are usually produced from two-component systems: component A contains polyol, including catalysts, stabilizers, and blowing agents, and component B is a polyisocyanate. Since the reaction between the diisocyanate and the diol is highly exothermic, it is possible to use inert, low-boiling liquids and/or water as blowing agents. Water reacts with the polyisocyanate to form carbon dioxide [4].

The high thermal efficiency of PURFs results from the combination of its chemical and structural characteristics and the thermal conductivity of the gas that fills its cells, the blowing agent. In fact, it has been showed that the gas trapped inside the cells is responsible for up to 60% of the total thermal insulation properties of the foam. The blowing agent has several roles in the production and lifetime of rigid polyurethane foam. In the foam manufacturing process its role as a processing aid includes viscosity reduction and aiding the flow of the reacting chemicals so that they can, for example, completely fill the cavity between the inner and outer walls of a refrigerator. During the exothermic reaction process, the blowing agent volatilizes: if it is a liquid it comes out of solution; if it is a gas it expands the foam by a factor of, typically, thirty times[5]. Finally, part of it remains in the foam cells to endow it with its characteristic high insulation value.

In order to perform these various functions there is a stringent specification for the “ideal” blowing agent. For optimum processing it should be soluble and stable in the liquid chemical reactants and have boiling point just above ambient temperature – in the range between 298.15 to 303.15K. It should also be non-flammable – an important characteristic for both the manufacturing and use stages. To give the foam optimum properties it should have very low gas thermal conductivity, low diffusivity through the foam matrix and low solubility in the plastic. This latter property, together with high vapor pressure in the foam cells gives an economic advantage of low practical density.

Until around 1995, the blowing agents selection of the PUR foams manufacturers was heavily based on CFC's, mainly CFC-11. However, due to the high Ozone Depletion Potential of this compound and within the Montreal Protocol, its use as blowing agent was abolished. From there, research on new blowing agents took two different paths, as North America's research focused mainly on HCFCs, which due to stricter regulations were later rejected as environmentally suitable blowing agents, and HFCs, which have zero Ozone Depletion Potential, while Europe focused mainly on hydrocarbons [6-10]. Halogen-free hydrocarbons, mainly pentanes, were considered the best alternatives in view of their environmental acceptability. The major drawback is their flammability[11]. Distilled water is one of the most widely used chemical-blowing agents. As was already mentioned, it reacts with diisocyanate generating gaseous carbon dioxide. The carbon

dioxide inflates the reactant mixture and a cellular structure is formed. When water is used as blowing agent, carbon dioxide is the by-product, producing a foam free of CFC. So, water is considered to be a very ecofriendly blowing agent in the preparation of PURF. However, there are some disadvantages of having water as a blowing agent: the system viscosity is high, the exothermicity is high while preparing the foam which may lead risk of fire and scorch the foam[3].

The present work focus the study of two blowing agent systems composed of binary mixtures of X3 and hydrocarbons, namely X1 or X2. All measurements were carried out using the Transient Hot Wire method, which is the IUPAC standard method for the determination of thermal conductivities of a gas [12]. These measurements were done for pressures up to 10 bar and for temperatures between 300K and 400 K.

2. Theoretical Basis

2.1. Thermal Conductivity Definition

Thermal conductivity of a fluid measures its propensity to dissipate energy when disturbed from equilibrium by the imposition of a temperature gradient. For isotropic fluids (fluids that have no preferential direction for heat conduction) the thermal conductivity coefficient, λ , is defined by the linear relationship known as Fourier's law (equation 2.1)[13],

$$\mathbf{q} = -\lambda \times \nabla T \quad \text{Equation 2.1}$$

Where \mathbf{q} represents the instantaneous heat flux, which corresponds to the heat rate per unit area, and λ is a proportionality constant called *thermal conductivity*. The minus sign is due to the fact that heat is transferred from the warm region to the cold region, direction in which the temperature decreases.

Thermal Conductivity, λ , is a physical property of a substance that depends on temperature and pressure. It measures the time rate of energy transfer by conduction when the material is perturbed from a state of equilibrium by the imposition of a temperature gradient. The SI units for thermal conductivity are Watt per meter per Kelvin ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

The effect of pressure on thermal conductivity can be divided in three different regions, very low pressure (below 10^{-3} bar), low or moderate pressure (from 10^{-3} to 10 bar) and high pressures (above the critical point). For the region of low temperatures, pressure has little effect on thermal conductivity as its values increase only 2% or less per bar for the majority of non polar gases. This behaviour is not observed in the high pressure region, where a small increase in pressure, raises substantially the values of thermal conductivity, especially in the proximity of the critical point, where λ values are quite sensitive to both



pressure and temperature[14]. The region of interest for this present work will be the second one, low or moderate pressures.

2.2. Thermal Conductivity Measurements

The methods usually used for the measurement of this transport property can be divided in two different categories, steady-state and transient methods [13]. In steady-state methods it is necessary to have an heat flux to maintain a temperature difference, constant in time, between two surfaces of the fluid. This kind of method is directly based on an integrated form of the Fourier's law (Equation 2.1) for steady conduction in a sample of fluid of specific geometry. The main limitation of steady-state methods is that special attention must be given to avoid a significant contribution from other forms of heat transfer, such as convection and radiation. This limitation is overcome by the second category of methods, the transient methods. The main aim of these techniques is the measurement of the temporal history of the fluid temperature as a result of a time-dependent perturbation, in the form of a heat flux, applied to a fluid initially in equilibrium. The thermal conductivity values are then obtained from a working equation relating the observed response of the fluid's temperature to the perturbation. The main advantage of this class of methods is the small measuring times required that avoids significant contribution of natural convection phenomena. This happens because the characteristic time for the acceleration of the fluid by buoyancy forces is much longer than the propagation time of a temperature wave originated by a strong and localised temperature gradient.

2.2.1. The Transient Hot-Wire Method

2.2.1.1. Ideal Model

The ideal model of the Transient Hot Wire Method assumes that the measuring instrument possesses an infinitely long, vertical, line source of heat. This source has zero heat capacity, infinite thermal conductivity and constant and radial heat dissipation. The ideal model also assumes that the fluid in which the heat source is immersed is infinite, isotropic and with physical properties independent of temperature [15].

The essential feature of the transient hot wire method is the precise determination of the transient temperature with a very thin metallic wire. This is determined from measurements of the resistance of the wire over a period of a few seconds, followed by the initiation of the heating cycle with a $\Delta T = (2.000 \pm 0.025)$ K. For cylindrical wires with radius r_0 , the ideal temperature rise ΔT on the surface of the wire can be calculated using Equation 2.2[15].

$$\Delta T_{id}(r_0, t) = \frac{q}{4\pi\lambda} \ln\left(\frac{4at}{r_0^2 C}\right) \quad \text{Equation 2.2}$$

where λ is the thermal conductivity at the temperature and density reference conditions, a is the thermal diffusivity, $a = \lambda / (\rho C_p)$, q is the heat flow through the wire, t is the time, and $C = \exp(\gamma) = 1.7811\dots$ is the exponential of Euler's constant γ .

Equation 2.2 is the fundamental working equation of the Transient Hot Wire Method. This equation allows the experimental determination of thermal conductivity, directly from the slope of the line obtained by plotting measured values of ΔT and $\ln t$.

2.2.1.2. Corrections to the Ideal Model of the Transient Hot Wire Method

Any practical implementation of the Transient Hot-Wire Method inevitably presents deviations from the ideal model. However, the success of this experimental method is due the fact that, by proper design, it is possible to construct an apparatus that matches closely the conditions and assumptions made by the ideal model and so making the deviations either negligible or very small. A summarized description of the ideal model conditions, possible deviations of experimental method and its corrections is presented in Table 2.1 and can be found in the available literature [6, 8-10, 12, 15-17].

Table 2.1 Ideal model conditions, possible deviations of the experimental method and its corrections. The type of corrections used for each kind of deviation is represented by a code: W (taken into account on the working equation), C (must use correction), D (minimize through proper design or adequate choice of parameters) and N (negligible or very small error)[18].

Correction	Ideal Model	Deviations	Code
1	Infinitesimal diameter of the wire, $r = 0$	Finite diameter, $r = r_b$	W
		Diameter not constant along the wire	C
2	Infinitely long wire without end effects	Finite wire with end effects	D
3	Infinite thermal conductivity of the wire	Finite thermal conductivity of the wire, $\lambda_w = \text{const}$	N
4	Wire with null heat capacity, $c_{p,w} = 0$	Wire with finite heat capacity, $c_{p,w} = \text{const}$	C
5	Infinite Fluid	Finite Fluid, effects at outer boundary	C
6	Continuous radial Temperature Profile	Temperature jump	N
7	Fluid with temperature independent physical properties	Fluid with temperature dependent physical properties	C
8	Pure heat conduction	Radial motion	N
		Free Convection	D
		Radiation	C

2.3. Empirical Models for Thermal Conductivity for Gas Mixtures

2.3.1. Wassiljewa Model

The thermal conductivity of a gas mixture is not usually a linear function of the mixture molar composition, meaning that the mixing rules usually used for the calculation of thermophysical properties of gases do not work for thermal conductivity. Several other mixing rules were proposed to calculate the thermal conductivity of gas mixtures. Among the most popular ones are the Wassiljewa mixing rules and the Wassiljewa mixing rules modified by Mason and Saxena [14, 19].

The Wassiljewa mixing rules state that the thermal conductivity of a gas mixture results from a combination of the pure components thermal conductivity in the form of equation 2.3.

$$\lambda_m = \frac{\sum_{i=1}^n y_i \lambda_i}{\sum_{j=1}^n y_j A_{ij}} \quad \text{Equation 2.3}$$

where λ_m is the thermal conductivity of the gas mixture and λ_i is the thermal conductivity of the pure component i , y_i and y_j are the molar fractions of components i and j , respectively and A_{ij} is the Wassiljewa function. For a binary mixture this equation can be simplified to equation 2.4.

$$\lambda_m = \frac{y_1 \lambda_1}{y_1 + y_2 A_{12}} + \frac{y_2 \lambda_2}{y_2 + y_1 A_{21}} \quad \text{Equation 2.4}$$

The main difference between the Wassiljewa mixing rules, proposed by Alexandra Wassiljewa in 1904, and the alternative proposed by Mason and Saxena is the calculation of Wassiljewa function, A_{ij} [14, 19]. The function derived by the first author for a binary mixture is shown in equation 2.5 and 2.6 while the general form of Wassiljewa function proposed by Mason and Saxena is presented in equation 2.7.



$$A_{ij} = \frac{1}{\sqrt{2}} \left(\frac{s_i + s_j}{2s_i} \right)^2 \sqrt{\frac{m_i + m_j}{m_j}} \quad \text{Equation 2.5}$$

$$A_{ji} = \frac{1}{\sqrt{2}} \left(\frac{s_i + s_j}{2s_j} \right)^2 \sqrt{\frac{m_i + m_j}{m_i}} \quad \text{Equation 2.6}$$

$$A_{ij} = \frac{\varepsilon \left[1 + \left(\frac{\lambda_{tri}}{\lambda_{tj}} \right)^{\frac{1}{2}} \left(\frac{M_i}{M_j} \right)^{\frac{1}{4}} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{\frac{1}{2}}} \quad \text{Equation 2.7}$$

where s_1 and s_2 are the molecules diameters (in meters), m_1 and m_2 are the molecules mass (in kg), M is the molecular weight (in g.mol⁻¹), λ_{tr} is the monatomic value of thermal conductivity and ε is a numerical constant close to unit.

The Wassiljewa method modified by Mason and Saxena (Equation 2.7) is usually associated with the Roy and Thodos equation[14, 19] (Equation 2.8), that allows the calculation of the monatomic thermal conductivities ratio as a function of reduced temperatures and critical properties of the components. .

$$\frac{\lambda_{tri}}{\lambda_{tj}} = \frac{\Gamma_i \left[e^{0.046T_{ri}} - e^{-0.241T_{ri}} \right]}{\Gamma_j \left[e^{0.046T_{rj}} - e^{-0.2412T_{rj}} \right]} \quad \text{Equation 2.8}$$

$$\Gamma = 210 \left(\frac{T_c M^3}{P_c^4} \right)^{\frac{1}{6}} \quad \text{Equation 2.9}$$

2.4. Extended Wassiljewa Model for Gas Mixtures

The Mason and Saxena modifications of the Wassiljewa function initially derived by Alexandra Wassiljewa introduced a new constant, ϵ , that is obtained by fitting of thermal conductivity experimental data. These authors, as well as other authors in literature[19], proposed that this constant should be close to unit and characteristic of each system, meaning that it should be constant for all compositions, temperatures and pressures of a mixture. In an attempt to develop a deeper understanding of the influence of ϵ in the mixture thermal conductivity calculation by Wassiljewa based methods, Fonseca[8] developed a new and simple mathematical model (Equation 2.10) that allows the calculation of ϵ for any temperature and pressure conditions

$$\epsilon = a.T^b \quad \text{Equation 2.10}$$

where a and b can be written as a pressure dependent two parameter equation each. The factor a will be given by as exponential function of pressure, whereas factor b will be described by a linear function. Replacing the two functions on equation 2.10, a new equation, which relates ϵ with temperature and pressure, is obtained (Equation 2.11)

$$\epsilon = A_1 e^{A_2 P} T^{A_3 P + A_4} \quad \text{Equation 2.11}$$

The values of the four parameters A_1 , A_2 , A_3 and A_4 are obtained by fitting the ϵ obtained from the application of the Wassiljewa method modified by Mason and Saxena to equation 2.11. In this way, if parameters in equation 2.11 are obtained for a specific mixture it is possible predict thermal conductivity values for that mixture at other temperature and pressure conditions.

3. Gas thermal conductivity apparatus

In the Figure 3.1 a schematic representation of the apparatus used in this work for gas thermal conductivity measurements is presented. This apparatus was developed at the Thermophysical Property's Laboratory of Bayer AG in co-operation with the University of Stuttgart and uses the Transient Hot-Wire Method.

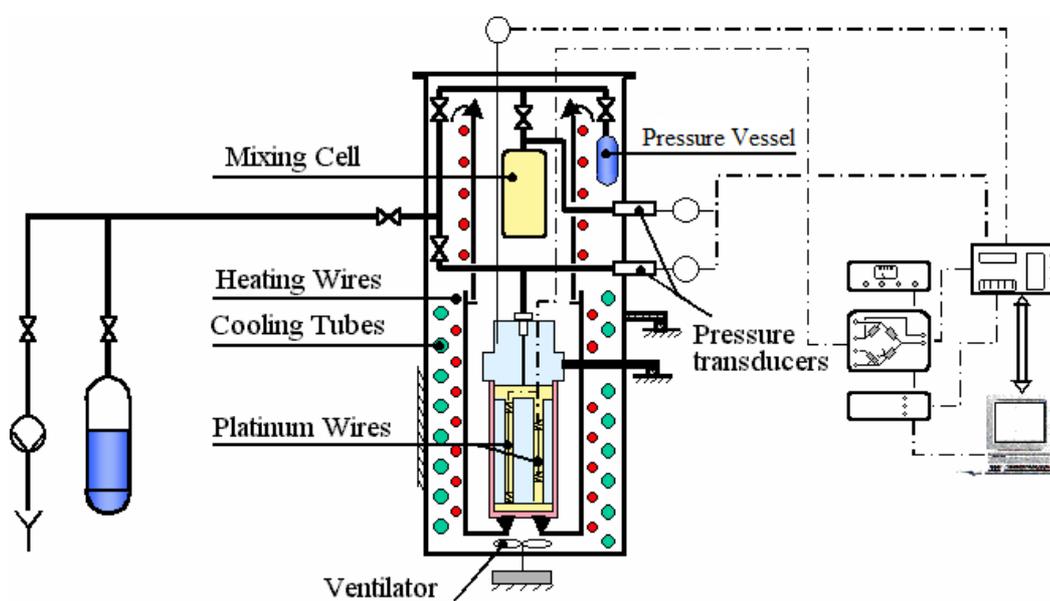


Figure 3.1 Schematic representation of the apparatus used in the present work to measure thermal conductivity.

In order to improve its performance, several modifications have been introduced in the apparatus over the years. Initially, to measure thermal conductivity of mixtures, the measuring cell was filled directly with the mixture previously prepared in a mixing cell. Due to problems with leaks and in order to avoid as much as possible related problems Fonseca [8] simplified the operation procedure: the mixing cell was taken out and the

mixture under study was prepared directly in the measuring cell. As will be explained later, this procedure is time consuming and so, in the present work, the use of the mixing cell was reintroduced along with some simplifications of the tubing and valves system in order to avoid leaks. In Figure 3.2 the new tubing system of the apparatus used in this work is depicted.

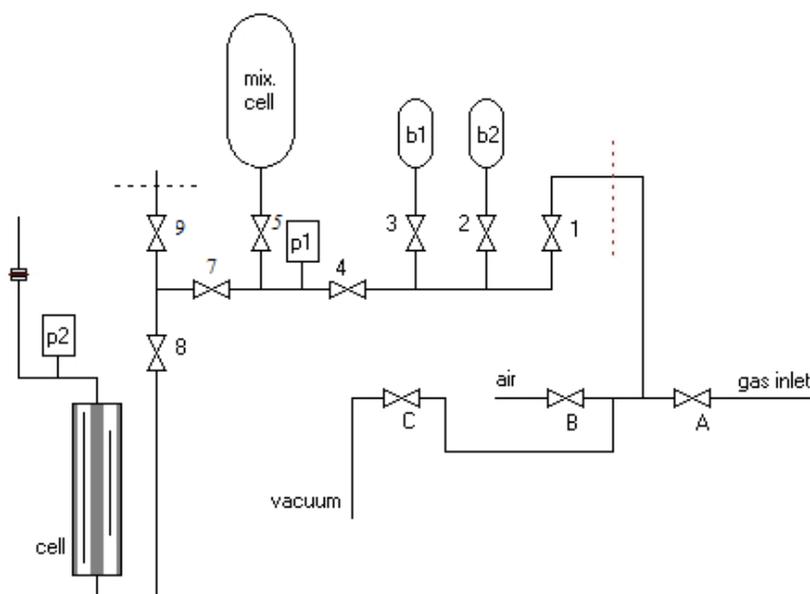


Figure 3.2 Schematic representation of the new tubing and valve system of the apparatus used in the present work. 1-8 are valves; A-C are valves; p1 and p2 are pressure transducers, b1 and b2 are pressure vessels.

This apparatus can be operated in a temperature range between 300 K and 500 K for pressures from 1 bar up to 18 bar. As a safety precaution the apparatus has a diaphragm that breaks for pressures above 20 bar. This diaphragm is directly connected to the measuring cell.

The apparatus used includes two pressure vessels (b1 and b2) where the fluids are initially transferred in order to obtain gas, the mixing cell where the mixture of the two gases are prepared, a measuring cell where the thermal conductivity measurements are performed, all the associated valves and tube system and the heating system (not depicted in Figure 3.2 but clearly seen in Figure 3.1). The electronic part is composed by a multimeter, a resistance decade, a power supply system, temperature controllers,

pressure sensors, as well data acquisition system. A photo of the apparatus itself is presented in Figure 3.3 and a photo of the electronic part is in Figure 3.4.



Figure 3.3 Photo of the apparatus.

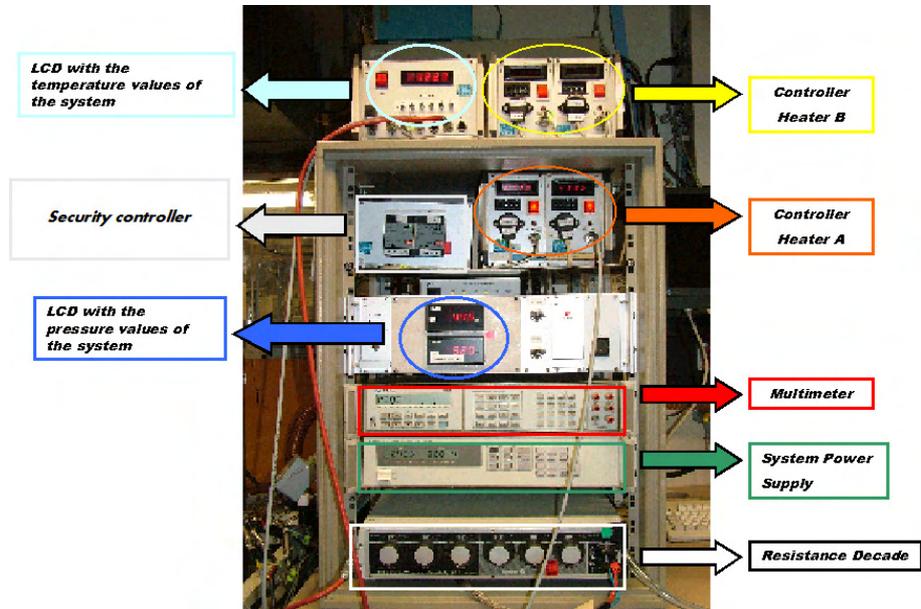


Figure 3.4 Photo of some of the electronic parts of the apparatus.

The pressure vessels, the mixing cell and the measuring cell are placed inside of a stainless steel thermostatic air bath composed of two concentric cylinders, both with 39 cm of inner diameter, and with a height of approximately 82 cm.

The air bath can be separated in a bottom part and an upper part. The bottom part contains a support for the measuring cell and around it there is an electrical resistance that is used as heat source. Under the support of the measuring cell there is a fan that provides a thermal homogeneity inside of the whole structure of the air bath. The bottom part is provided with a cooling system where cold water or liquid nitrogen can be used. In the upper part of the air bath another electrical resistance used as heat source.

