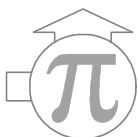


DISCLAIMER

THE INFORMATION PROVIDED IN THIS DOCUMENT HAS BEEN COMPILED CAREFULLY AND THE CALCULATION METHODS PRESENTED ARE, TO THE BEST OF OUR KNOWLEDGE, EQUIVALENT IN ACCURACY TO THE ORIGINAL MEASURED AND PUBLISHED DATA CONSIDERED. THIS DOCUMENT IS MADE AVAILABLE AS IS. THE AUTHOR AND HIS FIRM, **M. CONDE ENGINEERING**, CANNOT BE HELD LIABLE IN WHATEVER MANNER FOR EVENTUAL CONSEQUENCES, DIRECT OR IMPLIED, OF THE USE OR MISUSE OF THE MATERIAL CONTAINED AND DESCRIBED HEREIN.



Fluid Properties

The mathematical calculation and simulation models of components used in HVAC&R equipment and plants require the knowledge of a large number of thermodynamic and transport properties of the fluids they handle. In a model conceived for design purposes, those properties must be calculated for real fluids, as stressed by Black (1986)¹. The fluids used may be undergoing a cyclic process, such as the operating fluid in a chiller or heat pump, or may be totally or partially recirculated as the source and sink fluids, mostly humid air, water or a brine. The thermodynamic and transport properties of operating fluids are required for the liquid and the vapour phases, and for the two-phase liquid + vapour region as well. Water and brine properties are mostly necessary for the liquid phase, although solid water (frost and ice) properties may as well be required when the source fluid is atmospheric air, or an ice producing heat pump, for example.

This document describes the equations necessary for the calculation of the thermophysical (thermodynamic + transport) properties of { ammonia + water } mixtures in a coherent manner, and gives the necessary parameters.

¹ Black, C. 1986. Importance of thermophysical data in process simulation, *Int. J. Thermophysics*, 7(4), 987-1002.

Contents

1.	NOMENCLATURE USED IN PROPERTY CALCULATIONS	1
2.	INTRODUCTION	2
3.	FUNDAMENTAL PARAMETERS OF THE PURE SUBSTANCES	3
4.	VAPOUR - LIQUID EQUILIBRIUM AND THERMODYNAMIC PROPERTIES	3
5.	SOLUTION CRITICAL TEMPERATURE AND PRESSURE	8
6.	SPECIFIC THERMAL CAPACITY OF SATURATED LIQUID SOLUTIONS AT CONSTANT PRESSURE	9
7.	THERMAL CONDUCTIVITY OF LIQUID SOLUTIONS	11
8.	DYNAMIC VISCOSITY OF LIQUID SOLUTIONS	14
9.	SURFACE TENSION OF THE SOLUTIONS	17
10.	LIQUID SOLUTION DENSITY	18
11.	MASS DIFFUSIVITY (AMMONIA VAPOUR INTO AQUEOUS SOLUTIONS OF AMMONIA)	21
12.	THERMAL CONDUCTIVITY OF SOLUTIONS IN THE VAPOUR PHASE	22
13.	DYNAMIC VISCOSITY OF SOLUTIONS IN THE VAPOUR PHASE	25
14.	DENSITY OF SATURATED SOLUTIONS IN THE VAPOUR PHASE	26
15.	SPECIFIC THERMAL CAPACITY OF SATURATED SOLUTIONS IN THE VAPOUR PHASE	28
APPENDIX A - THE IAPWS FORMULATION FOR THE THERMAL CONDUCTIVITY OF ORDINARY WATER SUBSTANCE FOR INDUSTRIAL USE		29
APPENDIX B - THE IAPWS FORMULATION FOR THE DYNAMIC VISCOSITY OF ORDINARY WATER SUBSTANCE FOR INDUSTRIAL USE		30
APPENDIX C - THE FENGHOUR ET AL. (1995) ⁴² METHOD FOR THE CALCULATION OF THE VISCOSITY OF AMMONIA		31
APPENDIX D - THE SIMPLE ABSORPTION CYCLE WITH THE MIXTURE {AMMONIA + WATER}		33
APPENDIX E - A GAX ABSORPTION CYCLE WITH THE MIXTURE {AMMONIA + WATER}		34

Thermophysical Properties of NH₃ + H₂O solutions for the industrial design of absorption refrigeration equipment

Dr Manuel R. Conde-Petit
M. CONDE ENGINEERING
Zurich - SWITZERLAND

1. NOMENCLATURE USED IN PROPERTY CALCULATIONS

Symbol	Description	Unit
T	Temperature	K
p	pressure	bar
x	molar fraction of NH ₃ in the liquid phase	-
y	molar fraction of NH ₃ in the vapour phase	-
h	specific enthalpy	kJ.kg ⁻¹
C_p	specific thermal capacity at constant pressure	kJ.kg ⁻¹ .K ⁻¹
D	mass diffusivity	m ² .s ⁻¹
θ	reduced temperature	-
τ	reduced temperature complement to unity	-
ξ	mass fraction of liquid NH ₃ in the liquid phase	-
ζ	mass fraction of NH ₃ in the vapour phase	-
ρ	density	kg.m ⁻³
λ	thermal conductivity	mW.m ⁻¹ .K ⁻¹
η	dynamic viscosity	μPa.s
σ	surface tension	mN.m ⁻¹
ψ	association factor (Wilke & Chang Ref. 49)	-
Δ	deviation	
Subscripts		
c	at the critical point	
G	relating to the gaseous or vapour phase	
L	relating to the liquid phase	
t	at the triple point	
b	at the normal boiling point (sea level atmospheric pressure)	
sol	relating to the solution	
m	mixture	

2. INTRODUCTION

The engineering calculation and simulation of absorption refrigeration systems require the availability of simple and efficient mathematical methods for the determination of thermophysical property values of the operating fluid (solution). Values of the thermophysical properties are necessary both at key points in the cycle and along the processes taking place in the various components. The graphical methods described in the classical works of Merkel & Bošnjaković (1929)², Altenkirch (1954)³ and Niebergall (1959)⁴ are suitable for the analysis of the simpler cycles (see Appendix D for schematic diagrams). They get cumbersome and difficult to use for calculations of more complex cycles, such as GAX (Generator-Absorber heat eXchange), where the diluted solution is also used as heat transfer fluid between the absorber and the generator (see Appendix E for schematic diagram). In these cases, numerical simulation of the processes is practically unavoidable.

The first patent for an absorption refrigeration system operating with {ammonia + water} was issued to the french engineer Ferdinand Carré in 1859, in France⁵, and in 1860 in the United States. Despite the long history (in terms of refrigeration systems) of this technology, data and methods of calculation of thermophysical properties for {ammonia + water} solutions, in particular for transport properties, are sparse and do not cover various regions important in the design of absorption refrigeration equipment. The increasing interest in the utilization of binary mixtures as operating fluids for power cycles, particularly the Kalina cycle, has led to a significative research effort on the properties of the {ammonia + water} mixture. The results of this effort are reflected in the availability of new property formulations. These cover as well regions of interest in the design of absorption refrigeration equipment.

The availability of new experimental data, especially of the thermodynamic properties of the mixture, have allowed the formulation of unified and conceptually simple equations based upon the Helmholtz^{6,7} or Gibbs^{8,9,10} free energies. The importance of the development work done in these new formulations is excellently demonstrated by the adoption of the formulations proposed in Tillner-Roth and Friend⁶ by the International Association for the Properties of Water and Steam (IAPWS)¹¹ for the calculation of power cycles operated with the {ammonia + water} mixture. With the simplicity of the concepts concur numerical calculation methods of the derived properties that are difficult to

² Merkel, F., F. Bošnjaković 1929. Diagramme und Tabellen zur Berechnung der Absorptions-Kältemaschinen, Verlag von Julius Springer, Berlin.

³ Altenkirch, E. 1954. Absorptions-Kältemaschinen, VEB Verlag Technik, Berlin.

⁴ Niebergall, W. 1959. Sorptions-Kältemaschinen, Handbuch der Kältetechnik, 7. Band, Herausgegeben von R. Plank, Springer-Verlag, Berlin.

⁵ Carré, F. 1859. French Patent 41958. Brévets d'Inventions, Tome 74, Paris 1871.

⁶ Tillner-Roth, R. 1997. Eine umfassende kanonische Zustandsgleichung für das Gemisch Wasser/Ammoniak, DKV-Tagungsbericht, 24(II.1), 184-197.

⁷ Tillner-Roth, R., D. G. Friend 1998. A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture {Ammonia + Water}, J. Phys. Chem. Ref. Data, 27(1), 63-96.

⁸ Ziegler, B. 1982. Wärmetransformation durch einstufige Sorptionsprozesse mit dem Stoffpaar Ammoniak - Wasser, Dissertation ETH Zürich Nr. 7070.

⁹ Ibrahim, O. M., S. A. Klein 1993. Thermodynamic Properties of Ammonia - Water Mixtures, ASHRAE Transactions, 99, 1495-1502.

¹⁰ El-Sayed, Y. M., M. Tribus 1985. Thermodynamic Properties of Water-Ammonia Mixtures - Theoretical Implementation for Use in Power Cycles Analysis, ASME-AES - Vol. 1 - Analysis of Energy Systems — Design and Operation, The Winter Annual Meeting of the ASME, Nov. 17-22, 89-95.

¹¹ IAPWS 2001. Guideline on the IAPWS Formulation 2001 for the Thermodynamic Properties of Ammonia-Water Mixtures, Gaithersburg, MD, USA.

apply to the industrial sizing practice and even to the numerical simulation and computer assisted design of components and equipment. On the other hand, there is an important deficit of reliable experimental data on properties essential to the sizing of components and processes of absorption refrigeration cycles, namely for viscosity, thermal conductivity, mass diffusivity and surface tension of the mixture.

The need for practical and precise enough methods of property calculation, and considering the experimental data and formulations available, has led to a careful review of the literature. This included checking of the original sources of experimental data, and the verification and reformulation, in several cases, of the methods proposed in the literature.

The calculation methods described in the following include thermodynamic and transport properties of the liquid and vapour phase of the mixture, and whenever necessary the calculation methods for the pure components as well.

3. FUNDAMENTAL PARAMETERS OF THE PURE SUBSTANCES

These are the values as used in the determination of the parameters for the equations described in the following. They differ in some cases from those adopted by the IAPWS, for example. They are kept for the sake of compatibility of all equations.