3.1. The measuring cell

The measuring cell is placed inside of the thermostatic air bath, in the bottom part of the apparatus. It is made of stainless steel and has a cylindrical shape. Its external diameter is 48 mm and has a length of 200 mm. Inside of the measuring cell there are two parallel chambers with 16 mm of diameter each, where the two platinum wires of two different lengths and their supports can be found. The measuring cell photograph can be seen in the Figure 3.5. As it is possible to observe, it has a simple design that allows an easy assemble and disassemble. This fact is extremely important because the platinum wires inside of the cell are very thin (10 micro), and thus easy to break, and every time one wire breaks the cell has to be disassembled.

The two platinum wires have different lengths in order to minimize the end effects. The determination of the length of these wires is usually done together with the calibration of the apparatus. These two wires are welded with gold to a rigid and fixed wire made of platinum that gives them support and assures their positioning in the middle of the cell.

Whenever a new platinum wire is welded it is important to take into account the thermal expansion effects. Since the thermal expansion coefficient of stainless steel is approximately two times higher than that of platinum [8], a raise in temperature causes a larger dilatation in the stainless steel cell than in the platinum wires. In order to prevent

the breaking the wires, a system that allows the lower part of the cell to move was implemented. In this way, when the wires are being welded they should not be completely stretched, enabling their adjustment.



Figure 3.5 Photograph of the measuring cell used in the present work

The head of the cell has a ceramic sealing, which was found to be a better option than the previous Teflon® sealing. This sealing is made separately from the head of the cell and subsequently is welded to the upper part of the cell. Figure 3.6 shows a photo of the ceramic sealing of the upper part of the new cell. The ceramic sealing has four small metal tubes where the platinum wires are welded with gold. The outside part of the ceramic sealing is covered with metal and it is welded to the head of the cell.



Figure 3.6 Photograph of the head of the new cell used and the head sealing used on it.

However, this system still presents some drawbacks, such as less flexibility due of the welded platinum wires to the tubes in the ceramic sealing; if a wire breaks it is very difficult to replace it. Another aspect that must be taken in consideration is the protection of the upper part of the ceramic sealing from the liquids because otherwise the wires will be in electrical contact with the cell. When the platinum wires were being welded water condensation occurred. This happened because the gas used to weld the wires was hydrogen, and when it reacts with oxygen present in the air water is formed. Due to this fact, in the present work, the cell was placed inside of an oven for 24 hours.

The electrical connections between the platinum wires and the data acquisition system pass through the head of the cell to the outside where they connect to the electronic part of the apparatus.

3.2. Wheatstone Bridge- The most relevant electronic device

The most relevant electronic device in this apparatus is the Wheatstone bridge, which can be seen in Figure 3.7. Its function is to determine the variation of the wires potential with time and to calculate the temperature increase during the transient heating, enabling the determination of the thermal conductivity.

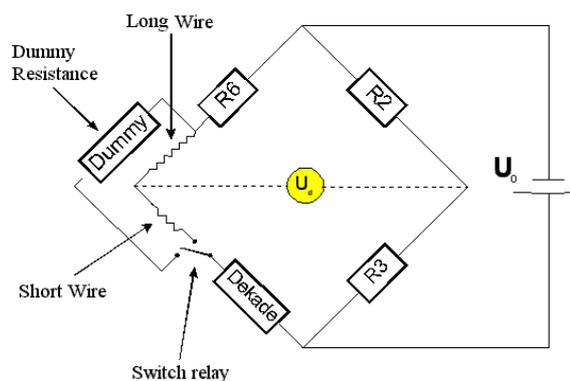


Figure 3.7 Schematic representation of the Wheatstone bridge.

All the electronic part of the apparatus is controlled by a program developed in C++ language called Lambda 2000 [20]. To run this program three different files are need. An output file (*.lda) which keeps all the information concerning each measuring data set, a file with the isobaric heat capacity for pressures between 1 bar and 20 bar (*.cp), property that is calculated with Aspen 2004.1 and a parameter data file (*.par) that includes, the Virial coefficients, the molar weight and the critical temperature of the mixture under study. It also contains the length of the platinum wires.

The program is also useful to verify the conditions inside the cell because, even after stabilized values of temperature and pressure, it is possible that the system is not stable enough to start the measurement. Furthermore, it enables the detection of convection inside the cell.

The identification of the stability state is done through the analysis of the graph $\Delta T=f(\ln t)$. In case of stability this graph is a straight line (Figure 3.8) and in case of non-stability state deviations from the linear behavior can be observed (Figure 3.8). Convection inside of the cell exists when a curve is obtained (Figure 3.8, right side).

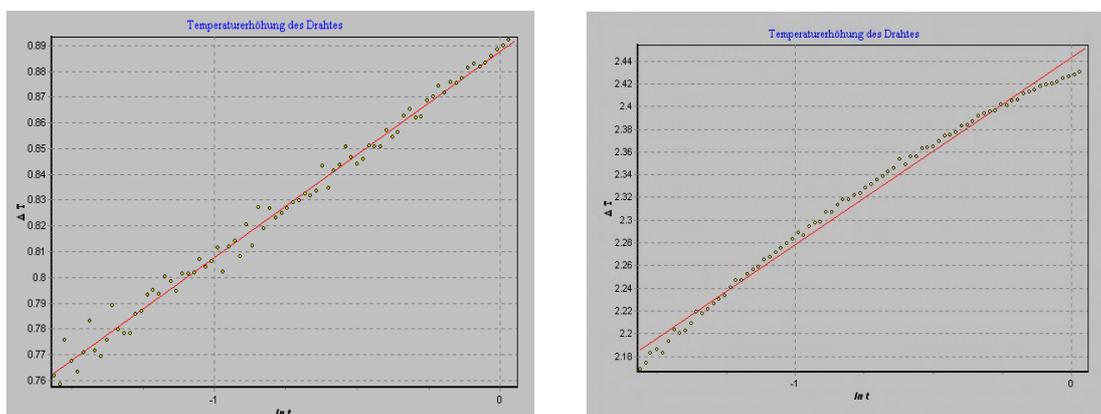


Figure 3.8 Left side: the equilibrium in the cell was reached; Right side: the cell presents a non-equilibrium state.

4. Experimental procedure

4.1. Cleaning the Apparatus

The first procedure that must be done is a leak test to the head sealing of the measuring cell. The cell is then placed inside of the apparatus and another air tightness test is done. All the leaks that are detected must be banned.

The next step is to clean the mixing cell, the measuring cell and all their associated piping system. For that purpose, vacuum must be done during a period of approximately one hour at 373.15K. It is important to do the vacuum during a long period at a high temperature to assure that all the thin pipes and all the connections that are in the piping system are clean. Then, the mixing cell and the measuring cell must be cleaned with the working gas(es) and the vacuum must be done again to assure the complete cleaning of the apparatus.

4.2. Degassing of the working fluids

If the fluid that will be studied is a gas at room temperature and atmospheric pressure, as for example nitrogen and carbon dioxide, it can be directly filled in from the bottle. If the fluid that will be studied is a liquid at room temperature and atmospheric pressure it must be compressed in one of the pressure vessels of the apparatus. So, it is extremely important to determine the maximum amount of liquid that the pressure vessel can contain, to avoid overpressure. After filling the pressure vessel with the fluid it is important to do its degassing to assure the total removal of all dissolved gases. The degassing is obtained doing cycles of cooling-vacuum-warming. Since in this procedure some mass can be loss an excess is weighted, relatively to the desired mass.

To fill the pressure vessel:

- The first step is to do vacuum in the pressure vessel and weighted it before filling.
- The maximum amount of liquid to be inserted in the pressure vessel must be calculated and it corresponds to the situation at which the pressure vessel has 90% of its volume filled at maximum working temperature, usually 373.15K for the mixtures under study.
- After filling the pressure vessel, it has to be weighted again in order to know exactly the mass of the compound.

Procedure to degass the fluid:

- The cooling step is done placing the pressure vessel in dry ice (solid carbon dioxide) for an half an hour.
- After cooling, vacuum is done for a few seconds (10 to 20 seconds) to remove any gas phase in contact with the solid phase inside of the pressure vessel.
- Then the warming step has to be done: the pressure vessel is placed in warm water to promote new liquid-gas equilibrium inside of the pressure vessel.
- At the end of each cycle the pressure vessel is carefully dried and weighted.
- To assure that the liquid is completed degassed the procedure described above must be repeated at least six times.

If at the end of the degassing process, the mass inside the pressure vessel is higher than the maximum calculated, the valve of the vessel must be open to release some gas; on contrary if the mass value is much smaller, more liquid must to be added to the vessel and all the degassing process repeated.

Finally, the pressure vessel is placed inside the apparatus and the desired temperature is set. Vacuum must be done again to clean the pipes that were exposed to the air during the placement of the pressure vessel.

4.3. Measurement procedure for thermal conductivity of pure gases

If the fluid in study is a gas than the measuring cell is filled with it directly from the bottle. If the fluid is a liquid it has to be firstly compressed in a pressure vessel (see Figure 3.2: b1 and b2) and then the measuring cell can be filled.

For fluids that present a high risk of condensation the maximum working pressure for each isotherm is only 80% of saturation pressure value at that temperature, in order to assure no condensation occurs.

The isotherms are obtained decreasing the pressure inside of the measuring cell within a range of interest, i.e. the measurement starts with the highest pressure. The decreasing of the pressure inside on the cell is achieved opening the valve 8 and 9 maintaining the valve 7 closed (see Figure 3.2, sub-chapter 3.1.).

After the determination of each isotherm, a new temperature is set. Usually it takes 5-7 hours for temperature stabilization.

4.4. Measurement procedure for thermal conductivity of mixtures

In this work, two procedures were used to measure thermal conductivity of mixtures: with and without the mixing cell. In both situations the mixture is prepared at the highest target temperature and pressure. Increments in temperature of approx. 10K and approx. 1 bar in pressure were used in this work.

With the mixing cell the measurements of each isotherm are carried out decreasing pressure by a fixed amount, as for pure components. Without the mixing cell the measurements are carried out by fixing the pressure (along isochors) and changing the temperature, within the temperature interval of interest. After measuring thermal conductivity at all desired temperatures some gas is released from the measuring cell, a new pressure is obtained, and the same process is repeated. Since the temperature of the gas inside the cell takes at least 5 hours to stabilize, this procedure is very time

consuming. Taking into account that the apparatus is not in a temperature-controlled room, the same set values for temperature controllers cannot be used from one experiment to the other. This leads to the fact that it is very difficult to measure isotherms without the mixing cell since there are always small fluctuations in temperature. This fact is very important for high temperatures where small differences in temperature lead to different thermal conductivity values. Another drawback associated to not using the mixing cell is that once the pressure inside the measuring cell is released, it is impossible to reproduce exactly the same composition inside of the measuring cell again.

The only case where the mixing cell cannot be used is for mixtures with high percentages of components with low vapor pressures. To use the mixing cell it is necessary to prepare a mixture with a total pressure of 20 bar so that three isotherms can be measured. Due to the low vapor pressure of X2, the mixture of X2 and X3 with high composition of X2 could not be measured with the mixing cell. For this system only the mixture with the lowest composition of X2 was prepared in the mixing cell. All the mixtures of X1 and X3 were measured using the mixing cell.

Before preparing the mixtures and in order to avoid possible condensation, VLE (vapor-liquid equilibrium) data needs to be checked, especially for mixtures with low vapor pressures components. The VLE data for the mixtures studied in the present work can be found in the appendix B.

Aspen 2004.1 was used to calculate the partial pressure of each component in the mixture. The calculation starts with the input of the pure component with the lowest vapor pressure at pressure and temperature working conditions since this component is the first one to be fed to the mixing/measuring cell. The partial pressure of the second component is determined by iterations, where the value of the total pressure is changed until the mixture density obtained matches the one previously calculated.

After preparing the mixture, its real composition and density needs to be calculated. The procedure is similar to the one used before but this time, to a fixed temperature and to

the total pressure of the mixture, the composition of the component with the lowest vapor pressure is changed until there is a convergence in these values.

For mixtures, every time that the valve 8 (Figure 3.2) is opened to release gas from the cell, condensation can occur due to adiabatic expansion of the gas mixture, the so-called Joule-Thompson effect. The condensation of the mixture leads to a changing in the gas mixture composition. To avoid the condensation, every time that the pressure is released the following procedure must be done: Maintaining valves 8 and 7 closed open valve 9 and vacuum is done. After evacuation, valve 9 must be closed, valve 7 must remain closed and valve 8 must be open during a short period in order to assure that the equilibrium is reached. Finally valve 8 must be closed and the described procedure must be repeated until the desired value of pressure is reached inside the cell.

During the present work Gas Chromatography (GC) analysis was used in order to evaluate if the mixtures composition changed between the initial measurement and the final one, due to eventual small leaks. It was concluded that the composition variation was negligible.

5. Presentation and Discussion of the Experimental Results

5.1. Wires calibration procedure

The first measurements with the new cell were done with nitrogen and it had the aim to calibrate the length of the platinum wires. This procedure is done whenever new wires are welded in the cell. Nitrogen was used because it is easy to find reliable data in the open literature. In the present work values from NIST[21] reference database were used. The calibration was done comparing the experimental values obtained for the nitrogen thermal conductivity with the reference values from NIST.

The sensor pressure was calibrated taking in account the procedure described in the appendix C.

The length of the wires was first measured with a cathetometer and the values were input in the lambda program. The initial values for the long and short wires were 0.11368m and 0.03836m, respectively. The first measurements were performed at 313.56 K. The isotherm that was obtained for this measurement is plotted in Figure 5.1.

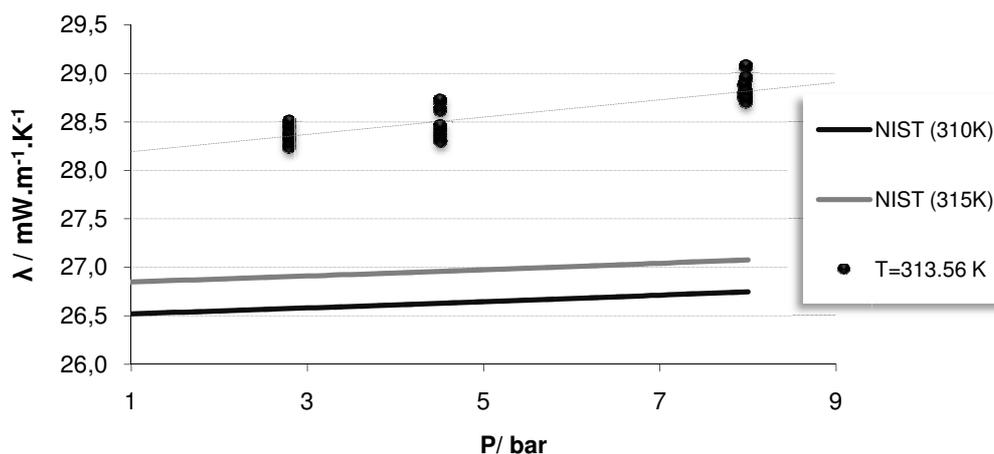


Figure 5.1 Thermal conductivity of nitrogen as function of pressure using length of the wires of 0.11368m and 0.03836m. Comparison with the values of NIST reference database.

Since the measured values for the thermal conductivity were too high, the length of the wires had to be modified. It was decided to change the length of the wires by more 5 % in each wire than the measured values with cathetometer. The isotherm that was obtained for this measurement is plotted in Figure 5.2.

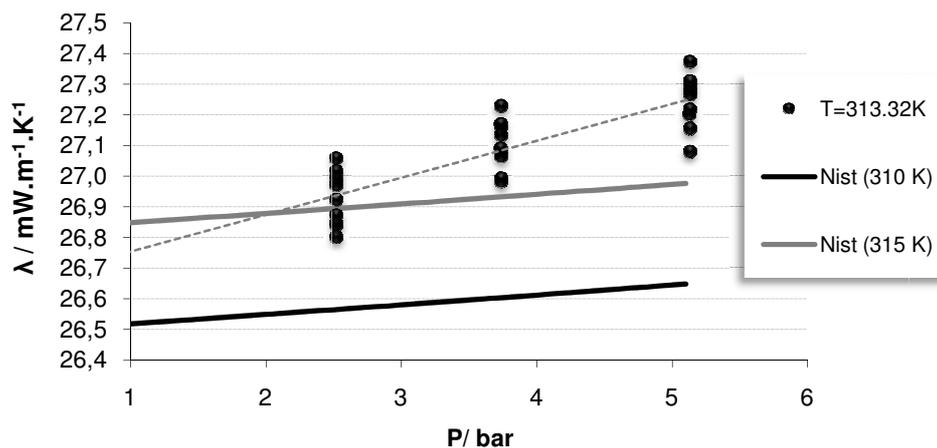


Figure 5.2 Thermal conductivity of nitrogen as function of pressure using length of the wires of 0.11936m and 0.040278m (5% more than the values measured with the cathetometer). Comparison with the values of NIST reference database.

As it can be seen in this figure, despite the fact that the extrapolation for 1 bar yielded a good value, the slope of the thermal conductivity as a function of pressure is too high. Taken into account that the short wire was less stretched than the long one inside of the cell, the length of the wires were changed in different proportions.

A good accuracy between experimental values and the NIST ones was found when the long wire length was 0.11823m (correction of around 4%) and the long wire length was 0.04124 mm (correction of around 7.5%). From this procedure it is possible to conclude that changing the length of the long wire it is possible manipulate the thermal conductivity value at 1 bar, and the pressure dependence of the thermal conductivity is related to the length of the short wire.

Just to confirm these values, two more temperatures were studied and good accuracy between experimental values and the NIST ones was once again verified, as it can be seen in Figure 5.3.

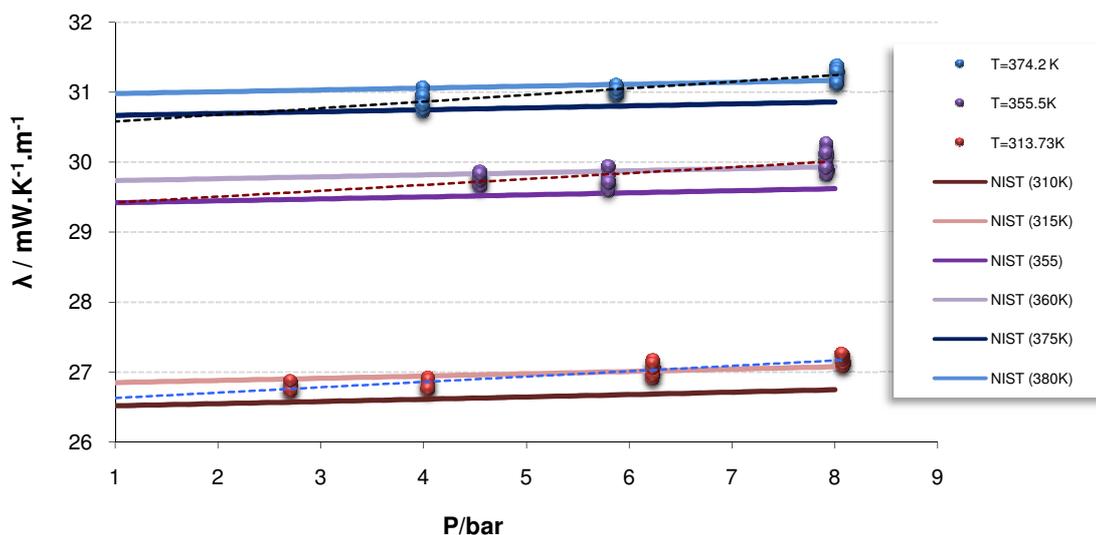


Figure 5.3 Thermal conductivity of nitrogen as function of pressure. Comparison with the values of NIST reference database.

Figure 5.3 shows that, for a fixed temperature, the thermal conductivity has a linear dependence with pressure.

$$\lambda \text{ (mW.m}^{-1}\text{.K}^{-1}\text{)} = a.P(\text{bar}) + b \quad \text{Equation 5.1}$$

where **a** is the slope and **b** is the intercept of the isotherm. The values of these constants for each isotherm for nitrogen are presented in Table 5.1. The magnitude of the slopes leads to the conclusion that the pressure dependence of the thermal conductivity is not very strong.

Table 5.1 Parameters a and b for nitrogen.

Temperature (K)	a	b
313.73	0.0763	26.554
355.52	0.0839	29.338
374.15	0.0941	30.489

Our interest is focused in the thermal conductivity values at 1 bar since this is pressure at each the foam finds its application. These values are obtained for each temperature by extrapolating the experimental results to 1 bar using Equation 5.1. It is important to note that due to operational conditions, the thermal conductivity values at 1 bar are always extrapolated from experimental data at higher pressures. The extrapolated values to 1 bar for nitrogen thermal conductivity can be seen in the Table 5.2.

Table 5.2 Thermal conductivity for nitrogen at 1 bar as a function of temperature.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹) → 1 bar
313.73	26.6303
355.52	29.4219
374.15	30.5831

In Figure 5.4 the extrapolated values are plotted together with the NIST values to 1 bar.

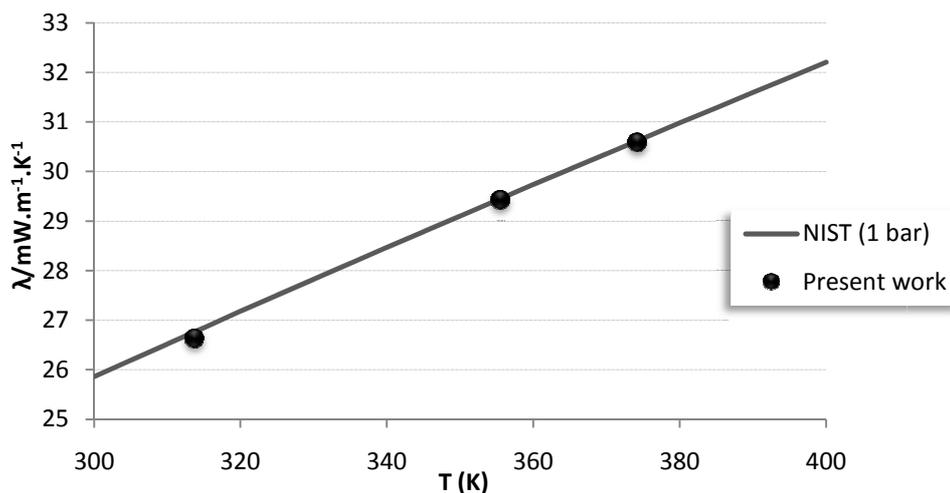


Figure 5.4 Extrapolation of Nitrogen's thermal conductivity to 1 bar. Comparison with NIST reference database.