		H ₂ O	NH ₃
T _c	[K]	647.14	405.4
p _c	[bar]	220.64	113.336
ρ _c	[kg.m ⁻³]	322	225
M	[kg.kmol ⁻¹]	18.015 268	17.030 26

4. VAPOUR - LIQUID EQUILIBRIUM AND THERMODYNAMIC PROPERTIES

For the calculation of thermodynamic properties, both in the vapour and liquid phases, as well as the vapour-liquid equilibrium, the simplified formulation proposed by Pátek & Klomfar¹², described by the following equations and parameter tables, is used.

Equations

$$T(p,x) = T_0 \sum_i a_i (1 - x)^{m_i} \left[\ln \left(\frac{p_0}{p} \right) \right]^{n_i}$$

Parameters

i	m _i	n _i	a _i
1	0	0	+0.322 302 × 10 ¹
2	0	1	-0.384 206 × 10 ⁰
3	0	2	+0.460 965 × 10 ⁻¹
4	0	3	-0.378 945 × 10 ⁻²
5	0	4	+0.135 610 × 10 ⁻³
6	1	0	+0.487 755 × 10 ⁰
7	1	1	-0.120 108 × 10 ⁰
8	1	2	+0.106 154 × 10 ⁻¹
9	2	3	-0.533 589 × 10 ⁻³
10	4	0	+0.785 041 × 10 ¹
11	5	0	-0.115 941 × 10 ²
12	5	1	-0.523 150 × 10 ⁻¹
13	6	0	+0.489 596 × 10 ¹
14	13	1	+0.421 059 × 10 ⁻¹
T ₀ = 100 K			p ₀ = 2 MPa

¹² Pátek, J., J. Klomfar 1995. Simple functions for fast calculations of selected thermodynamic properties of the ammonia-water system, Int. J. Refrig., 18(4), 228-234.

Equations

$$T(p,y) = T_0 \sum_i a_i (1 - y)^{m_i/4} \left[\ln \left(\frac{p_0}{p} \right) \right]^{n_i}$$

$$y(P,x) = 1 - \exp \left[\ln(1-x) \sum_i a_i \left(\frac{p}{p_0} \right)^{m_i} x^{n_i/3} \right]$$

$$h_L(T,x) = h_0 \sum_i a_i \left(\frac{T}{T_0} - 1 \right)^{m_i} x^{n_i}$$

Parameters

i	m _i	n _i	a _i
1	0	0	+0.324 004 x 10 ¹
2	0	1	-0.395 920 x 10 ⁰
3	0	2	+0.435 624 x 10 ⁻¹
4	0	3	-0.218 943 x 10 ⁻²
5	1	0	-0.143 526 x 10 ¹
6	1	1	+0.105 256 x 10 ¹
7	1	2	-0.719 281 x 10 ⁻¹
8	2	0	+0.122 362 x 10 ²
9	2	1	-0.224 368 x 10 ¹
10	3	0	-0.201 780 x 10 ²
11	3	1	+0.110 834 x 10 ¹
12	4	0	+0.145 399 x 10 ²
13	4	2	+0.644 312 x 10 ⁰
14	5	0	-0.221 246 x 10 ¹
15	5	2	-0.756 266 x 10 ⁰
16	6	0	-0.135 529 x 10 ¹
17	7	2	+0.183 541 x 10 ⁰
T ₀ = 100 K			p ₀ = 2 MPa

i	m _i	n _i	a _i
1	0	0	+1.980 220 17 x 10 ¹
2	0	1	-1.180 926 69 x 10 ¹
3	0	6	+2.774 799 80 x 10 ¹
4	0	7	-2.886 342 77 x 10 ¹
5	1	0	-5.916 166 08 x 10 ¹
6	2	1	+5.780 913 05 x 10 ²
7	2	2	-6.217 367 43 x 10 ⁰
8	3	2	-3.421 984 02 x 10 ³
9	4	3	+1.194 031 27 x 10 ⁴
10	5	4	-2.454 137 77 x 10 ⁴
11	6	5	+2.915 918 65 x 10 ⁴
12	7	6	-1.847 822 90 x 10 ⁴
13	7	7	+2.348 194 34 x 10 ¹
14	8	7	+4.803 106 17 x 10 ³
p ₀ = 2 MPa			

i	m _i	n _i	a _i
1	0	1	-0.761 080 x 10 ¹
2	0	4	+0.256 905 x 10 ²
3	0	8	-0.247 092 x 10 ³
4	0	9	+0.325 952 x 10 ³
5	0	12	-0.158 854 x 10 ³
6	0	14	+0.619 084 x 10 ²
7	1	0	+0.114 314 x 10 ²
8	1	1	+0.118 157 x 10 ¹
9	2	1	+0.284 179 x 10 ¹
10	3	3	+0.741 609 x 10 ¹
11	5	3	+0.891 844 x 10 ³
12	5	4	-0.161 309 x 10 ⁴
13	5	5	+0.622 106 x 10 ³
14	6	2	-0.207 588 x 10 ³
15	6	4	-0.687 393 x 10 ¹
16	8	0	+0.350 716 x 10 ¹
h ₀ = 100 kJ/kg		T ₀ = 273.16 K	

Equations

$$h_G(T, y) = h_0 \sum_i a_i \left(1 - \frac{T}{T_0} \right)^{m_i} (1 - y)^{n_i/4}$$

Parameters

i	m _i	n _i	a _i
1	0	0	+0.128 827 x 10 ¹
2	1	0	+0.125 247 x 10 ⁰
3	2	0	-0.208 748 x 10 ¹
4	3	0	+0.217 696 x 10 ¹
5	0	2	+0.235 687 x 10 ¹
6	1	2	-0.886 987 x 10 ¹
7	2	2	+0.102 635 x 10 ²
8	3	2	-0.237 440 x 10 ¹
9	0	3	-0.670 155 x 10 ¹
10	1	3	+0.164 508 x 10 ²
11	2	3	-0.936 849 x 10 ¹
12	0	4	+0.842 254 x 10 ¹
13	1	4	-0.858 807 x 10 ¹
14	0	5	-0.277 049 x 10 ¹
15	4	6	-0.961 248 x 10 ⁰
16	2	7	+0.988 009 x 10 ⁰
17	1	10	+0.308 482 x 10 ⁰
h ₀ = 1000 kJ/kg			T ₀ = 324 K

Although the Pátek & Klomfar¹² equations are of completely empirical nature, they allow the determinations of the properties of the mixture with accuracy acceptable for industrial use for pressures below 30 bar. Their numerical solution is significantly simpler than that of the formulation recently adopted by the IAPWS based upon the fundamental equations developed by Tillner-Roth & Friend 1998⁷, and that developed by Ziegler 1982⁸. They are also easily solved both explicitly and implicitly. The diagrams in Figures 1 to 3 show examples of application of this set of equations. Figure 1 shows vapour-liquid equilibrium curves at 5 and 18 bar. Figure 2 depicts an Othmer diagram (also called PTX diagram) for pressures up to 30 bar while Figure 3 illustrates various isobars, isotherms and isosters on the enthalpy - concentration ($H - \xi$) diagram.

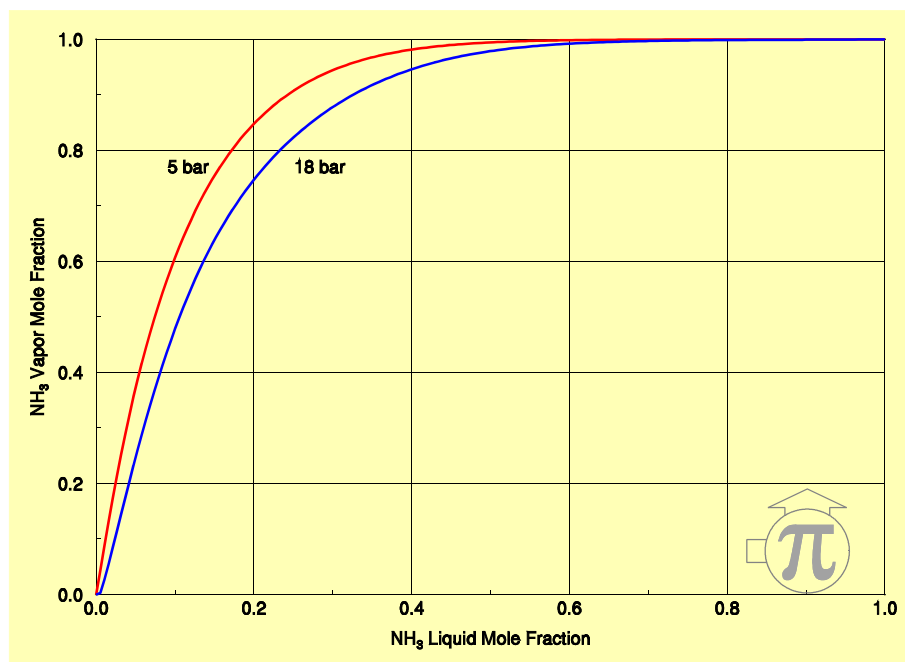


Fig. 1 - Vapour-liquid equilibrium curves at 5 and 18 bar.

Vapour-liquid equilibrium diagrams are useful in the determination of the theoretical number of stages in separation columns by the McCabe-Thiele¹³ method, while the $H - \xi$ diagram is used to the same effect and to general sizing by the Ponchon-Savarit¹⁴ method.