This figure also shows that the obtained values for the calibration are in good agreement to what could be expected from NIST reference data for 310 and 315 K. It can also be seen that the thermal conductivity for nitrogen has a linear dependence with temperature (Equation 5.2).

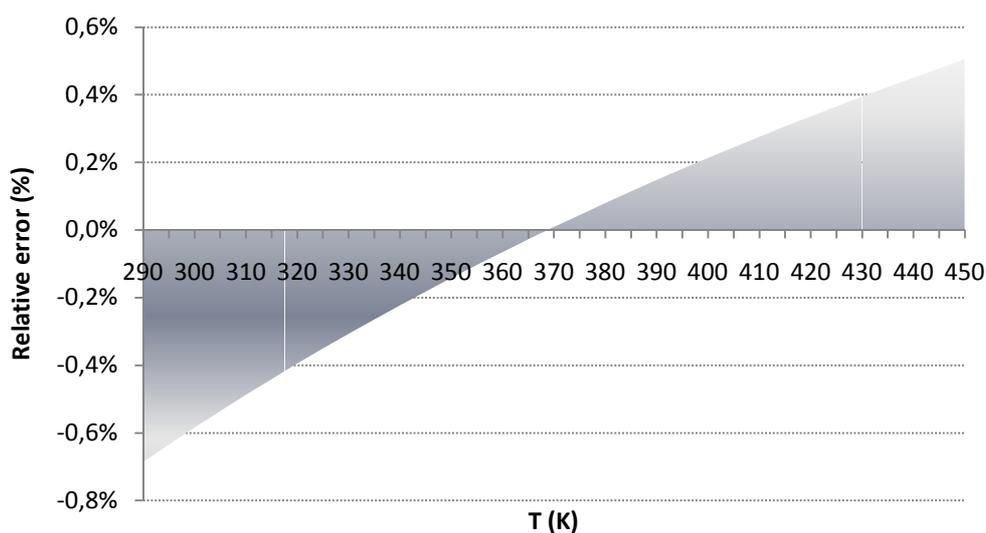
$$\lambda \text{ (mW.m}^{-1}\text{.K}^{-1}\text{)} = \alpha.T\text{(K)} + \beta \quad \text{Equation 5.2}$$

The parameters α and β obtained are presented in the Table 5.3, as well as the parameters obtained for the NIST reference values. Once again, comparing the values of the parameters obtained in the present work to the NIST values it can be concluded about feasibility of the calibration.

Table 5.3 Values for parameters α and β of Nitrogen at 1 bar obtained in the present work and NIST reference data values.

1 bar	α	β	R^2
Present Work	0.0656	6.0702	0.9997
NIST values	0.0634	6.8816	0.9998

To further verify the good agreement between the thermal conductivity values obtained in this work and NIST reference values, the relative deviations between them were calculated and are plotted in the Figure 5.5.

**Figure 5.5** Relative deviations between NIST reference thermal conductivity data and the values obtained in this work at 1 bar.

From this figure it can be concluded that the experimental values are within acceptable values. For the range of temperatures under study the deviations are always smaller than 0.6%. However, it can be seen that the deviations are not random and that the largest deviations occur at the lowest and the highest temperatures. This behavior is probably a

consequence of the chosen values for the length of the wires. However, it should be kept in mind that each data point is measured at least ten times, as depicted in Figure 5.3.

Yet, to further confirm the feasibility of the calibration, extrapolation of thermal conductivity values to 2 bar was done. The results are plotted in Figure 5.6 and the deviations in Figure 5.7. A good agreement can also be observed.

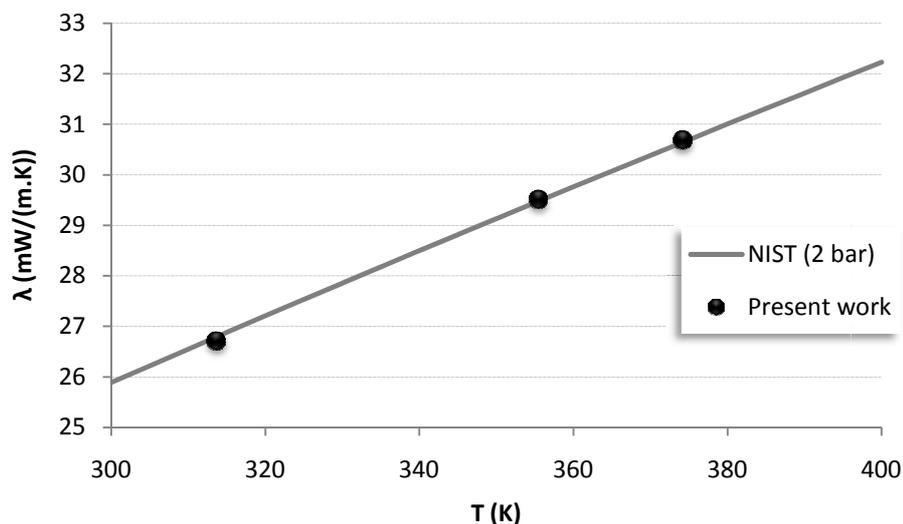


Figure 5.6 Extrapolation of Nitrogen's thermal conductivity to 2 bar. Comparison with NIST reference data.

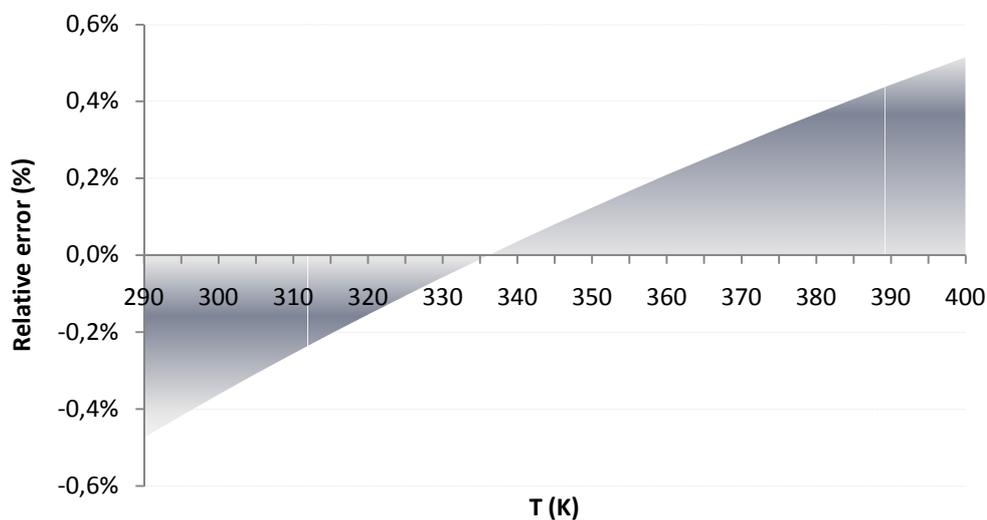


Figure 5.7 Relative deviations between the thermal conductivity extrapolated values for 2 bar obtained in the present work and the NIST reference data.

5.2. Gas Mixtures

5.2.1. X1 + X3

The first system studied in the present work was composed by X1 and X3. In order to evaluate how the thermal conductivity changes with the composition, three different compositions (20%, 50% and 80% (molar percentages)) were studied. These different compositions were prepared in the mixing cell and then introduced in the measuring cell for the thermal conductivity measurements. The experiments were performed at four different temperatures between 315K and 373K and pressures up to 5 bar. As it was mentioned before, these conditions were chosen taking into account the VLE diagram for each composition so that condensation can be avoided (see Figure B.1 in appendix B).

5.2.1.1. 20.10% X1+79.90% X3

The behavior of the thermal conductivity with temperature and pressure for this composition is presented in Table A.2 of appendix A and is depicted in Figure 5.8. The coefficients **a** and **b** of the equation 5.1 are presented in Table 5.4.

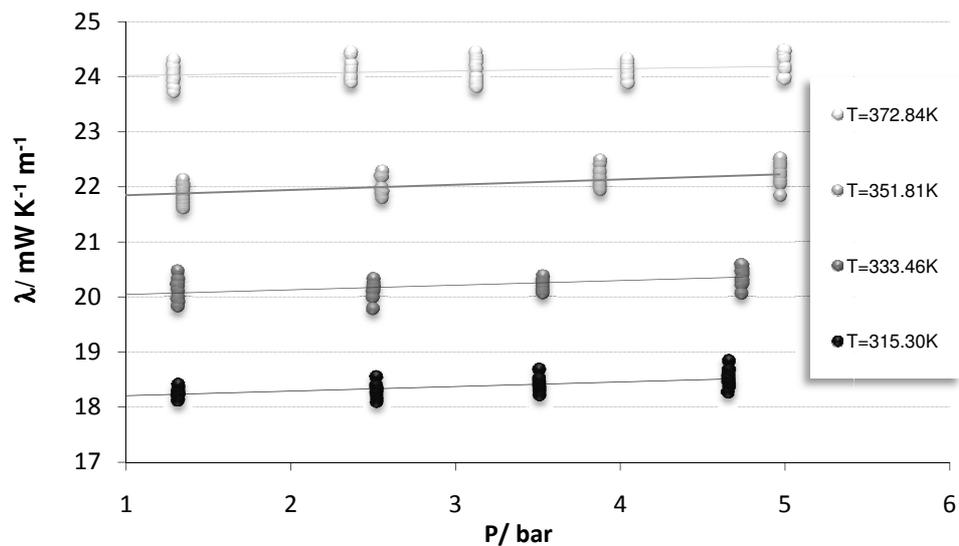


Figure 5.8 Thermal conductivity isotherms for the mixture 20.10% X1+79.90% X3. The symbols indicate the experimental values and the lines the linear behavior according to Equation 5.1.

Table 5.4 Coefficients a and b for each isotherm for the mixture 20.10% X1+79.90% X3.

Temperature (K)	a	b
315.30	0.0827	18.1275
333.46	0.0837	19.9628
351.81	0.0954	21.7542
372.84	0.0406	23.9856

Using equation 5.1 it is possible to calculate the thermal conductivity value at 1 bar for each studied temperature. These values are reported in Table 5.5.

Table 5.5 Thermal conductivity for the mixture 20.10% X1+79.90% X3 at 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹)→ 1 bar
315.30	18.2102
333.46	20.0465
351.81	21.8496
372.84	24.0262

5.2.1.2. 50.76% X1+49.24% X3

The thermal conductivity isotherms obtained for the present composition are presented in Table A.3 of appendix A and represented in Figure 5.9.

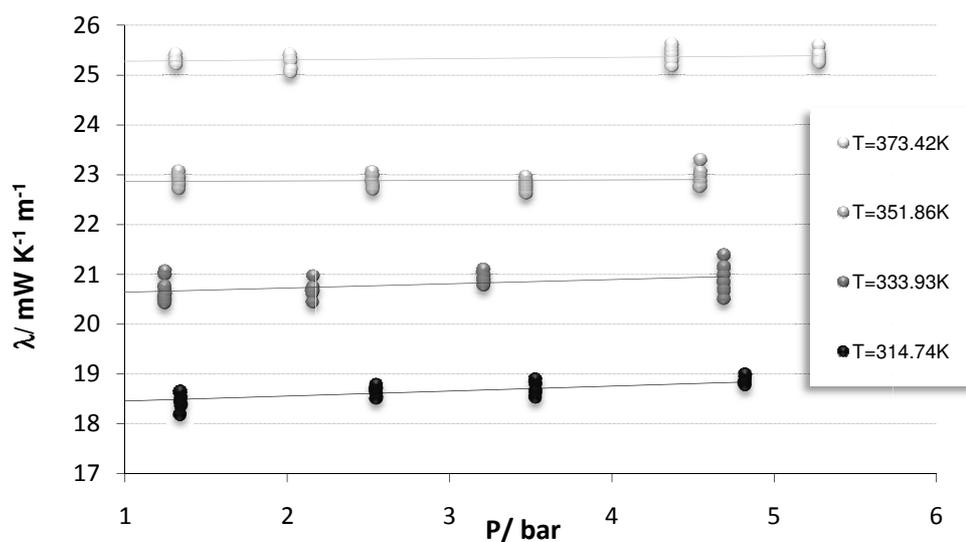


Figure 5.9 Experimental thermal conductivity isotherms for the mixture 50.76% X1+49.24% X3. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.1.

The coefficients a and b of the equation 5.1 are presented on Table 5.6 and the extrapolated thermal conductivity values for each temperature at 1 bar are presented on Table 5.7.

Table 5.6 Coefficients a and b for each isotherm of the mixture 50.76% X1+49.24% X3.

Temperature (K)	a	b
314.74	0.0996	18.358
333.93	0.0854	20.557
351.86	0.0103	22.857
373.42	0.0257	25.254

Table 5.7 Thermal conductivity for the mixture 50.76% X1+49.24% X3 extrapolated to 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹) → 1 bar
314.74	18.4576
333.93	20.6424
351.86	22.8673
373.42	25.2797

5.2.1.3. 77.12% X1+22.88% X3

The three isotherms obtained for the present composition are presented in Table A.4 of appendix A and represented in Figure 5.10. The coefficients a and b of the equation 5.1 are presented in Table 5.8 and the extrapolated thermal conductivity values for each temperature at 1 bar are presented in Table 5.9.

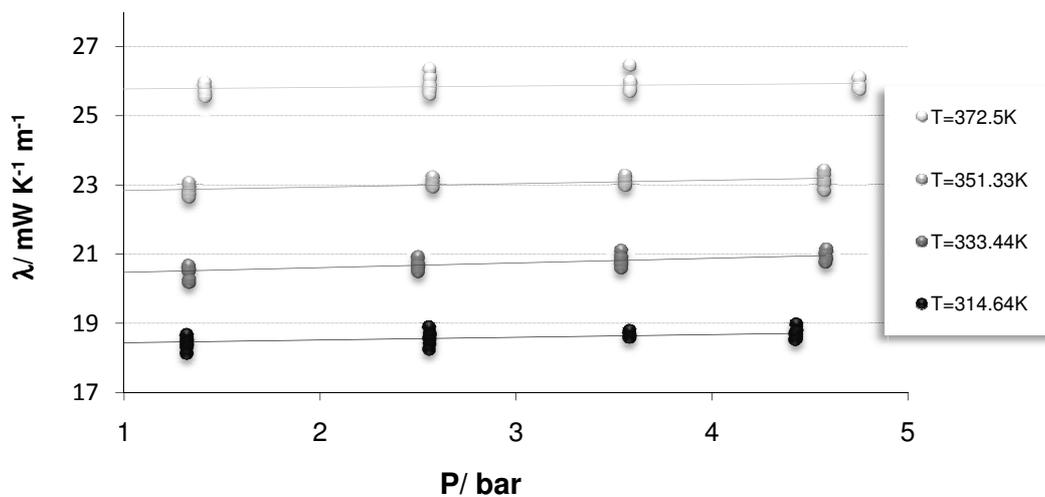


Figure 5.10 Experimental isotherms obtained for the mixture 77.12% X1+22.88% X3. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.1.

Table 5.8 Coefficients a and b for each isotherm of the mixture 77.12% X1+22.88% X3.

Temperature (K)	a	b
314.64	0.0783	18.3541
333.44	0.1350	20.3348
351.33	0.0980	22.7393
372.50	0.0421	25.7279

Table 5.9 Thermal conductivity for the mixture 77.12% X1+22.88% X3 extrapolated to 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹) → 1 bar
314.64	18.4324
333.44	20.4698
351.33	22.8373
372.50	25.7700

Another point to be mentioned is that the pressure inside of the measuring cell was never above 5 bar for both studied systems. The explanation for this is that during the calibration of the wires it was realized that for pressures over 5 bar the slope of the isotherm became steeper.

5.2.1.4. Discussion

In order to evaluate the thermal conductivity temperature dependence, the thermal conductivity extrapolated values to 1 bar were plotted as a function of each studied temperature and are presented in Figure 5.11. The thermal conductivity values for the pure components were taken from the literature [9, 10].

As expected, the thermal conductivity presents a linear dependence with temperature. The parameters α and β of equation 5.2 for each of the measured compositions are presented in Table 5.10 for 1 bar.

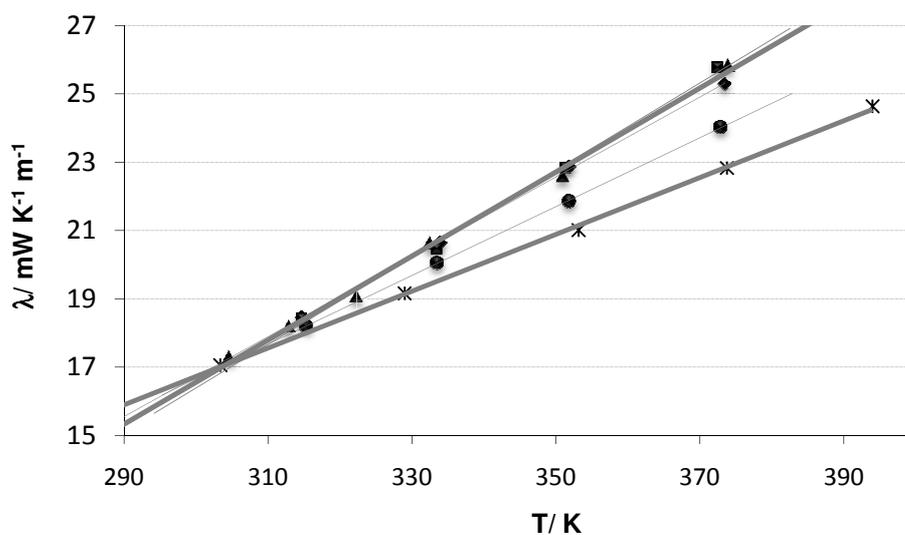


Figure 5.11 Extrapolation of the thermal conductivity data obtained for the system X1-X3 for a pressure of 1 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.10 Values of parameters α and β for all measured compositions of the system X1+X3 at 1 bar.

X1 %	α	β	R^2
0	0.0832	-8.2177	0.9991
20.10	0.1008	-13.5880	0.9999
50.76	0.1169	-18.3460	0.9996
77.12	0.1275	-21.8490	0.9969
100	0.1230	-20.3430	0.9966

A similar procedure was used for 2 bar, 3 bar and 5 bar and the results are presented in the next figures and tables.

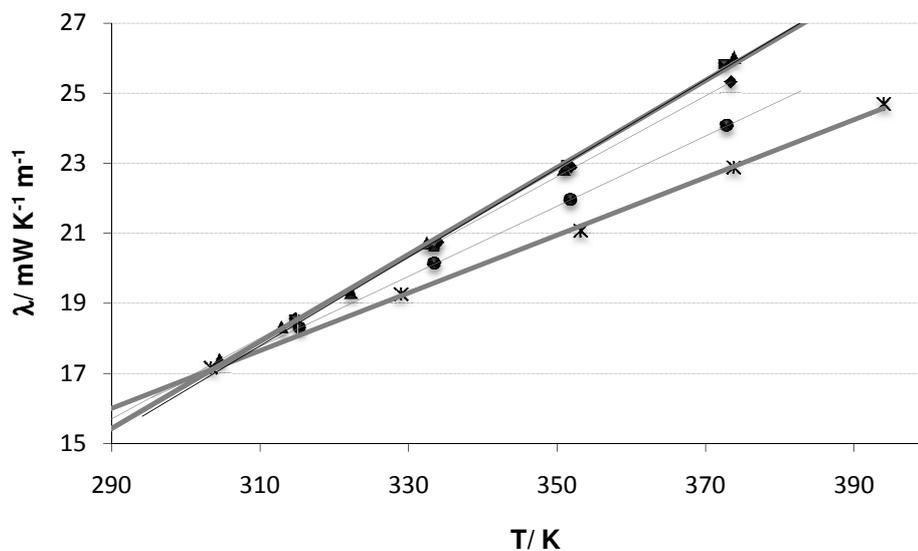


Figure 5.12 Interpolation of the thermal conductivity data obtained for the system X1-X3 for a pressure of 2 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.11 Values for parameters α and β for all the measured compositions of the system X1+X3 for a pressure of 2 bar.

X1 %	α	β	R^2
0	0,0825	-7,9285	0.9989
20.10	0,1002	-13,2980	1
50.76	0,1154	-17,7760	0.9999
77.12	0,1267	-21,4010	0.9979
100	0,1243	-20,6100	0.9980

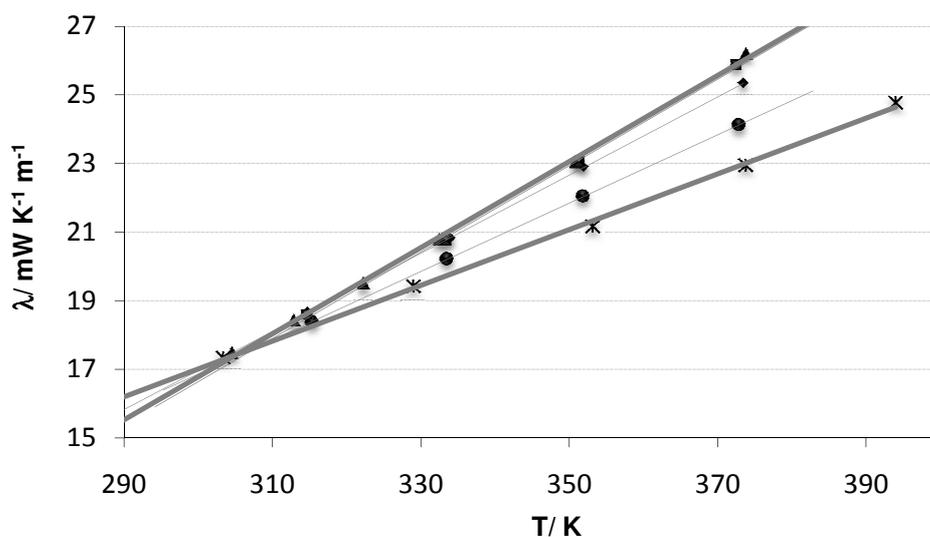


Figure 5.13 Interpolation of the thermal conductivity data obtained for the system X1-X3 for a pressure of 3 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.12 Values for parameters α and β for all the measured compositions of the system X1+X3 for a pressure of 3 bar.