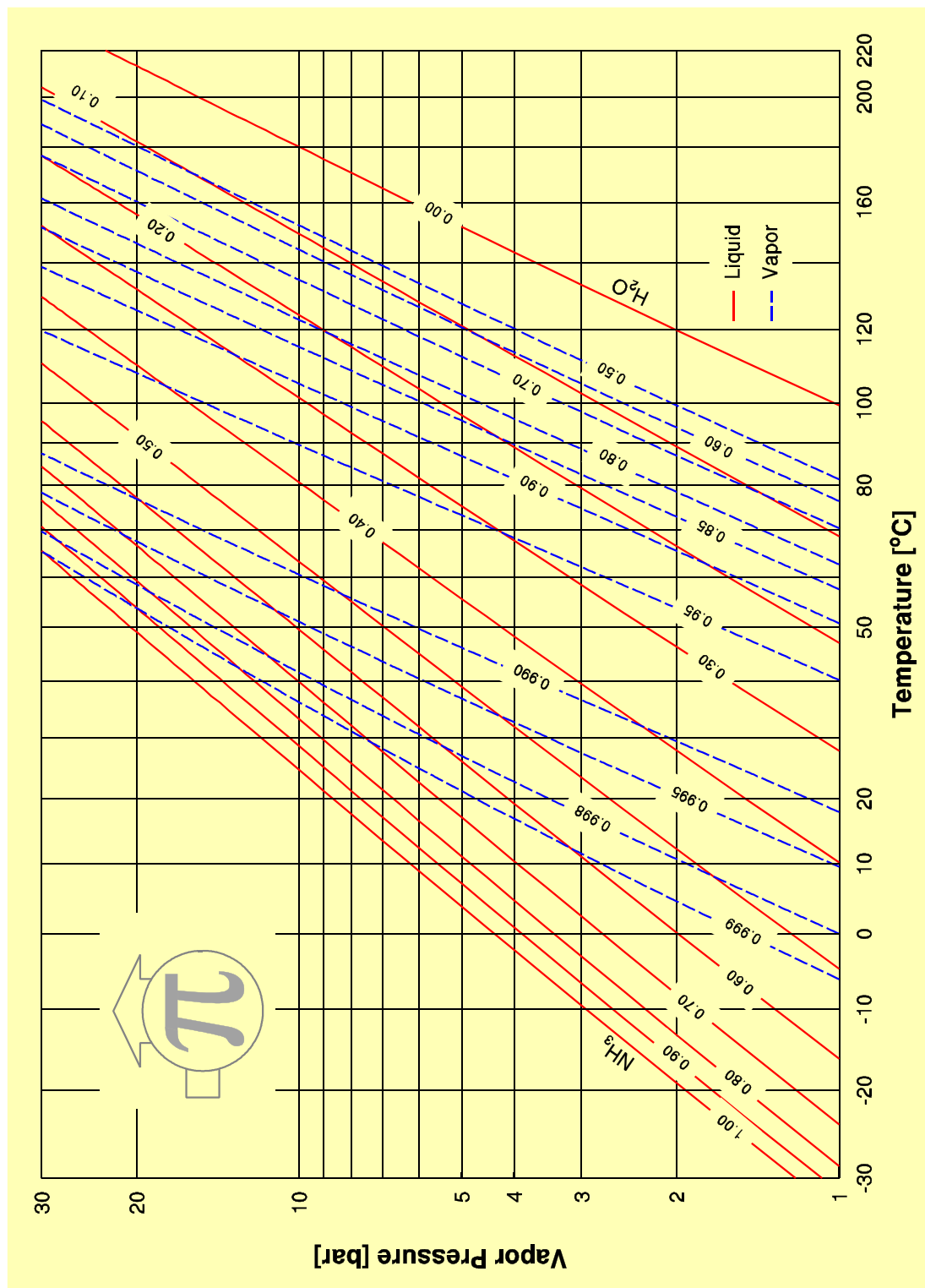


Fig. 2 - Othmer diagram (PTX) of the mixture ammonia - water.

¹³ McCabe, W. L., E. W. Thiele 1925. Graphical design of fractionation columns, I&EC, 17, 605-611.

¹⁴ Ponchon, M. 1921. Étude graphique de la distillation fractionnée industrielle, Parties 1 et 2, La Technique Moderne, 13(1), 20-24, 13(2), 55-58.