X1 %	α	β	R^2
0	0.0812	-7.3501	0.9985
20.10	0.0996	-13.0070	1
50.76	0.1139	-17.2060	1
77.12	0.1259	-21.1320	0.9988
100	0.1255	-20.8760	0.9988

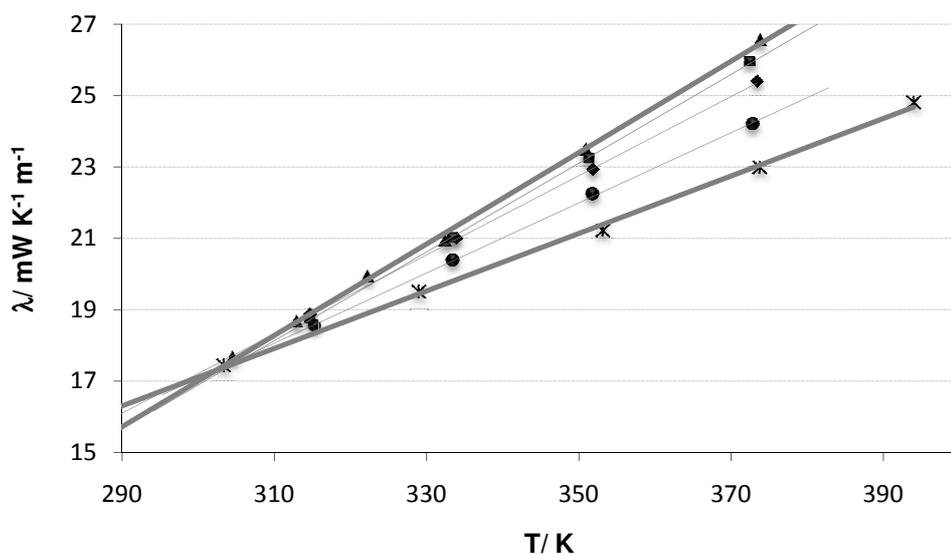


Figure 5.14 Interpolation of the thermal conductivity data obtained for the system X1-X3 for a pressure of 5 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.13 Values for parameters α and β for all the measured compositions of the system X1+X3 for a pressure of 5 bar.

X1 %	α	β	R^2
0	0.0805	-7.0609	0.9982
20.10	0.0983	-12.4260	0.9996
50.76	0.1109	-16.0660	0.9998
77.12	0.1243	-20.4160	0.9998
100	0.1280	-21.4100	0.9987

Analyzing the results obtained it can be concluded that the thermal conductivity presents a linear behavior with temperature and pressure but it does not present a linear dependence with the composition of the mixture. As can be seen in Figure 5.11, the mixtures with 50.76% and 77.12% of X1 present a behavior very close to the pure X1. This fact can be explained due to interactions between molecules. Although the dipole moment of X1 is near to zero ($\mu=0.132$ Db), it is not zero. So, this mixture can be considered a polar-nonpolar gas mixture because X3 has a null dipole moment. The observed behavior in the present mixture was the expected one taking in account the literature[22].

Another aspect that can be observed in this mixture is that there is a temperature where the thermal conductivity of both pure components is the same. This temperature will be referred from here on as cross temperature. This temperature for this system has a value of 304.66K which is very close to lowest temperature measured in this work. Note that for temperatures below the cross temperature X3 thermal conductivity is higher than that of X1 and for higher temperatures is the opposite behavior can be observed, X1 present higher values of thermal conductivity than X3.

5.2.2. X2 + X3

The second mixture studied in the present work was constituted by X2 and X3. As was done for the first mixture three different compositions (20%, 50% and 80% (molar percentages)) were studied to evaluate how the thermal conductivity changes with composition. Contrary to what happened to the mixtures of X1 and X3, these three different compositions were prepared directly in the measuring cell.

5.2.2.1. 20.42% X2+79.58% X3

The experiments for the present composition were performed at temperatures between 333K and 373K and pressures up to 5 bar so that condensation is avoided, according to the VLE diagram (see Figure B.2, appendix B). The measured thermal conductivity isotherms for the present mixture are presented in Table A.5 in appendix A and are depicted in Figure 5.15. The coefficients a and b of the equation 5.1 are presented in Table 5.14.

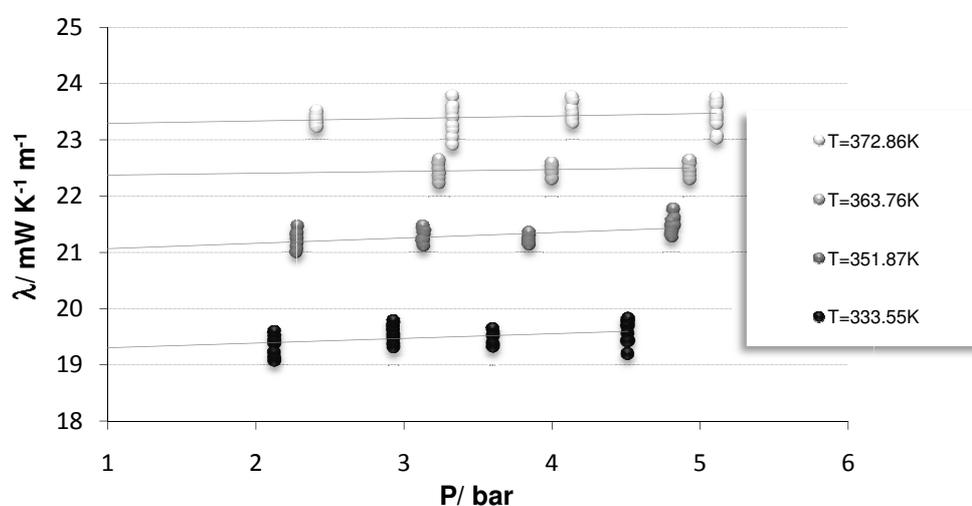


Figure 5.15 Thermal conductivity isotherms for the mixture 20.42% X2+79.58% X3. The symbols indicate the experimental values and the lines the linear behavior according to Equation 5.1.

Table 5.14 Coefficients a and b for each isotherm of the mixture 20.42% X2+79.58% X3.

Temperature (K)	a	b
333.55	0.0830	19.2225
351.87	0.0947	20.9714
363.76	0.0332	22.3414
372.86	0.0443	23.2468

To calculate the thermal conductivity value for each studied temperature the coefficients a and b are replaced in equation 5.1. The calculated values for each temperature are presented on Table 5.15.

Table 5.15 Thermal conductivity for the mixture 20.42% X2+79.58% X3 extrapolated to 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹)→ 1 bar
333.55	19.3055
351.87	21.0661
363.76	22.3746
372.86	23.2911

5.2.2.2. 45.88% X2+54.12% X3

For the present composition the temperature range of the experimental measurements is narrower (from 358 K to 385K) and the pressures were kept up to 5 bar. The working range of temperatures had to be adjusted due to condensation according the VLE diagram presented in the appendix B, Figure B.2. The thermal conductivity isotherms obtained for this composition are presented in Table A.6 in appendix A and plotted in Figure 5.16.

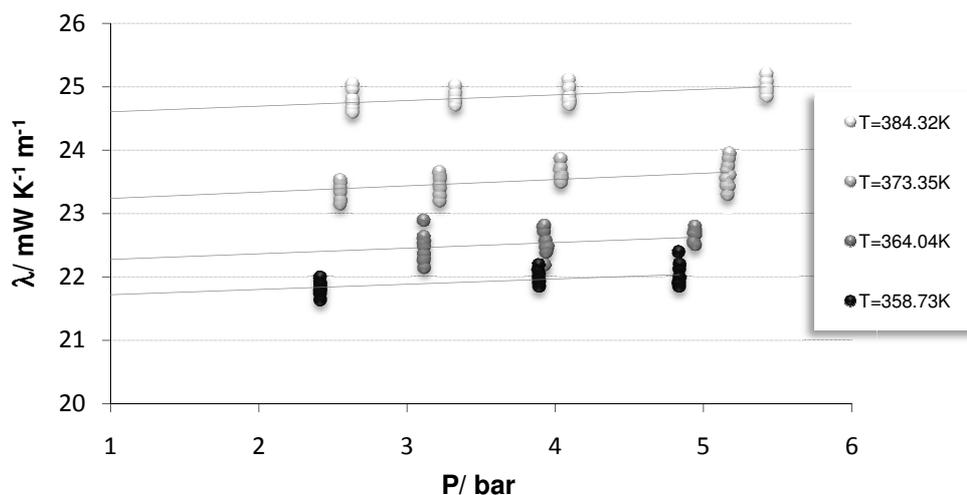


Figure 5.16 Thermal conductivity isotherms for the mixture 45.88% X2+54.12% X3. The symbols indicate the experimental values and the lines the linear behavior according to Equation 5.1.

The coefficients of the equation 5.1, a and b, are presented on Table 5.16 and the extrapolated thermal conductivity values to 1 bar are presented on Table 5.17.

Table 5.16 Coefficients a and b for each isotherm of the mixture 45.88% X2+54.12% X3.

Temperature (K)	a	b
358.73	0.0820	21.6393
364.04	0.0891	22.1888
373.35	0.0997	23.1386
384.32	0.0886	24.5188

Table 5.17 Thermal conductivity for the mixture 45.88% X2+54.12% X3 extrapolated to 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹) → 1 bar
358.73	21.7213
364.04	22.2779
373.35	23.2383
384.32	24.5188

5.2.2.3. 78.10% X2+21.90% X3

For this last mixture the experimental thermal conductivity measurements were carried out at temperatures between 364K and 393K.

The isotherms obtained for the present composition are presented in Table A.6 and plotted in Figure 5.17. The coefficients of the equation 5.1, a and b, are presented on Table 5.18 and the extrapolated thermal conductivity values to 1 bar are presented on Table 5.19.



Figure 5.17 Thermal conductivity isotherms for the mixture 78.10% X2+21.90% X3. The symbols indicate the experimental values and the lines the linear behavior according to Equation 5.1.

Table 5.18 Coefficients a and b for each isotherm of the mixture 78.10% X2+21.90% X3.

Temperature (K)	a	b
364.55	0.0619	22.1051
374.74	0.0739	23.2890
383.53	0.0239	24.6423
392.66	0.0567	25.6468

Table 5.19 Thermal conductivity for the mixture 78.10% X2+21.90% X3 extrapolated to 1 bar.

Temperature (K)	λ (mW.m ⁻¹ .K ⁻¹)→ 1 bar
364.55	22.1670
374.74	23.3629
383.53	24.6662
392.66	25.7035

5.2.2.4. Discussion

Comparing the thermal conductivity isotherms obtained for the 3 different X1 and X3 mixtures with those obtained for the 3 different X2 and X3 mixtures it is possible to see a difference in the scattering of the thermal conductivity values. For the first mixture the obtained values were more consistent than those obtained for the second one. This fact can be explained by the method that was used. The use of the mixing cell for X1 and X3 mixtures enabled the thermal conductivity measurements along isotherms by changing the pressure. For X2 and X3 system, the mixtures were directly prepared in the measuring cell and thus the thermal conductivity was acquired along isochors by changing temperature. With the present set-up it is difficult to obtain the exactly same temperature again since the apparatus is not in a temperature controlled room. This problem is more visible at high temperatures where a small deviation in temperature leads to a large deviation in thermal conductivity. To minimize this problem for high temperatures, the temperature control was done by “hand”, i.e. the set temperature in the controller was introduced by hand with a trial and error procedure so that the temperature of the apparatus was as close as possible to the previous measurement. This difference at low temperatures is negligible.

As was done with the isotherms obtained for the previous mixture, the extrapolation of the experimental data for a pressure of 1 bar was plotted as function of each studied temperature as well as an interpolation to 2 bar and 3 bar, in order to study the influence of temperature in the thermal conductivity values for each composition. The results obtained for 1 bar are shown in Figure 5.18, while the results for 2 bar, 3 bar and 5 bar are presented in Figure 5.19, Figure 5.20 and Figure 5.21, respectively. Once again, as was expected the thermal conductivity presents a linear dependence with temperature and with pressure.

The parameters α and β from equation 5.2 for each of the measured compositions are presented in Table 5.20 for 1 bar, in Table 5.21 for 2 bar, Table 5.22 presents the results for 3 bar and Table 5.23 for 5 bar. The thermal conductivity values for the pure components, X2 and X3, were taken from literature [8, 18].

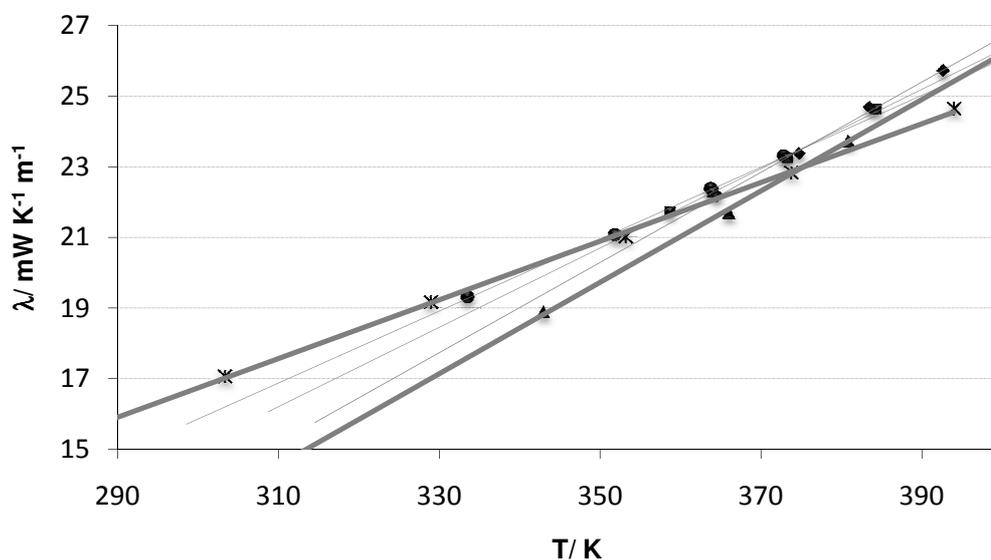


Figure 5.18 Extrapolation of the thermal conductivity data obtained for the system X2-X3 for a pressure of 1 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.20 Values for parameters α and β for all the measured compositions of the system X2+X3 for a pressure of 1 bar.

X2 %	α	β	R^2
0	0.0832	-8.2177	0.9991
20.42	0.1019	-14.7070	0.9992
45.88	0.1123	-18.6200	0.9976
78.10	0.1278	-24.4560	0.9975
1	0.1294	-25.5789	0.9995

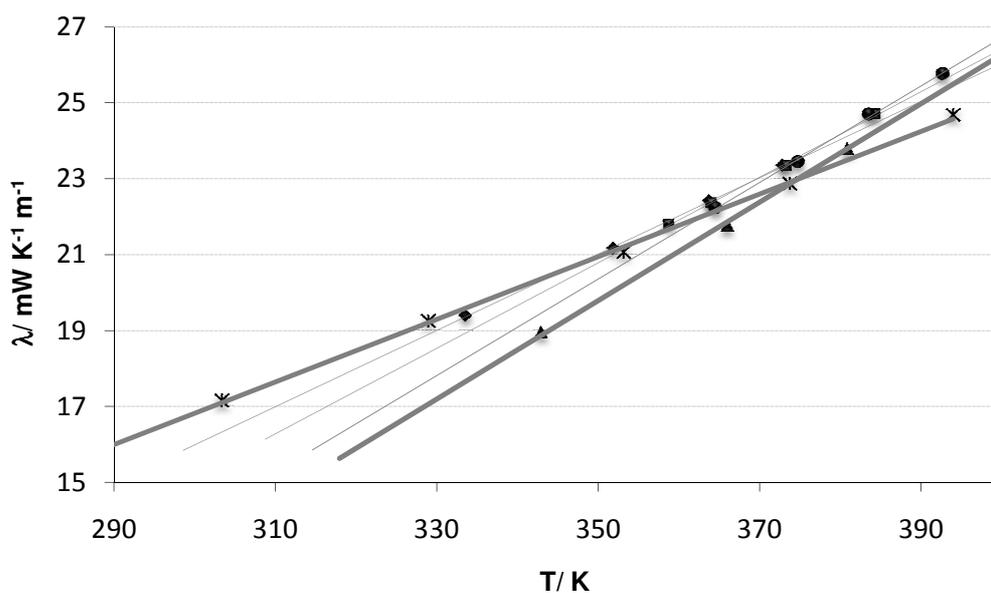
**Figure 5.19** Interpolation of the thermal conductivity data obtained for the system X2-X3 for a pressure of 2 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.21 Values for parameters α and β for all the measured compositions of the system X2+X3 for a pressure of 2 bar.

X2 %	α	β	R^2
0	0.0825	-7.9285	0.9989
20.42	0.1006	-14.1800	0.9997
45.88	0.1126	-18.6360	0.9981
78.10	0.1271	-24.1420	0.9986
100	0.1297	-25.6200	0.9995

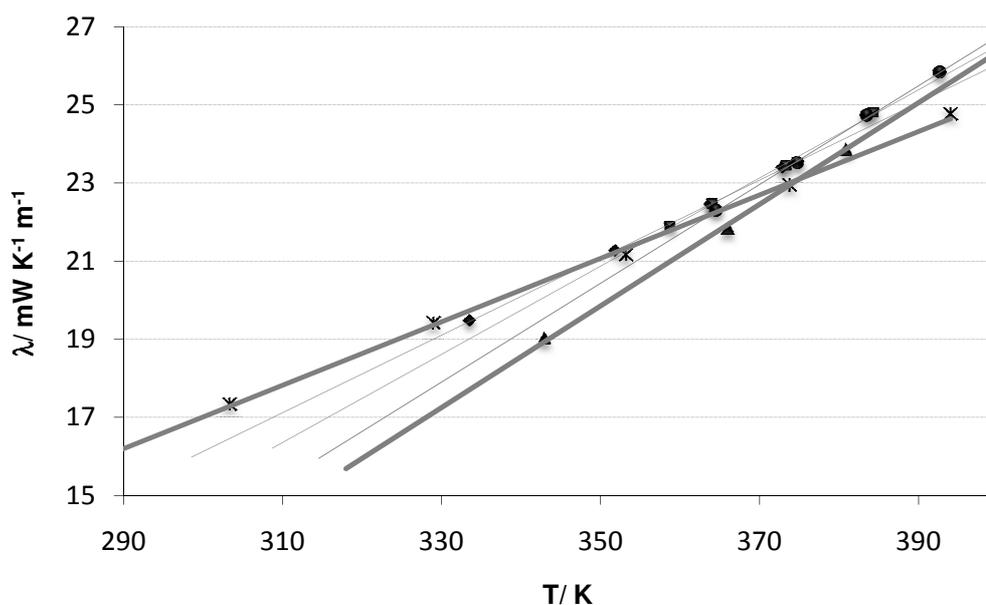
**Figure 5.20** Interpolation of the thermal conductivity data obtained for the system X2-X3 for a pressure of 3 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.22 Values for parameters α and β for all the measured compositions of the system X2+X3 for a pressure of 3 bar.

X2 %	α	β	R^2
0	0.0812	-7.3501	0.9985
20.42	0.0993	-13.6540	0.9999
45.88	0.1129	-18.6510	0.9985
78.10	0.1265	-23.8270	0.9993
100	0.1301	-25.6650	0.9994

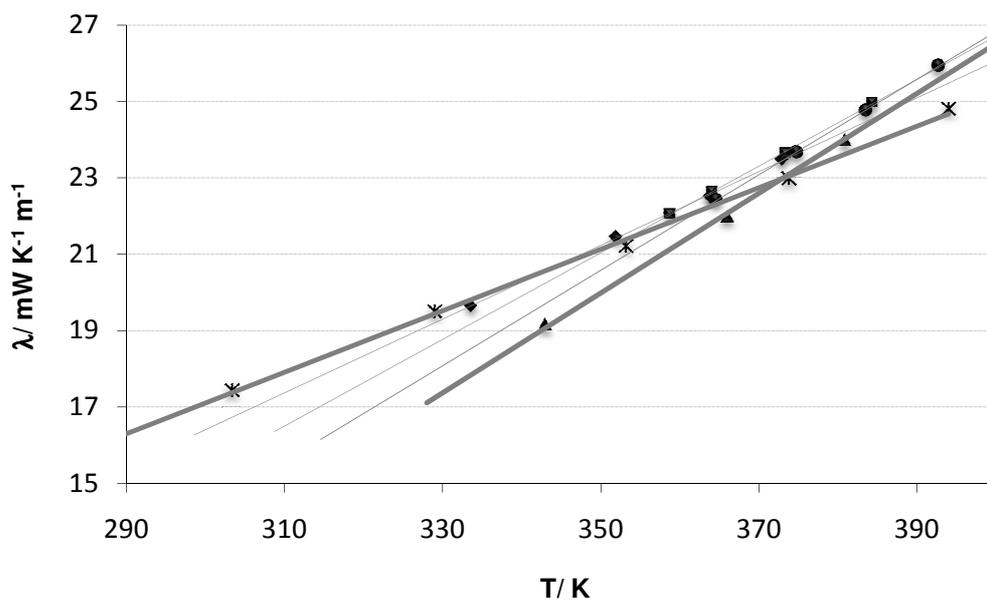
**Figure 5.21** Interpolation of the thermal conductivity data obtained for the system X2-X3 for a pressure of 5 bar. The symbols indicate the experimental values and the lines the linear behavior according to equation 5.2.