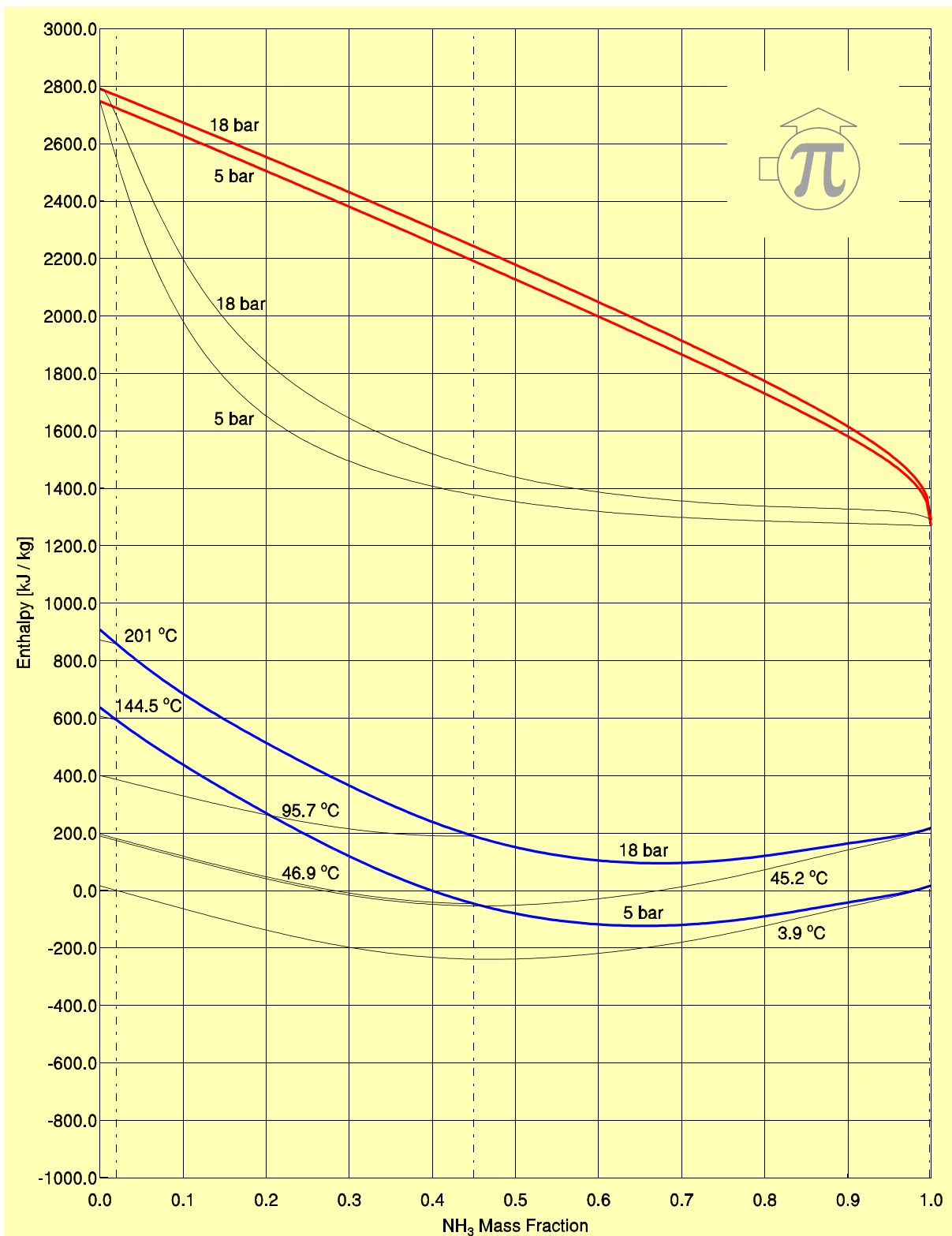


Fig. 3 - H - ξ enthalpy - concentration diagram. Examples of isobars, isotherms and isosters.

5. SOLUTION CRITICAL TEMPERATURE AND PRESSURE

The solution critical temperature and pressure depend upon its composition. Experimental data from Sassen et al. (1990)¹⁵ were used to establish the equations below for the calculation of the critical temperature and pressure of the solution as function of composition.

$$T_{c,sol} = \sum_{i=0}^4 a_i x^i$$

$$P_{c,sol} = \sum_{i=0}^4 b_i x^i$$

i	a _i	b _i
0	647.14	220.64
1	-199.822 371	-37.923 795
2	109.035 522	36.424 739
3	-239.626 217	-41.851 597
4	88.689 691	-63.805 617

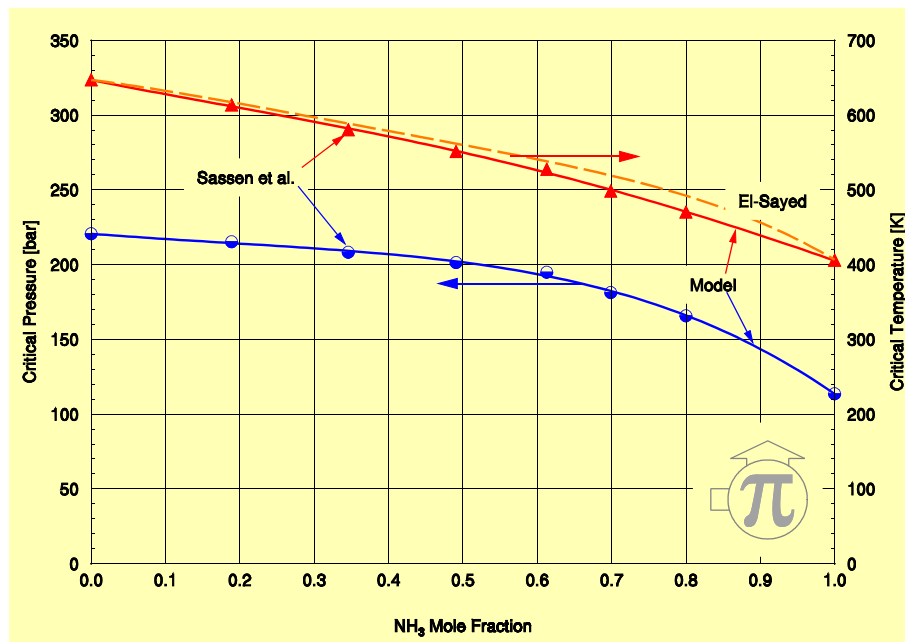


Fig. 4 - Solution critical temperature and pressure. Comparison of the experimental data of Sassen et al. (1990) with the model proposed here, and with that proposed by El-Sayed & Tribus (1985).

Figure 4 depicts a comparison between the experimental data of Sassen et al.¹⁵, values calculated with the above equations, and values calculated with the equation proposed by El-Sayed & Tribus¹⁰ with the corrections introduced by Thorin¹⁶ for the calculation of the critical temperature.

¹⁵ Sassen, C. L., R.A.C. van Kwartel, H.J. van der Kooi, J. de Swan Arons, 1990. Vapor - Liquid Equilibria for the System Ammonia + Water up to the Critical Region, J. Chem. Eng. Data, 35(1990), 140-144.

¹⁶ Thorin, E. 2000. On Thermophysical Properties of Ammonia-Water Mixtures for Prediction of Heat Transfer Areas in Power Cycles, Proc. 14th Symposium on Thermophysical properties, Boulder - Colorado, June 25-30 (Pre Prints).