Table 5.23 Values for parameters α and β for all the measured compositions of the system X2+X3 for a pressure of 5 bar.

X2 %	α	β	R^2
0	0.0805	-7.0609	0.9982
20.42	0.0967	-12.6010	0.9994
45.88	0.1135	-18.6830	0.9992
78.10	0.1251	-23.1980	0.9999
100	0.1307	-25.7530	0.9994

It can be seen that for the X2 and X3 mixture there is also a temperature where the values of thermal conductivity are the same for both components. For temperatures below this cross temperature, X3 presents higher values of thermal conductivity, for temperatures higher the cross temperature is X2 that presents higher thermal conductivity values. For this particular systems the cross temperature at 1 bar is 375.78K, which is a much higher value than the one found for the isobutene and X3 system. Once again the dipole moment of X2 is very close to zero ($\mu=0.37$ Db) but it is not null, so this mixture is a polar-nonpolar gas mixture, too. In the present mixture, analyzing the Figure 5.18 and Figure 6.10 that is presented in the next chapter, it is clear a presence of a maximum in thermal conductivity values, this behavior is normal in this kind of mixtures [22].

6. Correlation of the experimental results using the Extended Wassiljewa model

In the present chapter, the Extended Wassiljewa model is used to correlate the experimental results obtained. The novelty introduced in this work was the fitting of the ϵ parameter to all data results for a specific system using Equation 2.11. In this way, instead of having an ϵ parameter that is temperature dependent as it was previously done, an analysis of the pressure and temperature dependence of the ϵ parameter can be done. Some authors consider this parameter constant and close to unit [14, 19, 22]

Until the present work the ϵ parameter from Wassiljewa model modified by Mason and Saxena was fitted individually for each temperature. Then, with these values, the parameters of the Equation 2.11 were calculated, enabling the calculation of the ϵ parameter for any temperature and pressure, and therefore to calculate the thermal conductivity of the mixture in study for any temperature or pressure.

In the present work all the process was done simultaneously, e.g. it was used directly the Extended Wassiljewa model. The parameter ϵ was fitted for each temperature and pressure but it was not fitted individually. All the fitting process was done using simultaneously different temperatures and different pressures, taking in account that the thermal conductivity values for these temperatures and pressures.

For both mixtures studied in the present work the values of thermal conductivity do not increase in a regular way with the composition of the mixture.

6.1. X1 + X3

In Figure 6.1 the experimental values of thermal conductivity as well as the Extended Wassiljewa model for 1 bar are depicted. It is possible to see that as the X1 content increases, the thermal conductivity of the mixture shows an higher dependence on the temperature.

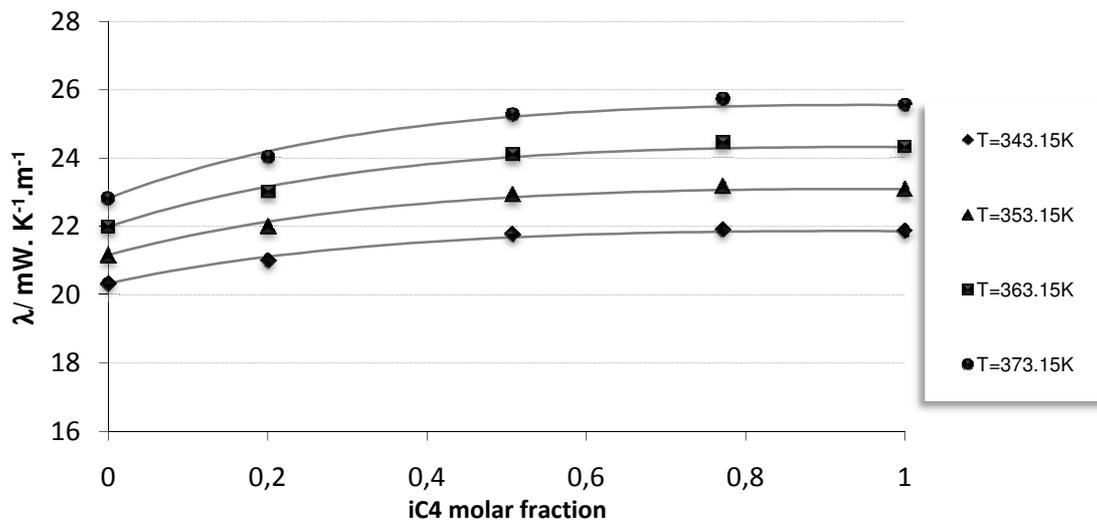


Figure 6.1 Thermal conductivity X1 + X3 mixture_at 1 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

The deviations between the experimental values and the Extended Wassiljewa model are presented in Figure 6.2. There is a good agreement between experimental values and the values obtained with the Extended Wassiljewa model, being the deviations always smaller than $\pm 0.80\%$.

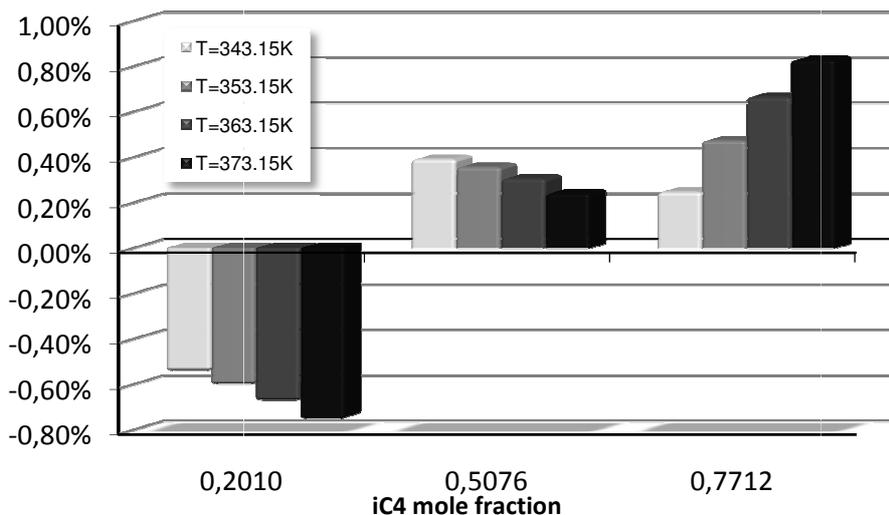


Figure 6.2 Deviations between the experimental results and the Extended Wassiljewa model at 1 bar for the three compositions measured.



The extended Wassiljewa model was also used to correlate the experimental data obtained at 2, 3 and 5 bar. The results for 2, 3 and 5 bar are shown in Figure 6.3, Figure 6.4 and Figure 6.7, respectively.

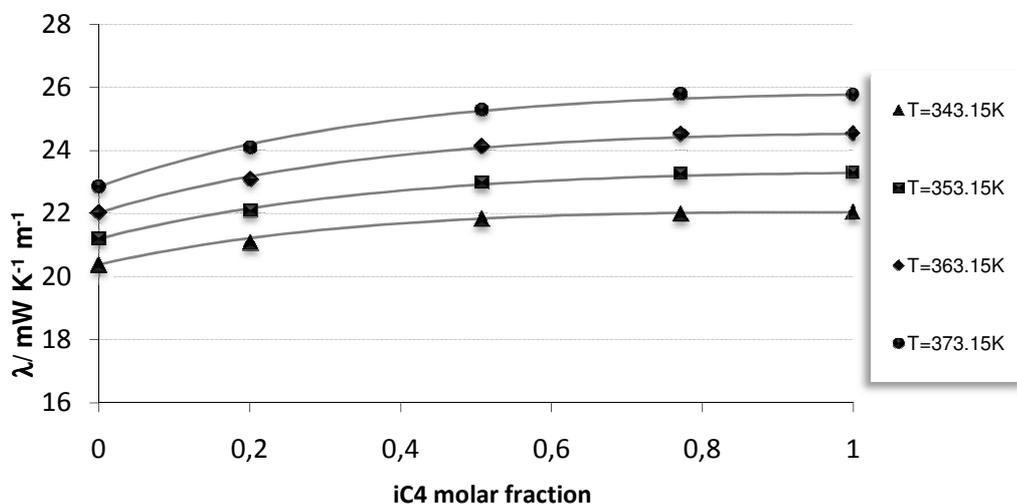


Figure 6.3 Thermal conductivity X1 + X3 mixture at 2 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

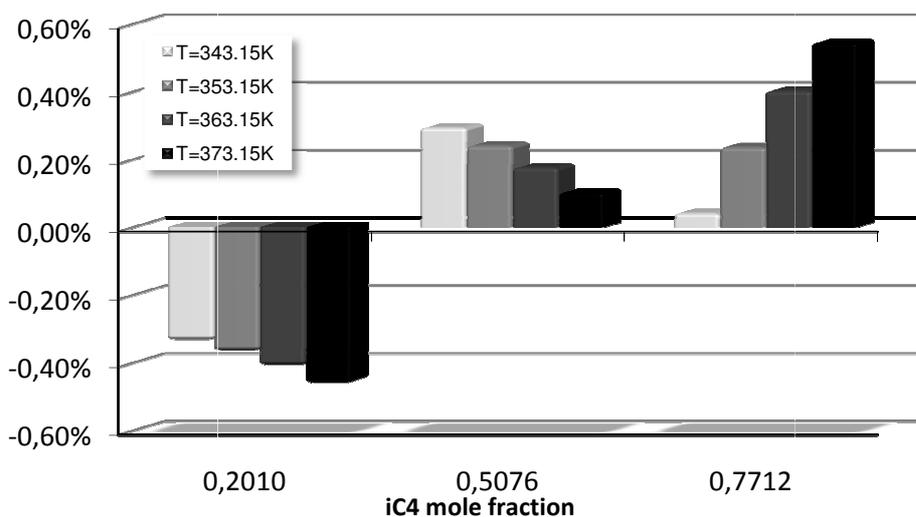


Figure 6.4 Deviations between the experimental results and the Extended Wassiljewa model at 2 bar for the three compositions measured.



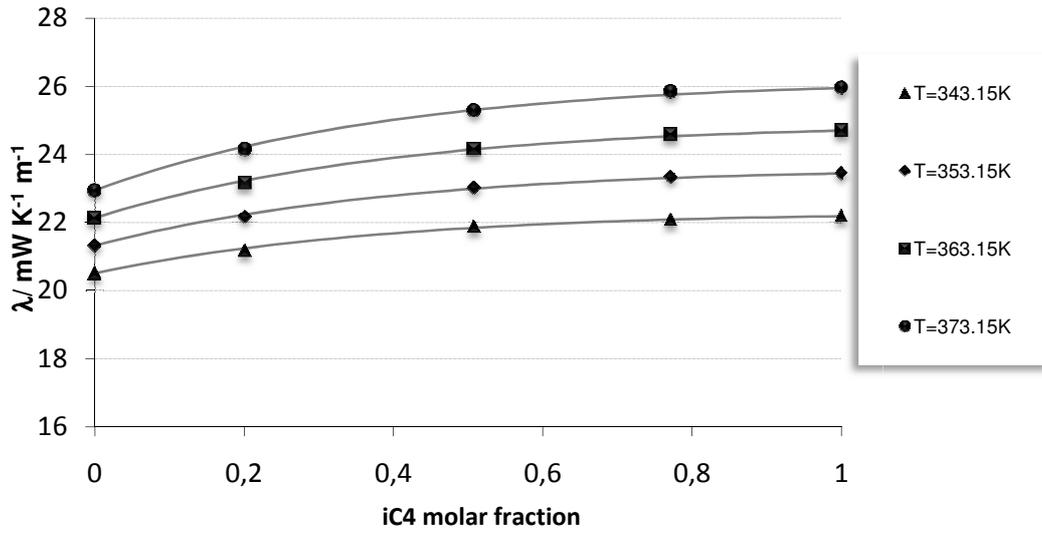


Figure 6.5 Thermal conductivity X1 + X3 mixture at 3 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

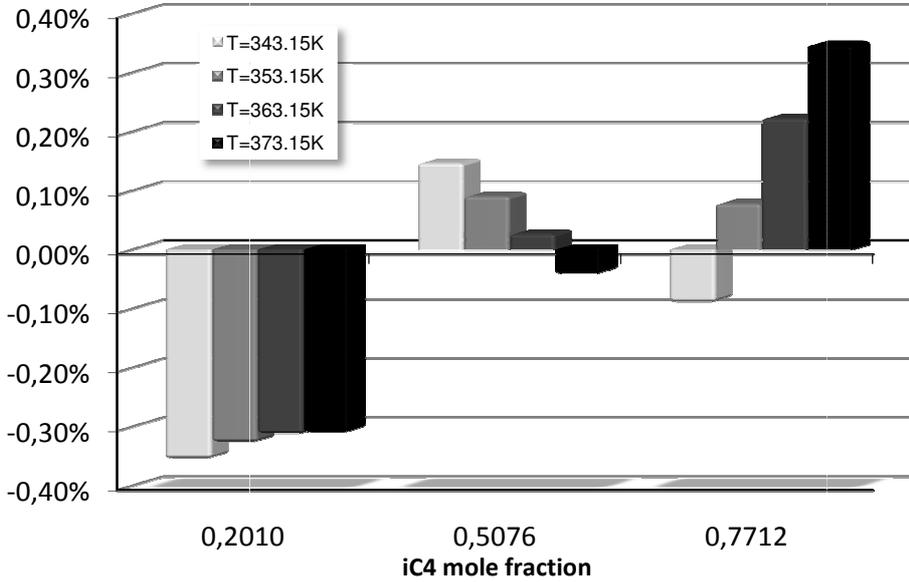


Figure 6.6 Deviations between the experimental results and the Extended Wassiljewa model at 3 bar for the three compositions measured.

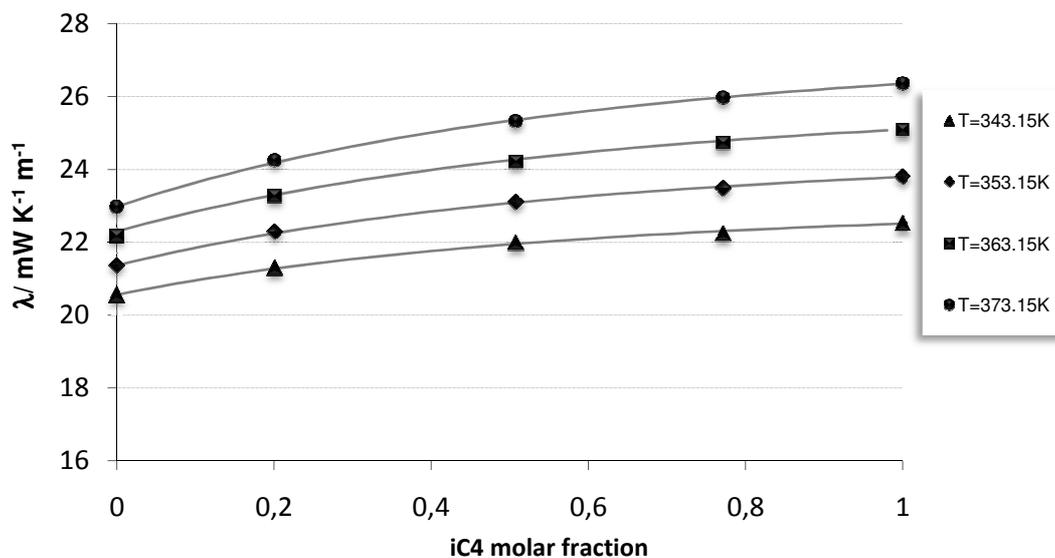


Figure 6.7 Thermal conductivity X1 + X3 mixture at 5 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

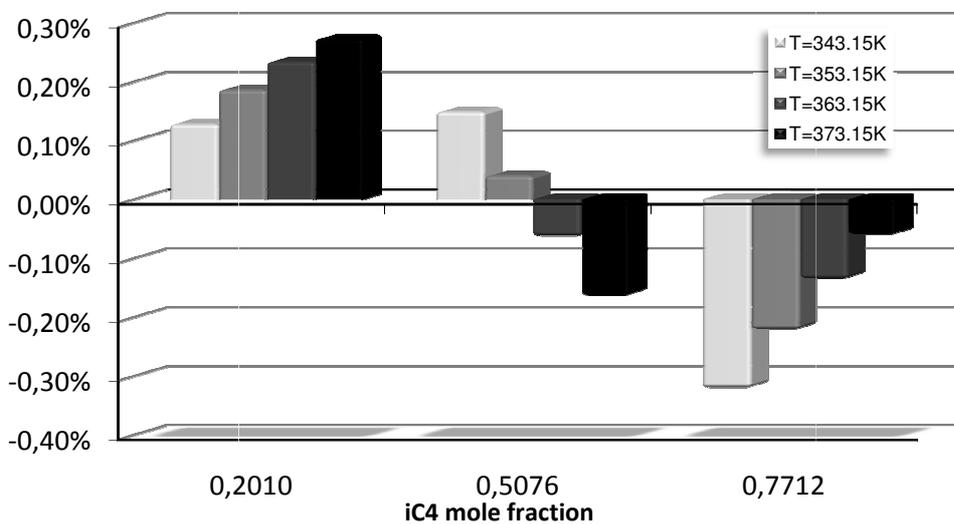


Figure 6.8 Deviations between the experimental results and the Extended Wassiljewa model at 5 bar for the three compositions measured.

The ϵ parameter was fitted to the four different temperatures and four different pressures. The parameters obtained for the equation 2.11 are presented in Table 6.2 and on Table 6.1 can be seen the results for the fitting of the parameter ϵ .

Table 6.1 ϵ parameter of the extended Wassiljewa model for X1+X3 system.

Pressure	$\epsilon_{343.15K}$	$\epsilon_{353.15K}$	$\epsilon_{363.15K}$	$\epsilon_{373.15K}$
1	0.9287	0.9222	0.9159	0.9098
2	0.9338	0.9284	0.9232	0.9181
3	0.9390	0.9347	0.9305	0.9265
5	0.9495	0.9474	0.9454	0.9435

Table 6.2 Values of the parameters of the equation 2.11 for the X1+X3 system.

A1	A2	A3	A4
4.9285	-0.2413	0.0423	-0.2868

It is possible to see an excellent agreement between experimental values and the Extended Wassiljewa model. Although small (below 0.8%) the highest deviations were observed for the pressure of 1 bar. It is possible to conclude that the Extended Wassiljewa model performs very well in the description of the thermal conductivity of this mixture.

Relatively to the dependence of the ϵ parameter on temperature and pressure for the present mixture X1+X3, it can be seen in Table 6.1 that, it is not a constant as it is sometimes assumed in literature [14, 19] and also it is not close to unit. The ϵ parameter is in fact smaller than unit and it shows a more marked dependence on pressure than temperature, increasing with pressure and decreasing with temperature.

After the fitting procedure it is possible to predict the values of the thermal conductivity for lower temperatures. The lower temperatures are interesting since it is at these temperatures that the studied mixtures will be used as blowing agents. In Figure 6.9 the prediction for 1 bar and 283.15K (10°C) are presented.

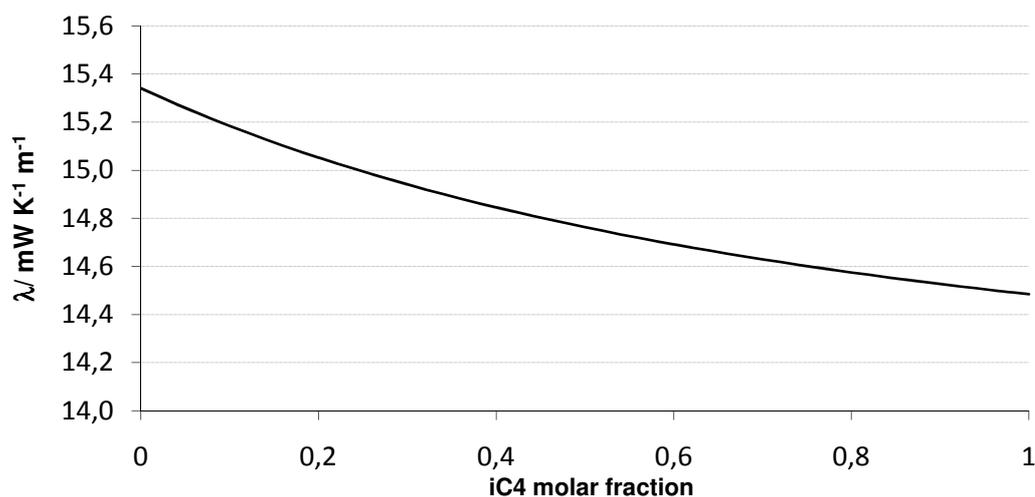


Figure 6.9 Thermal conductivity predicted with the Extended Wassiljewa model for the mixture X1+X3 at 283.15K and 1 bar.

The most striking feature found in this graph is the fact that for 283.15K and 1 bar the thermal conductivity behavior of the mixture is the opposite of the one found for high temperatures. This result can be explained by the fact that this temperature is smaller than the system cross temperature. Due to experimental reasons, the thermal conductivity of this mixture was measured at temperatures above the cross temperature but the temperatures interesting for their application are located below it. This means that the more efficient blowing agents are those mixtures with high content of X1, contrary to what could be expected from the behavior of the thermal conductivity for high temperatures.

6.2. X2 + X3

The experimental values of the thermal conductivity experimental values as well as the Extended Wassiljewa model the for three mixtures of X2 + X3 at 1,2, 3 and 5 bar and temperatures of 343.15, 353.15, 363.15 and 373.15 K are shown in the next figures. Observing the figures it can be noticed that as the temperature approaches the cross temperature the presence of a maximum in thermal conductivity can be detected.