6. SPECIFIC THERMAL CAPACITY OF SATURATED LIQUID SOLUTIONS AT CONSTANT PRESSURE

Values of the specific thermal capacity of the solution were reported by Wrewsky & Kaigorodof¹⁷, Hildenbrand & Giauque¹⁸ e Chan & Giauque¹⁹. In a recent analysis of these data Tillner-Roth & Friend²⁰ show they are incompatible with the solution enthalpy measurements by Zinner²¹. On the other hand, El-Sayed & Tribus¹⁰ present an equation, without referring the data used in its derivation, that like the data of Chan & Giauque and Hildenbrand & Giauque yields values incompatible with the more coherent formulations and the measurements of Zinner. Taking this into account, it was decided to adopt a practical solution for the calculation of specific thermal capacity, that, nevertheless, agrees well with the values obtained by Tillner-Roth & Friend from the measurements of Zinner, even considering the solution as quasi-ideal.

$$Cp_m = x Cp_{NH_3, T_{NH_3}^*} + (1 - x) Cp_{H_2O, T_{H_2O}^*}$$

$$Cp_{T^*} = A_{cp} + B_{cp} \tau^{-1}$$

$$\tau \equiv 1 - \theta \equiv 1 - \frac{T^*}{T_c}$$

$$\theta \equiv \frac{T_{sol}}{T_{c,sol}} = \frac{T_{NH_3}^*}{T_{c,NH_3}} = \frac{T_{H_2O}^*}{T_{c,H_2O}}$$

The values of the specific thermal capacity of the pure substances are calculated asThe parameters for the equations of the pure substances are:

	A_{cp}	B_{cp}	$\bar{\Delta}$	Δ_{max}
NH ₃	3.875 648	0.242 125	0.0252 %	1.15 %
H ₂ O	3.665 785	0.236 312	0.0183%	3.649 %

These parameters were obtained from data by Haar & Gallagher (1978)²² for ammonia and from Wagner & Kruse (1998)²³ on the basis of IAPWS - IF97²⁴ for water.

¹⁷ Wrewsky, M., A. Kaigorodof 1924. Wärmekapazität wässriger Lösungen von Chlorwasserstoff und Ammoniak bei verschiedenen Temperaturen, Zeit. Phys. Chem., 112, 83-89

¹⁸ Hildenbrand, D. L., W. F. Giauque 1953. Ammonium Oxide and Ammonium Hydroxide. Heat Capacities and Thermodynamic Properties from 15 to 300 K, J. Amer. Chem. Society, 75, 2811-2818.

¹⁹ Chan, J. P., W. F. Giauque 1964. The Entropy of NH₃ 2H₂O. Heat Capacity from 15 to 300 K, The Journal of Physical Chemistry, 68(10), 3053-3057.

²⁰ Tillner-Roth, R., D. G. Friend 1998. Survey and Assessment of Available Measurements on Thermodynamic Properties of the Mixture {Water + Ammonia}, J. Phys. Chem. Ref. Data, 27(1), 45-61.

²¹ Zinner, K. 1934. Wärmetönung beim Mischen von Ammoniak und Wasser in Abhängigkeit von Zusammensetzung und Temperatur, Zeit. für die gesamte Kälte-Industrie, 41(2), 21-29.

²² Haar, L., J. S. Gallagher 1978. Thermodynamic properties of Ammonia, Journal of Physical and Chemical Reference Data, 7, 635-792.

²³ Wagner, W., A. Kruse 1997. Properties of Water and Steam — The Industrial Standard IAPWS - IF97 for the Thermodynamic Properties and Supplementary Equations for Other Properties, Springer-Verlag, Berlin.

²⁴ The International Association for the Properties of Water and Steam, 1997. Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam, IAPWS, London.

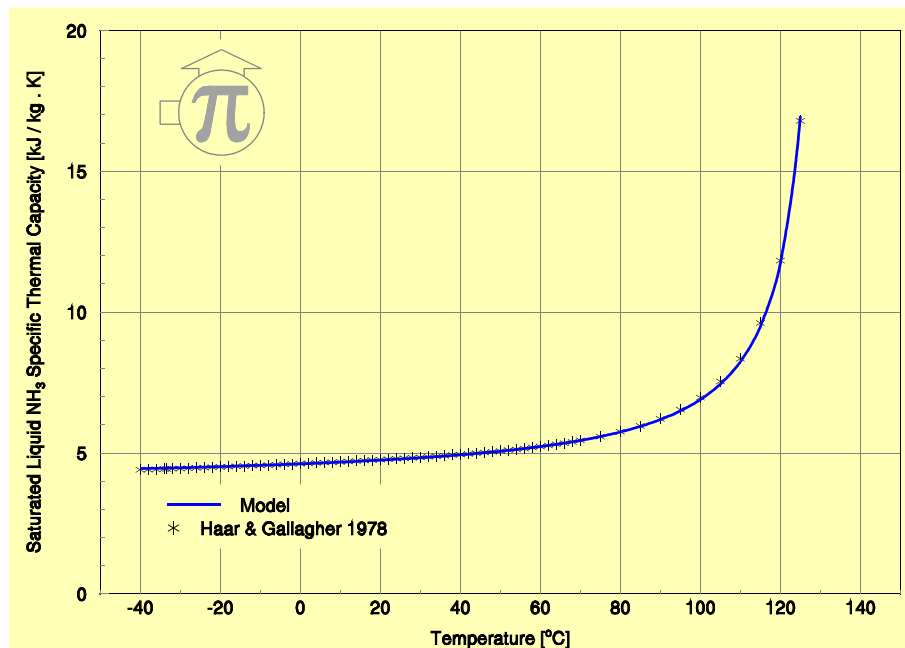


Fig. 5 - Specific thermal capacity for saturated liquid ammonia.