Again the deviations between the experimental values and the Extended Wassiljewa model for each pressure presented for 1, 2, 3 and 5 bar, allow the conclusions that the model also performs very well in the description of thermal conductivity of this mixture. The highest deviations correspond to the mixture with high content of X2. This fact was expectable because it was needed to use high temperatures to study it and, as was already mentioned in the present work, it contributes to the instability of the measurements. In spite of this, it can be stated that the Extended Wassiljewa model performs very well in the description of the thermal conductivity of this mixture.

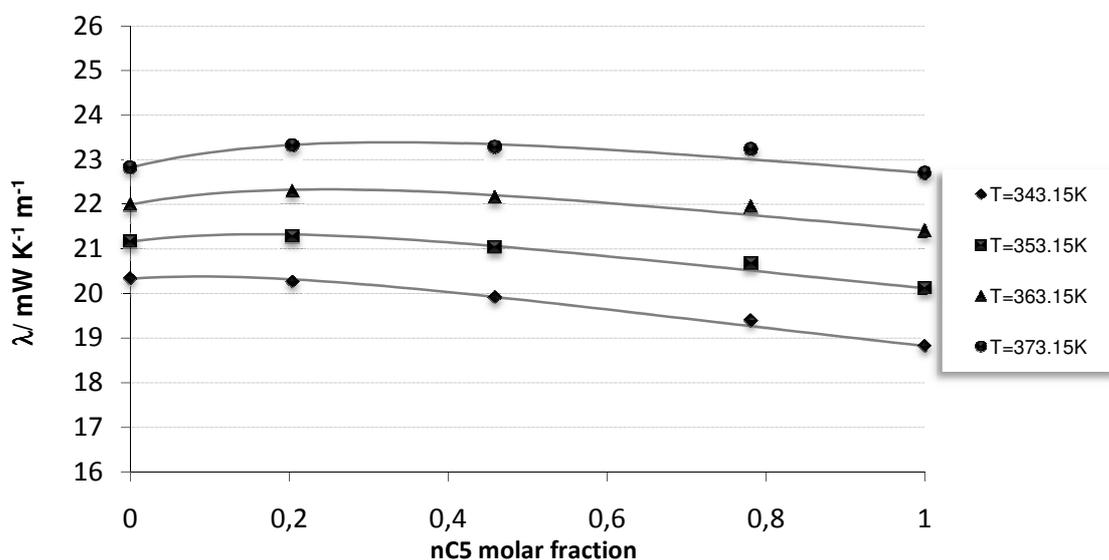


Figure 6.10 Thermal conductivity X2 + X3 mixture at 1 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

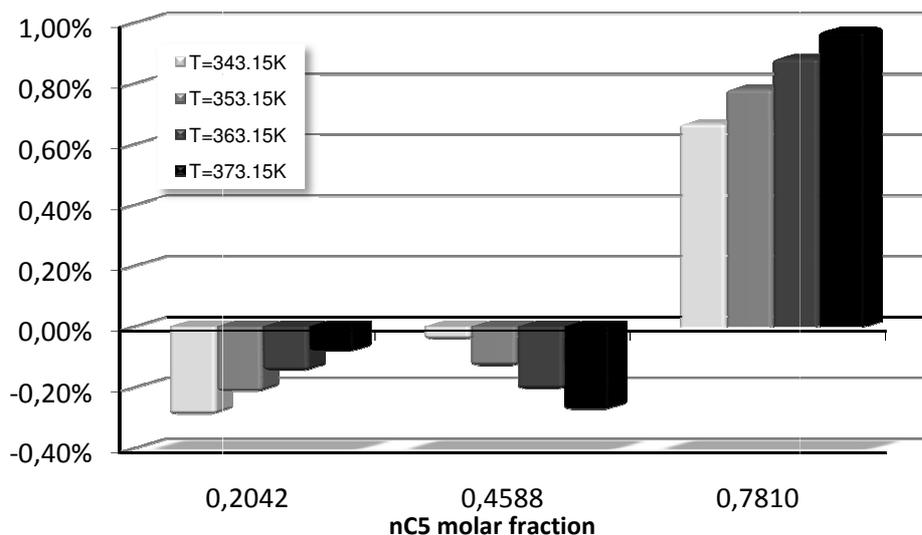


Figure 6.11 Deviations between the experimental results and the Extended Wassiljewa model at 1 bar for the three compositions measured.

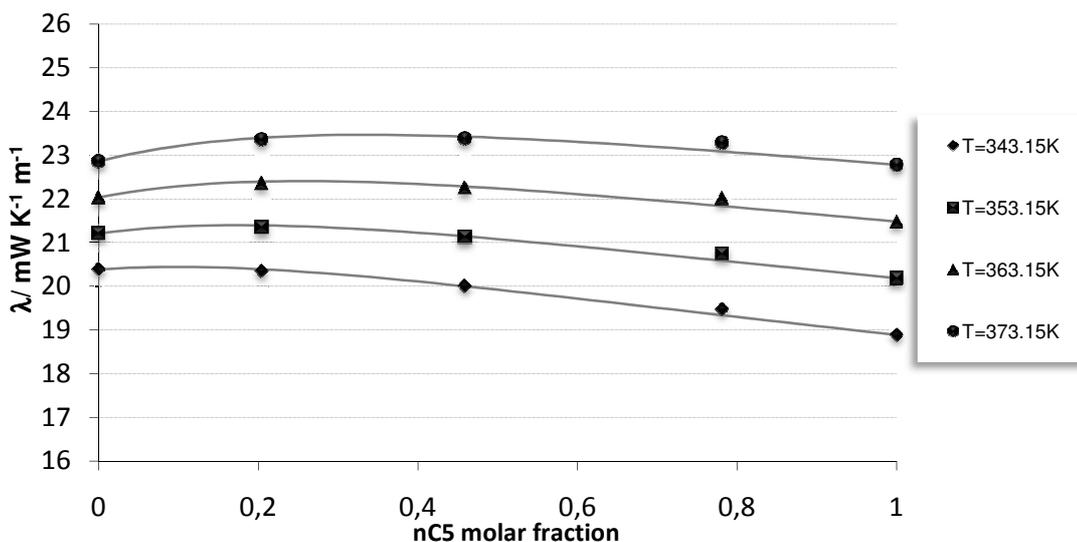


Figure 6.12 Thermal conductivity X2 + X3 mixture at 2 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.



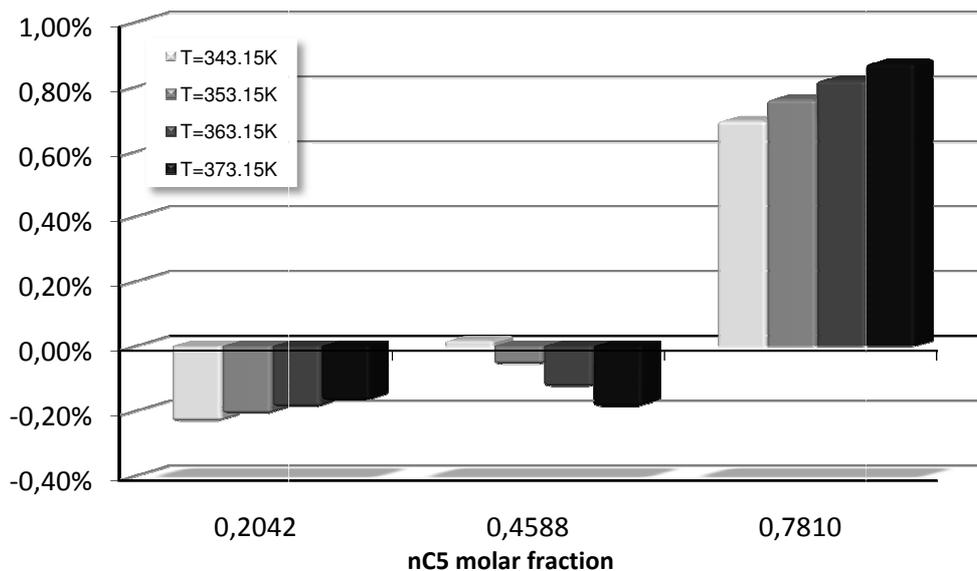


Figure 6.13 Deviations between the experimental results and the Extended Wassiljewa model at 2 bar for the three compositions measured.

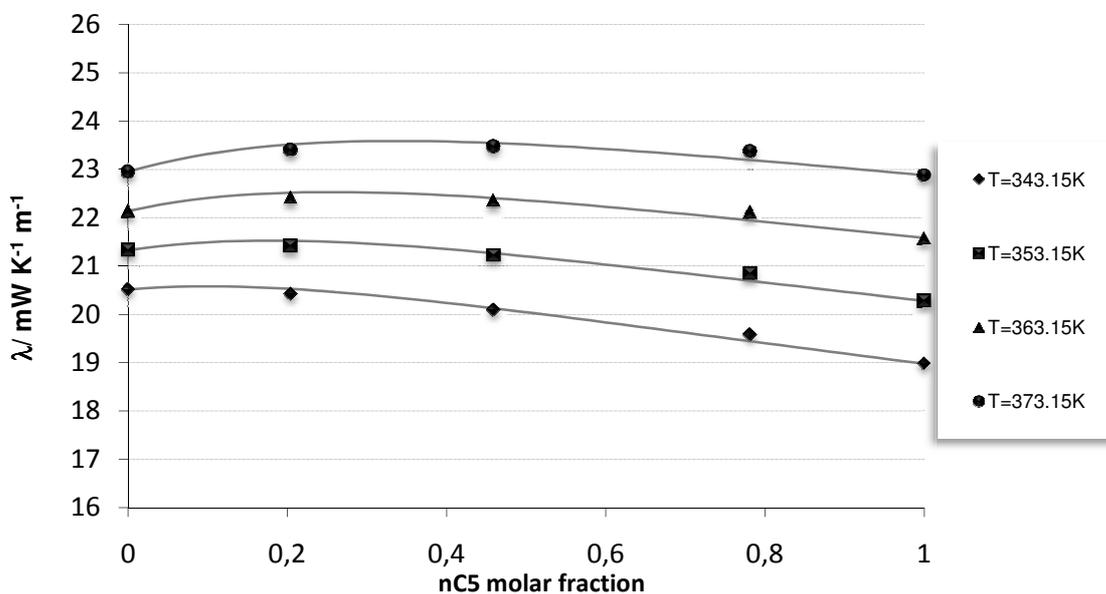


Figure 6.14 Thermal conductivity X2 + X3 mixture at 3 bar for the three studied compositions. The lines refer to the Extended Wassiljewa model.

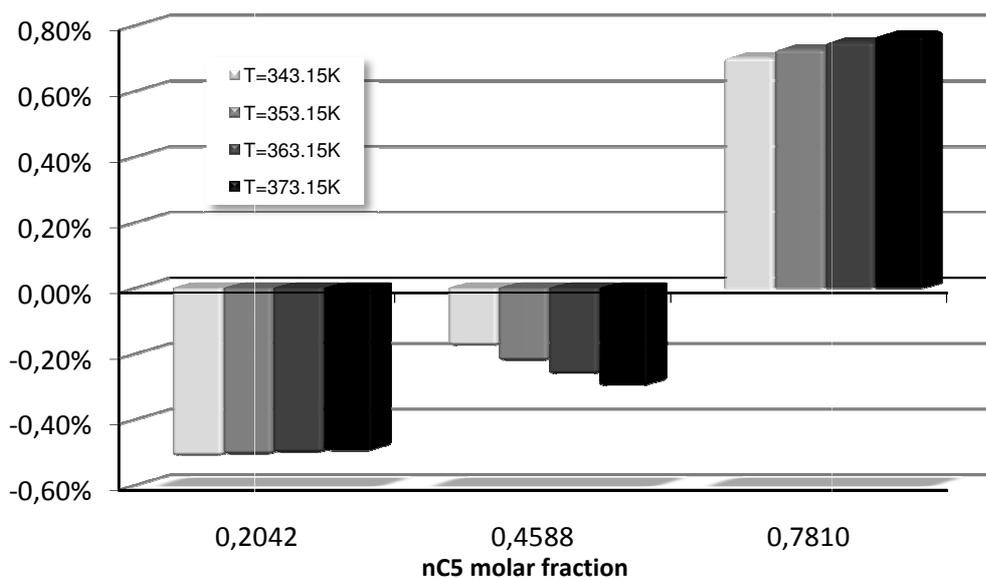


Figure 6.15 Deviations between the experimental results and the Extended Wassiljewa model at 3 bar for the three compositions measured.

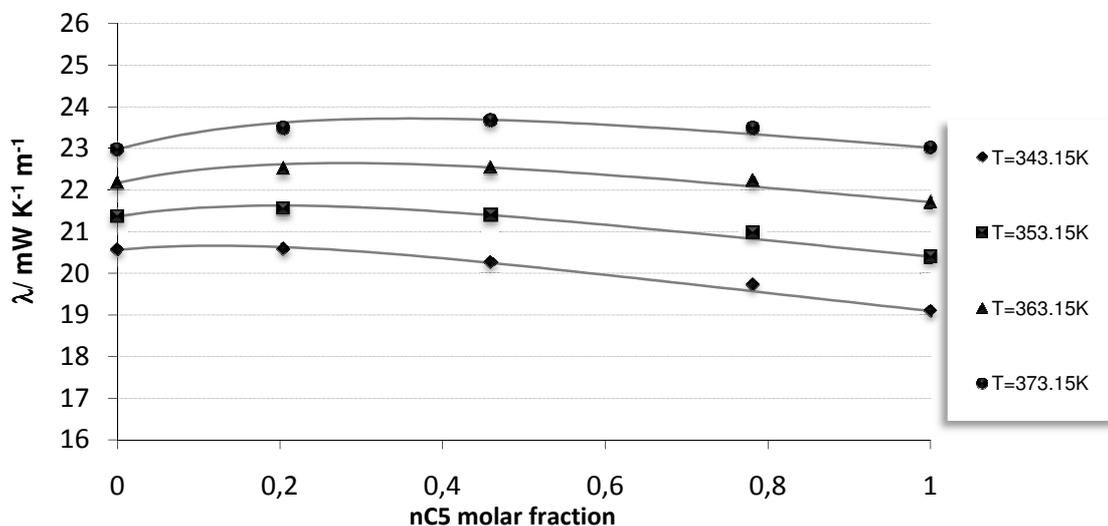


Figure 6.16 Deviations between the experimental results and the Extended Wassiljewa model at 5 bar for the three compositions measured.



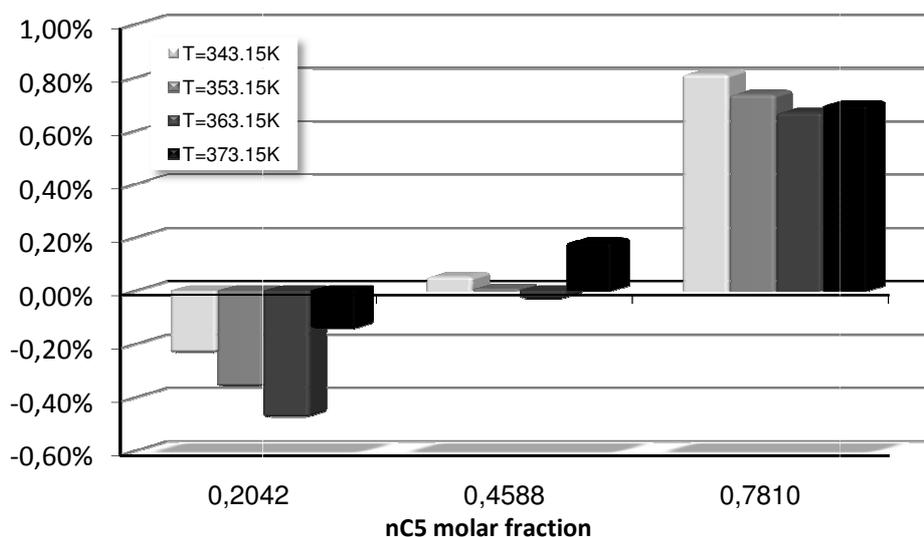


Figure 6.17 Deviations between the experimental results and the Extended Wassiljewa model at 5 bar for the three compositions measured.

The ϵ parameter was fitted for the four different temperatures and four different pressures. The parameters of the equation 2.11 are presented in Table 6.4 and in Table 6.3 the parameters of the correlation of the ϵ parameter with temperature and pressure can be analyzed.

Table 6.3 ϵ parameter of the extended Wassiljewa model for X2+X3 system.

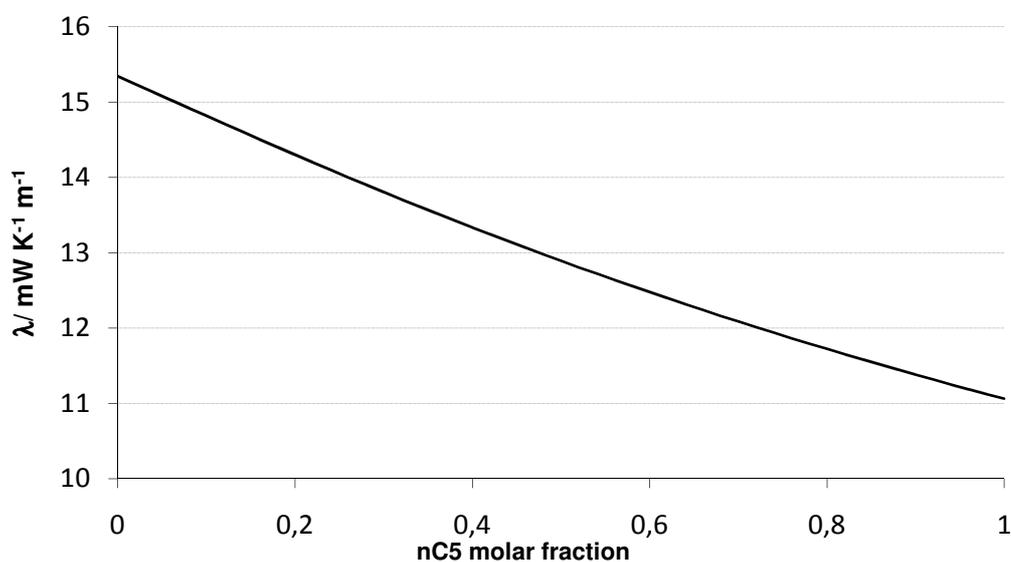
Pressure	$\epsilon_{343.15K}$	$\epsilon_{353.15K}$	$\epsilon_{363.15K}$	$\epsilon_{373.15K}$
1	0.9035	0.9037	0.9039	0.9041
2	0.9019	0.9020	0.9022	0.9024
3	0.9003	0.9004	0.9005	0.9007
5	0.8971	0.8971	0.8972	0.8972

Table 6.4 Values of the parameters of the equation 2.11 for the system X2+X3.

A1	A2	A3	A4
0.8532	0.0076	-0.0016	0.0101

Again the ϵ parameters are always smaller than the unit. More constant parameters (less dependent on the temperature and pressure conditions) were found for X2+X3 than for X1+X3. Relatively to the temperature and pressure dependence, the behavior found for this system is the opposite of that obtained for X1+X3, the parameter ϵ decreases with pressure and increases with temperature.

The predicted values of the thermal conductivity for 1 bar and for 283.15K (10°C) using the Extended Wassiljewa model are shown in Figure 6.18.

**Figure 6.18** Predicted thermal conductivity values with the Extended Wassiljewa model for the mixture X2+X3 at 283.15K to 1 bar.

It can be noticed that at 283.15K that there is a considerable difference in the thermal conductivity for the pure components. The difference was not so large at the temperatures where the experimental results were measured because they were closer to the cross temperature. Again the thermal conductivity mixture behavior at 283.15 K is not the expected one from the high temperature thermal conductivity experimental values.

As for X1+X3, the most interesting compositions to use as blowing agent are those with high content of hydrocarbon because they present lower thermal conductivity values.

7. Conclusion and Future Work

7.1. Conclusion

In the present work the transient hot wire method was used to measure the thermal conductivity of two gas binary systems composed of X3 + hydrocarbon. The studied hydrocarbons were X1 and X2. Three different compositions for each mixture were studied from 300 to 400 K and pressures between 1 and 5 bar.

Two different methods to prepare the mixtures were used: for the X1+ X3 mixtures the mixing cell was used and for X2 + X3 the mixture was directly prepared in the measuring cell. The choice of different mixture methods was due to the low vapour pressure of X2 at the studied temperatures. From the analysis of the obtained result it can be concluded that the introduction of the mixing cell improved the quality of the results while saving time.

The thermal conductivity results obtained showed in general very small deviations. However, at high temperatures the scattering of the data increases. This was observed not only for the studied mixtures but also for the calibration with nitrogen. This fact can be explained by the probable occurrence of convection inside of the measuring cell. As it is known, the wires inside of the cell work as heating source, and for higher temperatures and pressures above 5 bar a non-uniform heating of the wire might occur leading to the development of buoyancy forces in the gas that surrounds the wire which will result in convective heat transport. Although the convection could exist it is not significant enough to affect the linearity between ΔT and t .

The Extended Wassiljewa Model was used to correlate the thermal conductivity results of both mixtures performing very well. The ϵ parameter is always small than the unit and presents opposite behavior for the two mixtures. For the mixture constituted by X1 and X3 the ϵ parameter increases with pressure and decreases with temperature, while for the mixture constituted by X2 and X3 the ϵ parameter decreases with pressure and increases with temperature.

From the analysis of the results of the mixtures studied in the present work it can be concluded that the mixture constituted by X2 and X3 displays better thermal properties to be used as blowing agent.

7.2. Future Work

The future work should focus on the measurement of more systems that contain X3. X3 is always present in the foam's cells and so it is vital to understand of the behavior of its mixture with other hydrocarbons, namely cyclopentane.

In terms of apparatus improvement the temperature controllers should be replaced and the Lambda program should be revised. It would also be valuable to place to the apparatus in a temperature controlled room.

8. References

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Appendix A

Table A.1 Results obtained in calibration with nitrogen.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]	T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
314,03	2,709	26,8569	355,55	4,549	29,742
314,03	2,709	26,8002	355,56	4,548	29,807
314,08	2,708	26,7336	355,55	4,547	29,7202
314,10	2,707	26,8174	355,52	4,547	29,7371
314,05	2,706	26,7301	355,53	4,546	29,7762
314,05	2,706	26,7323	355,54	4,546	29,8166
314,02	2,704	26,8684	355,53	4,545	29,8328
313,67	8,091	27,1259	355,54	4,544	29,818
313,62	8,085	27,2260	355,52	7,933	29,8744
313,61	8,083	27,1329	355,50	7,93	30,1121
313,58	8,081	27,0832	355,52	7,928	29,9037
313,62	8,078	27,2333	355,48	7,925	30,0865
313,70	8,077	27,1117	355,50	7,923	29,9293
313,69	8,076	27,1700	355,44	7,921	29,9715
313,67	8,074	27,2019	355,40	7,918	29,8158
313,64	8,072	27,2260	355,41	7,917	30,2166
313,60	8,068	27,2535	355,45	7,916	30,2587
313,67	6,241	27,0582	355,46	7,915	30,0215
313,66	6,240	27,1226	355,49	7,913	30,1284
313,63	6,238	27,0573	355,50	7,912	29,9053
313,62	6,238	27,0389	355,52	7,912	30,114
313,61	6,236	26,9642	355,53	5,801	29,9325
313,58	6,233	26,9408	355,53	5,800	29,8128
313,57	6,232	27,0296	355,55	5,799	29,7302
313,58	6,232	27,1651	355,55	5,799	29,6903
313,58	6,228	26,9067	355,56	5,798	29,5876
313,58	6,228	26,9393	355,53	5,796	29,7488
313,59	6,227	27,0430	355,53	5,796	29,6817
313,70	6,227	27,1190	355,57	5,796	29,7514
313,64	4,046	26,8556	355,57	5,795	29,6838
313,65	4,045	26,8938	355,55	5,794	29,9264
313,62	4,045	26,9135	355,53	5,793	29,6968
313,72	4,043	26,8787	374,01	8,030	31,2831
313,74	4,044	26,7568	374,00	8,028	31,1762
313,79	4,043	26,7683	374,01	8,028	31,2585
313,78	4,043	26,7848	373,99	8,026	31,3534
313,82	4,042	26,7547	373,98	8,025	31,1359
355,57	4,551	29,6719	374,00	8,023	31,3738
355,58	4,550	29,8597	374,04	8,022	31,3295
355,57	4,550	29,6522	374,07	8,018	31,2839

Table A.2 Results obtained for the mixture 20.10% X1+79.90% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
372,93	4,999	24,1371
372,92	4,998	23,9686
372,89	4,997	24,1789
372,88	4,997	24,4616
372,84	4,996	24,1438
372,82	4,995	24,3553
372,76	4,994	24,3144
372,75	4,993	24,4684
372,75	4,993	24,4011
372,77	4,992	24,3337
372,78	4,991	23,9591
372,74	4,044	23,8922
372,73	4,045	24,0203
372,73	4,044	23,8828
372,67	4,043	24,1729
372,65	4,042	24,3079
372,67	4,042	24,1192
372,67	4,042	23,9885
372,68	4,043	23,9966
372,67	4,042	24,2539
372,68	4,042	23,8819
372,69	4,043	24,2494
372,70	4,042	24,0908
372,70	3,123	23,9229
372,71	3,124	24,1653
372,72	3,124	24,0070
372,71	3,123	24,4334
372,71	3,124	24,3176
372,71	3,124	24,1403
372,71	3,123	24,2024
372,72	3,123	23,8940
372,75	3,124	23,8979
372,74	3,125	24,3303
372,74	3,125	24,2491
372,79	3,124	23,9435
372,80	3,124	23,8100
372,81	3,124	23,8543
372,85	3,124	24,3751
372,93	2,365	24,4344
372,92	2,364	23,9530
372,92	2,364	24,3974
372,92	2,365	24,1249
372,93	2,365	23,9752
372,95	2,365	24,1088
372,97	2,365	24,0047
372,97	2,365	23,8914
372,98	2,365	24,1298
372,99	2,365	24,1293
372,99	2,365	23,8949
372,99	2,366	24,1598
373,00	2,366	24,2293
373,01	2,366	24,1106

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
373,08	1,289	23,9627
373,07	1,289	24,2928
373,04	1,289	23,7975
373,01	1,289	24,2772
372,98	1,288	23,7170
372,98	1,289	24,1753
372,96	1,288	24,0863
372,94	1,288	23,9618
372,93	1,287	24,1184
372,91	1,288	24,0030
372,89	1,286	24,0621
372,87	1,287	24,0646
372,86	1,286	23,8198
372,86	1,286	23,9134
372,82	1,286	24,2041
372,83	1,286	24,1684
372,80	1,285	24,0457
351,72	4,971	22,4868
351,73	4,970	22,1929
351,75	4,970	21,8340
351,75	4,970	22,3553
351,74	4,971	22,5097
351,75	4,970	22,2670
351,77	4,970	22,2491
351,77	4,970	22,2144
351,78	4,969	22,3758
351,82	4,969	22,2025
351,82	4,970	22,2012
351,82	4,969	22,1054
351,85	4,969	22,1064
351,86	4,970	22,4329
351,88	4,970	22,0497
351,96	3,879	22,0433
351,99	3,879	22,1144
351,99	3,879	22,0044
352,02	3,879	21,9758
352,03	3,879	22,4084
352,04	3,878	21,9369
352,03	3,878	22,0185
352,02	3,878	21,9581
352,04	3,878	21,9524
352,04	3,879	22,0022
352,06	3,879	22,1673
352,06	3,879	22,4728
352,07	3,879	22,2800
352,06	3,879	21,9862
352,08	3,878	22,2571
352,04	2,557	21,9061
352,03	2,556	21,9145
352,02	2,556	22,2753
351,99	2,555	22,1888
351,99	2,555	21,8912

(continuation)

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
351,97	2,554	21,9026
351,97	2,553	21,7930
351,93	2,551	21,8451
351,91	2,551	21,9770
351,92	2,550	21,9344
351,89	2,550	22,2042
351,86	2,550	22,1707
351,88	2,549	21,8871
351,85	2,548	22,1807
351,47	1,345	22,0498
351,48	1,345	21,7737
351,48	1,345	21,9721
351,47	1,346	21,7102
351,50	1,345	21,9739
351,49	1,345	21,7950
351,49	1,345	21,6076
351,48	1,346	21,9627
351,50	1,345	21,8698
351,50	1,346	22,1216
351,51	1,345	21,9390
351,53	1,346	21,6473
351,52	1,346	21,7794
351,53	1,347	22,0013
351,54	1,347	22,0490
333,74	4,742	20,4102
333,71	4,741	20,5647
333,68	4,741	20,4574
333,71	4,740	20,2445
333,69	4,739	20,5568
333,69	4,739	20,5134
333,68	4,738	20,2967
333,67	4,737	20,5482
333,63	4,737	20,3173
333,64	4,736	20,0618
333,67	4,736	20,2817
333,67	4,736	20,2152
333,66	4,736	20,4504
333,67	4,735	20,5771
333,11	3,531	20,2673
333,09	3,530	20,2830
333,11	3,531	20,1321
333,09	3,530	20,3061
333,13	3,530	20,0635
333,11	3,530	20,3496
333,11	3,530	20,1179
333,09	3,530	20,3743
333,13	3,530	20,3243
333,14	3,530	20,2629
333,16	3,530	20,3460
333,17	3,530	20,1904

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
333,16	3,530	20,2596
333,17	3,531	20,1047
333,18	3,531	20,1045
333,22	2,499	20,1005
333,22	2,499	19,7838
333,23	2,499	19,9884
333,28	2,500	20,1190
333,29	2,500	20,1612
333,32	2,501	20,0927
333,34	2,501	20,1616
333,39	2,502	20,1628
333,38	2,501	20,1751
333,40	2,502	20,1129
333,43	2,503	20,2182
333,43	2,503	20,3220
333,41	2,503	20,1183
333,42	2,504	20,1890
333,44	2,503	20,2518
333,60	1,311	20,2219
333,64	1,312	19,9470
333,68	1,312	19,8303
333,74	1,313	20,1371
333,79	1,314	20,1901
333,77	1,314	20,1901
333,75	1,314	19,9970
333,71	1,315	19,9395
333,71	1,315	20,4574
333,69	1,315	19,9581
333,69	1,316	19,9103
333,68	1,316	20,1028
333,67	1,317	20,3207
333,69	1,317	20,2006
333,68	1,316	20,2347
314,64	4,660	18,4524
314,64	4,660	18,3675
314,62	4,660	18,4040
314,62	4,660	18,5065
314,61	4,659	18,6707
314,59	4,659	18,6471
314,59	4,658	18,6036
314,60	4,658	18,5695
314,55	4,657	18,5932
314,60	4,657	18,8322
314,61	4,657	18,4392
314,59	4,657	18,4691
314,62	4,656	18,6124
314,58	4,655	18,2661
314,58	4,655	18,4519
314,56	4,654	18,5314
314,59	3,510	18,5140

(continuation)

T [K]	P [bar]	λ [mW.m⁻¹.K⁻¹]
314,58	3,510	18,4379
314,60	3,510	18,3846
314,62	3,510	18,6749
314,61	3,510	18,4422
314,61	3,511	18,3568
314,61	3,511	18,2913
314,62	3,510	18,4820
314,62	3,511	18,2142
314,64	3,511	18,3112
314,89	2,519	18,2621
314,90	2,520	18,2597
314,91	2,520	18,2171
314,98	2,521	18,5417
314,99	2,521	18,3879
315,03	2,522	18,1485
315,06	2,521	18,3487
315,06	2,523	18,2843
315,08	2,523	18,0948
315,09	2,524	18,3407
315,28	1,314	18,2116
315,37	1,316	18,1145
315,42	1,317	18,3954
315,44	1,317	18,2860
315,45	1,318	18,3630
315,49	1,318	18,4020
315,52	1,319	18,1270
315,53	1,319	18,2392
315,53	1,320	18,3056
316,54	1,322	18,2472

Table A.3 Results obtained for the mixture 50.76% X1+49.24% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
373,32	5,274	25,2579
373,33	5,273	25,4249
373,32	5,272	25,2658
373,32	5,272	25,2435
373,32	5,272	25,3252
373,30	5,272	25,3602
373,31	5,272	25,3844
373,34	5,273	25,2924
373,36	5,271	25,5726
373,38	5,271	25,3642
373,48	4,367	25,1702
373,51	4,367	25,3260
373,54	4,368	25,5512
373,54	4,367	25,4050
373,56	4,367	25,4199
373,59	4,367	25,2881
373,59	4,368	25,6041
373,61	4,368	25,5743
373,63	4,368	25,5122
373,62	4,367	25,3137
373,62	4,367	25,4913
372,57	2,823	25,0582
372,59	2,822	24,9545
372,59	2,823	24,8685
372,60	2,823	24,9338
372,59	2,823	25,2327
372,62	2,824	25,1791
372,61	2,824	24,9925
372,63	2,824	25,2988
372,67	2,825	24,9860
372,67	2,827	25,2551
372,85	2,508	25,0417
372,88	2,509	25,2795
372,89	2,510	24,7868
372,90	2,509	24,6330
372,91	2,510	25,0209
372,93	2,511	25,0985
372,96	2,511	25,0743
372,99	2,511	25,1333
373,00	2,512	25,0853
373,02	2,512	25,3478
373,06	2,512	25,1078
373,17	2,015	25,2835
373,17	2,016	25,0483
373,19	2,016	25,4009
373,19	2,017	25,3037
373,23	2,018	25,3607
373,27	2,019	25,1282
373,30	2,018	25,0973
373,35	2,018	25,3537
373,35	2,017	25,2779
373,35	2,018	25,3316

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
373,49	1,312	25,4094
373,52	1,312	25,2056
373,52	1,312	25,3098
373,49	1,312	25,3701
373,52	1,312	25,2768
373,51	1,312	25,3998
373,51	1,310	25,2824
373,53	1,309	25,2956
373,53	1,309	25,2829
351,73	4,543	23,0433
351,74	4,543	23,0565
351,73	4,543	22,8611
351,68	4,543	22,9825
351,66	4,543	22,8692
351,65	4,542	22,7645
351,65	4,542	22,9822
351,62	4,540	22,9912
351,62	4,540	23,2877
351,62	4,539	22,7496
351,64	3,468	22,7886
351,63	3,468	22,8324
351,62	3,468	22,7763
351,63	3,468	22,6941
351,62	3,468	22,9286
351,63	3,467	22,8775
351,66	3,467	22,9543
351,65	3,467	22,6189
351,68	3,467	22,8893
351,72	3,467	22,7600
351,86	2,520	22,8581
351,86	2,520	22,9934
351,85	2,520	22,8769
351,86	2,521	22,8265
351,90	2,521	23,0494
351,91	2,522	22,9813
351,94	2,523	22,7757
351,99	2,523	22,6964
352,02	2,523	22,7169
352,05	2,524	22,9980
352,13	1,328	23,0167
352,12	1,328	22,9618
352,15	1,329	22,7084
352,18	1,329	22,9419
352,19	1,329	22,8847
352,24	1,330	22,7239
352,26	1,330	22,9574
352,27	1,330	23,0636
352,28	1,331	22,8003
352,28	1,331	22,9451
352,34	1,333	22,8663
352,39	1,333	23,2848

(continuation)

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
352,40	1,334	22,7798
352,43	1,335	22,8171
352,43	1,335	22,7639
352,48	1,335	23,2500
352,50	1,335	22,8252
352,48	1,331	22,8670
352,49	1,330	22,8815
333,71	1,243	20,9943
333,68	1,243	20,7094
333,72	1,242	20,5515
333,71	1,242	20,4870
333,70	1,243	20,4200
333,71	1,243	20,4715
333,69	1,243	20,5159
333,74	1,245	20,7546
333,73	1,245	20,6072
333,72	1,246	21,0601
333,75	4,688	20,9851
333,75	4,687	20,5073
333,74	4,687	20,8338
333,75	4,686	20,8519
333,76	4,686	21,1190
333,79	4,686	20,7111
333,84	4,686	21,1469
333,85	4,686	20,8518
333,86	4,686	20,6679
333,87	4,686	21,3762
334,01	3,206	20,7759
334,03	3,206	20,8711
334,03	3,206	21,0445
334,04	3,206	20,9130
334,07	3,206	21,0695
334,13	3,206	21,0234
334,14	3,207	21,0868
334,16	3,207	20,9848
334,18	3,207	20,8390
334,22	3,207	20,8989
334,18	2,159	20,7349
334,16	2,158	20,6730
334,14	2,158	20,9591
334,12	2,157	20,7373
334,13	2,155	20,4396
334,11	2,153	20,6193
334,08	2,152	20,6090
334,05	2,152	20,6409
334,04	2,152	20,7119
334,02	2,151	20,6672
314,66	4,818	18,7879
314,65	4,818	18,7756
314,65	4,819	18,9565

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
314,62	4,818	18,8251
314,62	4,817	18,7888
314,62	4,816	18,9806
314,59	4,816	18,8706
314,61	4,815	18,8228
314,59	4,815	18,8122
314,58	4,815	18,8024
314,63	3,526	18,8265
314,65	3,526	18,6235
314,66	3,526	18,7980
314,63	3,526	18,5248
314,63	3,526	18,5519
314,68	3,527	18,8848
314,70	3,527	18,6452
314,69	3,527	18,5517
314,70	3,527	18,6595
314,69	3,526	18,6231
314,71	2,544	18,6963
314,70	2,545	18,7228
314,69	2,545	18,7271
314,74	2,545	18,6862
314,78	2,545	18,6164
314,78	2,546	18,5210
314,78	2,546	18,7654
314,79	2,546	18,5078
314,80	2,546	18,7204
314,79	2,546	18,7743
314,85	1,338	18,6276
314,87	1,339	18,4389
314,89	1,339	18,1834
314,91	1,339	18,4365
314,91	1,340	18,6438
314,93	1,341	18,4784
314,92	1,341	18,5862
314,96	1,342	18,3608
314,96	1,342	18,5238
315,06	1,344	18,3862

Table A.4 Results obtained for the mixture 77.12% X1+22.88% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
372,51	4,751	25,8634
372,51	4,751	26,0706
372,48	4,749	25,8066
372,48	4,749	25,8340
372,46	4,749	26,0857
372,46	4,748	25,7340
372,46	4,747	25,8542
372,47	4,747	26,0486
372,48	4,746	26,0707
372,48	4,746	25,7633
372,55	3,583	25,9209
372,56	3,583	25,9666
372,55	3,583	25,7156
372,52	3,582	25,7450
372,52	3,582	25,9131
372,54	3,581	25,7684
372,51	3,581	25,9612
372,50	3,580	25,6713
372,49	3,580	26,4264
372,50	3,579	25,7329
372,61	2,560	26,0954
372,60	2,560	25,7324
372,57	2,559	25,8528
372,56	2,559	25,7017
372,53	2,559	25,7340
372,51	2,558	25,7666
372,51	2,558	25,7140
372,50	2,558	25,6527
372,52	2,558	26,3215
372,52	2,558	25,6009
372,52	2,558	26,0730
372,51	2,558	25,8931
372,51	2,557	26,0659
372,50	2,557	25,8810
372,49	2,556	25,8091
372,50	1,410	25,6746
372,47	1,409	25,8802
372,42	1,409	25,8635
372,43	1,410	25,8395
372,41	1,410	25,8321
372,41	1,410	25,8327
372,42	1,411	25,9400
372,44	1,412	25,6295
372,47	1,412	25,5361
372,48	1,412	25,5955
351,35	4,571	22,8216
351,34	4,571	23,2894
351,36	4,571	23,0471
351,37	4,570	23,0141
351,38	4,570	23,1136
351,35	4,570	23,3508
351,35	4,569	23,3501

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
351,31	4,569	23,0884
351,30	4,568	23,0478
351,33	4,568	23,4073
351,29	3,558	23,0039
351,32	3,558	23,1282
351,31	3,557	22,9884
351,32	3,557	22,9572
351,32	3,557	23,0273
351,32	3,557	23,1388
351,33	3,557	22,9676
351,34	3,557	23,2371
351,33	3,556	23,2509
351,35	3,555	23,2214
351,31	2,573	23,1574
351,30	2,573	23,1583
351,31	2,573	22,9632
351,29	2,573	23,1988
351,30	2,574	23,2065
351,31	2,574	23,0667
351,30	2,574	23,1114
351,30	2,574	22,9158
351,29	2,574	22,9638
351,33	1,328	22,7164
351,34	1,329	22,7799
351,33	1,330	22,7234
351,36	1,329	22,8063
351,35	1,329	22,6873
351,36	1,329	22,6249
351,37	1,330	22,9902
351,37	1,331	22,9611
351,38	1,331	22,8499
351,38	1,331	23,0399
333,45	4,583	21,0477
333,46	4,583	20,8939
333,44	4,583	20,8387
333,40	4,582	20,9074
333,37	4,581	20,8640
333,36	4,581	21,1227
333,36	4,580	21,0258
333,36	4,580	21,0180
333,38	4,580	21,0175
333,40	4,580	20,7409
333,38	3,535	20,8177
333,39	3,536	20,7649
333,41	3,536	20,9084
333,40	3,536	20,6886
333,38	3,536	21,0854
333,38	3,536	20,8995
333,40	3,536	20,7362
333,39	3,535	20,8809
333,40	3,534	20,6978
333,38	3,535	20,5811

(continuation)

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
333,40	2,502	20,6268
333,37	2,501	20,8429
333,38	2,501	20,5505
333,33	2,500	20,9019
333,33	2,501	20,8638
333,34	2,501	20,7159
333,34	2,500	20,7237
333,37	2,501	20,4743
333,40	2,501	20,6124
333,43	2,502	20,6932
333,54	1,327	20,5392
333,56	1,327	20,5620
333,56	1,328	20,4887
333,56	1,328	20,6194
333,59	1,329	20,6507
333,58	1,329	20,5081
333,59	1,330	20,1655
333,63	1,330	20,6325
333,65	1,331	20,5588
333,67	1,331	20,2590
314,42	4,430	18,5961
314,41	4,429	18,5367
314,42	4,428	18,7135
314,39	4,428	18,7233
314,36	4,427	18,9521
314,37	4,427	18,7601
314,37	4,426	18,6667
314,34	4,425	18,5077
314,35	4,425	18,6929
314,39	4,425	18,6724
314,43	3,578	18,6396
314,41	3,578	18,6349
314,39	3,577	18,5718
314,41	3,577	18,6774
314,45	3,578	18,5761
314,50	3,578	18,6903
314,54	3,579	18,7679
314,55	3,579	18,6255
314,53	3,579	18,7367
314,54	3,579	18,5719
314,65	2,556	18,2385
314,68	2,556	18,5541
314,68	2,556	18,8755
314,71	2,557	18,8500
314,74	2,558	18,5488
314,76	2,559	18,5554
314,78	2,559	18,5445
314,87	2,560	18,6721
314,89	2,560	18,3892
314,91	2,560	18,5107

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
314,94	1,319	18,6538
314,93	1,319	18,4782
314,92	1,319	18,4030
314,92	1,319	18,1160
314,90	1,320	18,2996
314,89	1,320	18,3427
314,90	1,320	18,4805
314,92	1,320	18,5910
314,92	1,321	18,3733
314,93	1,321	18,6245
314,94	1,321	18,5116

Table A.5 Results obtained for the mixture 20.42%X2+79.58% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
372,85	5,107	23,4396
372,84	5,106	23,0647
372,86	5,106	23,7442
372,85	5,106	23,4228
372,86	5,107	23,6804
372,86	5,107	23,2854
372,88	5,107	23,6197
372,86	5,107	23,4094
372,88	5,108	23,0251
372,88	5,108	23,4534
372,90	5,109	23,6305
372,92	5,109	23,3700
372,92	5,109	23,6720
373,04	4,138	23,6949
372,99	4,137	23,3034
372,97	4,137	23,3079
372,93	4,136	23,4707
372,91	4,136	23,3895
372,88	4,135	23,3681
372,88	4,134	23,3414
372,87	4,134	23,7322
372,87	4,132	23,5543
372,88	4,132	23,7573
372,93	3,326	23,7744
372,92	3,326	23,5478
372,90	3,327	23,2529
372,85	3,326	23,2507
372,86	3,326	22,9112
372,88	3,327	23,4010
372,85	3,327	23,1773
372,84	3,327	23,5946
372,80	3,326	23,5144
372,83	3,326	23,0473
372,84	3,326	23,5615
372,86	3,326	23,5039
372,84	2,411	23,3806
372,81	2,411	23,5059
372,81	2,410	23,4025
372,78	2,410	23,2289
372,77	2,410	23,4678
372,77	2,411	23,3234
372,78	2,411	23,3069
372,77	2,410	23,2705
372,78	2,412	23,3136
372,80	2,413	23,2383
364,00	4,928	22,2986
363,93	4,926	22,6346
363,93	4,926	22,6223
363,90	4,925	22,5783
363,89	4,925	22,4561
363,88	4,925	22,3686
363,84	4,924	22,4895

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
363,83	4,923	22,6301
363,85	4,924	22,4613
363,83	4,923	22,6012
363,87	3,999	22,3168
363,87	3,999	22,5407
363,87	3,998	22,5523
363,84	3,998	22,4253
363,82	3,997	22,4997
363,81	3,997	22,4407
363,83	3,997	22,5807
363,86	3,997	22,4130
363,88	3,997	22,3009
363,53	3,237	22,4053
363,53	3,237	22,6431
363,56	3,237	22,6128
363,59	3,236	22,2328
363,57	3,235	22,5681
363,56	3,235	22,5751
363,58	3,236	22,3917
363,57	3,236	22,3206
363,58	3,235	22,3671
363,58	3,235	22,4812
352,12	4,822	21,6110
352,11	4,820	21,4801
352,11	4,817	21,7628
352,08	4,812	21,4469
352,08	4,811	21,4240
352,08	4,809	21,5552
352,07	4,809	21,3872
352,13	4,806	21,3261
352,15	4,806	21,4738
352,14	4,805	21,2825
351,63	3,844	21,3105
351,61	3,845	21,1435
351,59	3,844	21,2414
351,54	3,844	21,2018
351,52	3,844	21,3479
351,53	3,843	21,2014
351,53	3,842	21,1765
351,51	3,843	21,3110
351,51	3,843	21,3252
351,50	3,842	21,1376
351,98	3,137	21,3935
351,92	3,134	21,3344
351,88	3,132	21,2268
351,85	3,131	21,2438
351,80	3,130	21,3648
351,80	3,129	21,1222
351,77	3,128	21,2379
351,77	3,128	21,4152
351,75	3,127	21,4611
351,74	3,126	21,1976

(continuation)

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
352,05	2,280	21,4630
352,02	2,279	21,2515
352,01	2,277	21,1756
351,97	2,277	21,3455
351,94	2,276	21,0531
351,92	2,275	21,0682
351,93	2,274	21,3125
351,95	2,274	21,2510
352,03	2,273	21,1024
352,07	2,272	21,0021
333,93	4,513	19,7013
333,91	4,512	19,7439
333,91	4,511	19,8163
333,87	4,510	19,4288
333,83	4,508	19,1920
333,81	4,508	19,5604
333,82	4,507	19,4184
333,80	4,506	19,6895
333,79	4,505	19,7925
333,76	4,504	19,6915
333,51	3,600	19,6386
333,53	3,600	19,3507
333,53	3,599	19,3282
333,54	3,600	19,5091
333,52	3,599	19,3253
333,50	3,599	19,5395
333,48	3,599	19,6114
333,46	3,598	19,3305
333,48	3,598	19,3813
333,47	3,597	19,5164
333,45	2,930	19,5391
333,47	2,930	19,3656
333,43	2,929	19,5340
333,43	2,929	19,5024
333,41	2,929	19,4650
333,39	2,929	19,3118
333,39	2,928	19,6878
333,39	2,928	19,6270
333,38	2,928	19,6234
333,39	2,928	19,7788
333,39	2,928	19,7432
333,48	2,126	19,5837
333,44	2,125	19,1326
333,45	2,126	19,3897
333,45	2,125	19,4042
333,44	2,125	19,5244
333,43	2,125	19,4104
333,44	2,125	19,4361
333,41	2,124	19,2136
333,43	2,125	19,3797
333,42	2,125	19,0759

Table A.6 Results obtained for the mixture 45.88%X2+54.12% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
384,31	5,422	24,9628
384,31	5,423	24,9161
384,35	5,421	24,9352
384,39	5,421	25,1952
384,38	5,421	25,0812
384,42	5,422	24,9908
384,44	5,422	25,1921
384,44	5,421	24,8454
384,48	4,095	24,8518
384,45	4,096	24,7817
384,42	4,095	24,9976
384,37	4,094	24,7367
384,31	4,092	24,9740
384,28	4,091	24,7957
384,30	4,089	24,8233
384,34	4,089	24,7800
384,35	4,090	24,8171
384,38	4,089	24,7060
384,38	4,089	25,1078
384,29	3,324	24,7917
384,29	3,325	24,8068
384,27	3,325	24,9080
384,27	3,325	24,8789
384,25	3,326	24,7029
384,28	3,326	25,0102
384,28	3,327	24,7592
384,34	2,634	24,7532
384,33	2,633	24,6125
384,30	2,633	24,9544
384,21	2,633	24,6144
384,19	2,632	25,0328
384,21	2,633	24,6690
384,21	2,632	24,5943
384,23	2,633	24,7577
384,20	2,633	24,8089
373,33	5,174	23,9401
373,33	5,172	23,5972
373,26	5,170	23,8588
373,23	5,168	23,7452
373,17	5,166	23,4297
373,09	5,161	23,4738
373,04	5,160	23,2905
373,01	5,158	23,6688
372,98	5,154	23,5500
372,94	5,152	23,4351
373,42	4,043	23,5616
373,41	4,041	23,6113
373,37	4,040	23,6113
373,30	4,037	23,5928
373,30	4,037	23,7153
373,29	4,036	23,8564
373,28	4,036	23,4859

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
373,26	4,035	23,7052
373,26	4,034	23,6747
373,23	4,033	23,5567
373,49	3,222	23,3943
373,50	3,222	23,5390
373,47	3,221	23,6050
373,47	3,221	23,5652
373,48	3,221	23,2719
373,46	3,220	23,6260
373,45	3,220	23,2936
373,43	3,220	23,6519
373,41	3,220	23,4412
373,39	3,220	23,1913
373,50	2,549	23,3924
373,47	2,548	23,1458
373,46	2,549	23,3408
373,45	2,549	23,3329
373,45	2,549	23,5262
373,47	2,549	23,2170
373,49	2,549	23,4831
373,52	2,550	23,4131
373,53	2,551	23,4963
373,56	2,551	23,1833
364,17	4,941	22,7902
364,15	4,941	22,7387
364,12	4,939	22,4990
364,09	4,938	22,7065
364,08	4,937	22,6794
364,10	4,936	22,6587
364,07	4,935	22,5416
364,07	4,934	22,6769
364,07	4,933	22,5448
364,06	4,933	22,5204
364,18	3,921	22,7789
364,16	3,923	22,7051
364,16	3,926	22,8019
364,17	3,930	22,1837
364,15	3,933	22,5661
364,11	3,936	22,4660
364,11	3,939	22,3850
364,11	3,942	22,4037
364,12	3,946	22,4871
364,14	3,948	22,4705
363,76	3,112	22,2540
363,83	3,113	22,5283
363,88	3,115	22,4740
363,91	3,115	22,6073
363,91	3,115	22,3615
363,90	3,115	22,2884
363,88	3,115	22,8853
363,88	3,115	22,6246
363,85	3,116	22,1442

(Continuation)

T [K]	P [bar]	λ [mW.m⁻¹.K⁻¹]
363,86	3,116	22,5716
358,70	4,833	22,3865
358,71	4,833	21,8982
358,73	4,834	21,9940
358,74	4,834	21,8465
358,77	4,835	21,8920
358,77	4,835	22,1179
358,79	4,836	21,8991
358,80	4,836	21,9225
358,79	4,837	21,9684
358,82	4,837	22,1949
358,76	3,890	22,0175
358,74	3,890	22,0528
358,74	3,889	21,9285
358,72	3,889	22,1861
358,72	3,889	22,0331
358,68	3,888	21,9766
358,71	3,888	22,0921
358,72	3,888	21,8992
358,73	3,889	21,8439
358,75	3,889	21,9408
358,77	2,416	21,8942
358,69	2,415	21,8366
358,63	2,415	21,6369
358,60	2,414	21,7342
358,62	2,414	21,7845
358,68	2,416	21,9855
358,78	2,416	21,7880
358,75	2,416	21,8864

Table A.7 Results obtained for the mixture 78.10%X2+21.90% X3.

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
392,56	4,135	25,9701
392,59	4,134	25,7254
392,77	4,133	25,6510
392,79	4,133	26,1829
392,82	4,133	26,0500
392,82	4,132	25,7402
392,83	4,132	25,7804
392,82	4,131	25,9132
392,82	4,130	25,7177
392,84	4,129	25,7024
392,92	2,932	25,6147
392,81	2,931	26,1479
392,69	2,931	26,0514
392,62	2,929	25,9847
392,57	2,929	25,7170
392,53	2,928	26,1680
392,54	2,927	25,8284
392,54	2,926	26,0098
392,58	2,925	25,9797
392,60	2,925	25,8289
392,94	2,895	25,9820
392,71	2,470	25,7880
392,66	2,469	26,1587
392,54	2,469	25,7393
392,51	2,468	25,4822
392,50	2,468	25,7696
392,48	2,468	25,6324
392,46	2,468	25,3150
392,46	2,468	25,5743
392,42	2,468	25,6248
383,88	4,976	24,7733
383,88	4,975	24,6913
383,85	4,972	24,5846
383,80	4,970	24,8576
383,73	4,968	25,1715
383,72	4,966	24,7051
383,72	4,964	24,9410
383,69	4,963	24,6524
383,68	4,962	25,0034
383,68	4,960	24,6361
383,33	4,073	24,6149
383,34	4,067	24,8405
383,33	4,065	24,9385
383,33	4,064	24,3860
383,33	4,062	24,5149
383,33	4,061	24,3795
383,33	4,060	24,9113
383,33	4,060	24,8851
383,35	4,060	24,5885
383,45	2,828	24,6659
383,41	2,825	24,8420
383,40	2,823	24,6089

T [K]	P [bar]	λ [mW.m ⁻¹ .K ⁻¹]
383,39	2,821	24,6107
383,43	2,819	24,6551
383,46	2,819	24,9225
383,40	2,818	24,5640
383,34	2,817	24,8413
383,32	2,817	24,7257
383,33	2,817	24,5533
383,62	2,392	24,7724
383,56	2,392	24,6702
383,53	2,393	24,7524
383,52	2,393	24,7209
383,54	2,393	24,8878
383,57	2,393	24,6183
383,60	2,395	24,4042
383,64	2,394	24,7542
383,70	2,397	24,6376
383,75	2,397	25,0768
374,99	4,731	23,6807
374,91	4,728	23,7389
374,87	4,726	23,8147
374,87	4,723	23,6844
374,83	4,721	23,8450
374,81	4,719	23,4765
374,76	4,716	23,4002
374,75	4,714	23,6759
374,71	4,712	23,7878
374,68	4,710	23,2004
374,78	3,913	23,6340
374,81	3,913	23,4486
374,80	3,913	23,6472
374,77	3,913	23,8777
374,73	3,913	23,5893
374,75	3,913	23,4940
374,76	3,913	23,3508
374,77	3,913	23,3445
374,81	3,914	23,9012
374,85	3,914	23,4072
374,85	3,914	23,7809
374,45	2,726	23,3327
374,55	2,725	23,4862
374,57	2,725	23,4075
374,61	2,724	23,4526
374,63	2,724	23,6937
374,65	2,723	23,3990
374,68	2,722	23,5942
374,67	2,721	23,4498
374,69	2,721	23,4076
374,67	2,721	23,5827
374,67	2,720	23,5418
364,60	4,551	22,7719
364,60	4,550	22,6319
364,58	4,550	22,2058

(continuation)

T [K]	P [bar]	λ [mW.m⁻¹.K⁻¹]
364,55	4,549	22,0788
364,54	4,547	22,5018
364,51	4,547	22,3661
364,50	4,546	22,2643
364,52	4,547	22,3317
364,51	4,547	22,2998
364,53	4,546	22,1790
364,53	3,696	22,5781
364,50	3,693	22,3579
364,45	3,692	22,2939
364,45	3,690	22,4421
364,49	3,688	22,4956
364,53	3,687	22,4311
364,60	3,686	22,3031
364,63	3,684	22,5067
364,57	3,684	22,1388
364,54	3,682	22,1947
364,58	2,606	22,2150
364,58	2,610	22,0282
364,60	2,614	22,1286
364,62	2,618	22,0841
364,62	2,623	22,3461
364,56	2,629	22,3117
364,54	2,632	22,3327
364,53	2,633	22,3385
364,51	2,635	22,3496
364,51	2,635	22,3647

Appendix B

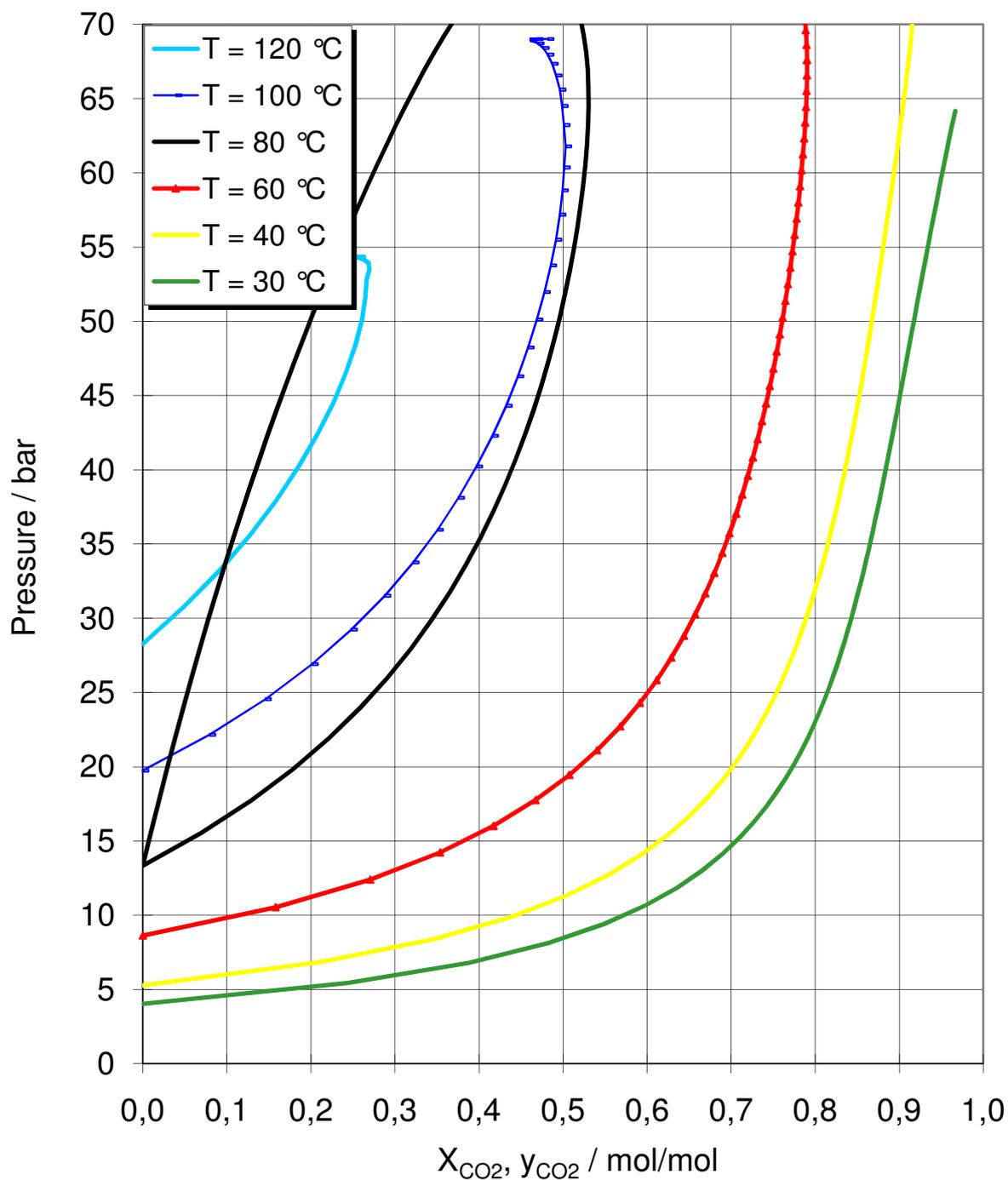


Figure B.1 Vapor-Liquid Equilibrium (VLE) diagram for the mixture constituted by X1 and X3.

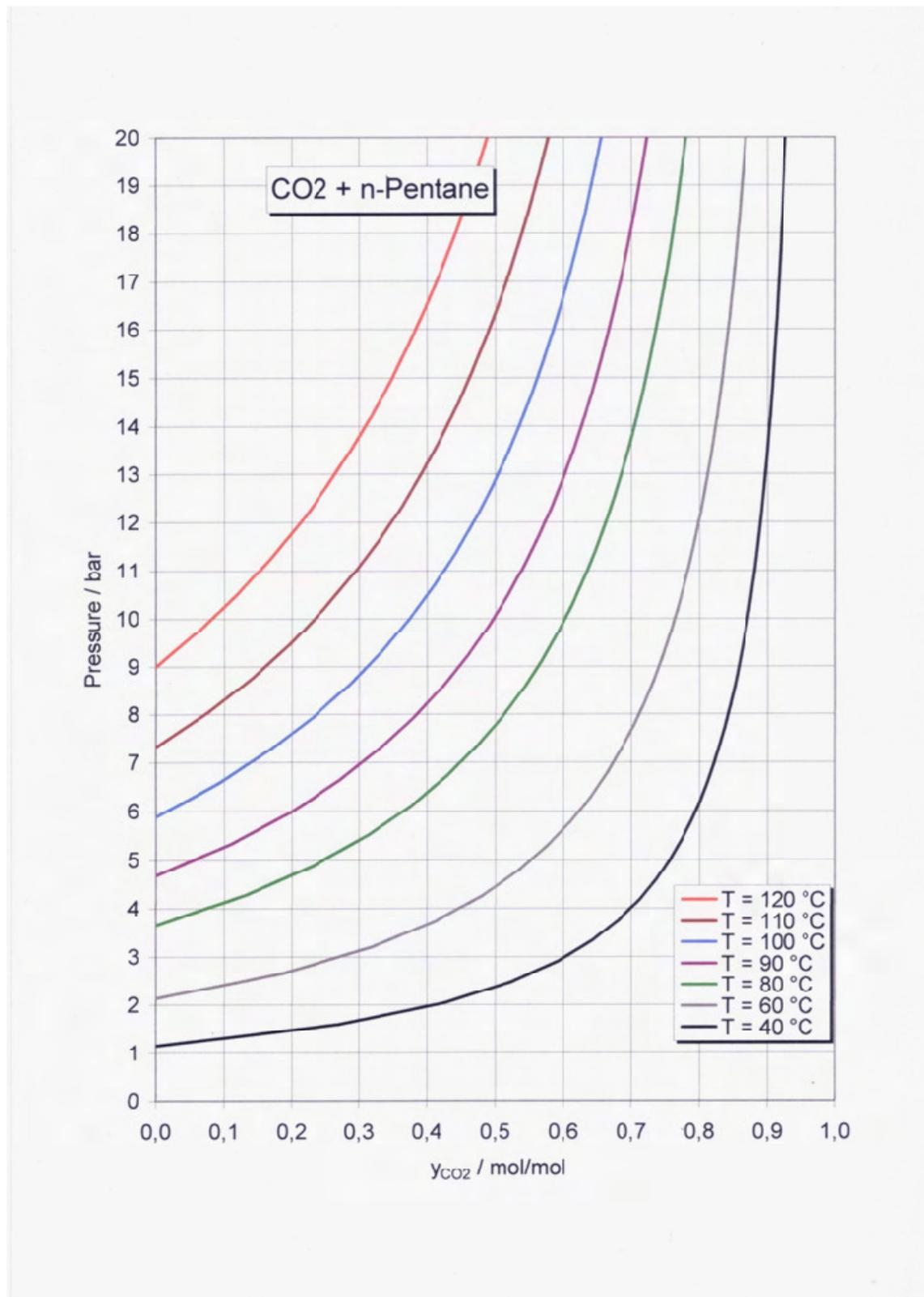


Figure B.2 Vapor-Liquid Equilibrium (VLE) diagram for the mixture constituted by X₂ and X₃.

Appendix C

Pressure calibration (calibration of the sensor pressure)

The calibration of the sensor pressure should be made periodically. In the present work the calibration was initialized with the connection of the calibrator machine directly to the cell. Vacuum was done and the calibration parameters on the parameter data file of the lambda program were changed until the pressure that was being calculated with lambda program was the same as were shown in the calibration machine. Only vacuum was used for the calibration because in this case the pressure inside of the cell is constant. For higher pressures the pressure inside of the cell is always changing and the procedure becomes complicated to perform.