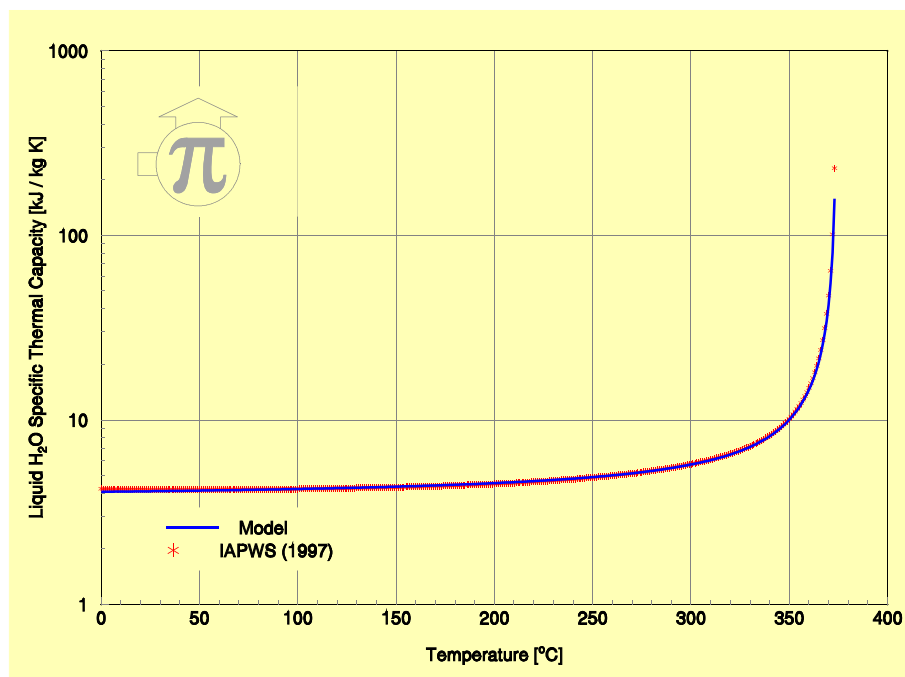


Fig. 6 - Specific thermal capacity of saturated liquid water.

Figures 5 and 6 show graphs of the specific thermal capacity of NH_3 and H_2O , respectively, while Figure 7 depicts curves of liquid solution thermal capacity for various pressures, as function of the NH_3 mass fraction.

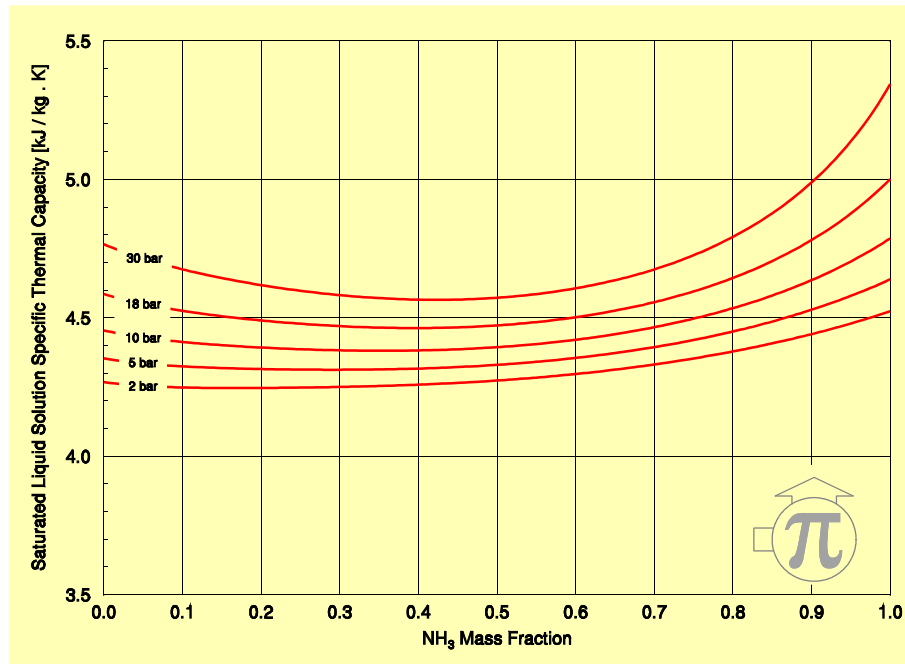


Fig. 7 - Specific thermal capacity of saturated liquid solution at constant pressure.

7. THERMAL CONDUCTIVITY OF LIQUID SOLUTIONS

The experimental data for the thermal conductivity of the liquid solution available from the literature, Lees (1898)²⁵, Braune (1937)²⁶ and Baranov et al. (1997)²⁷, show remarkable inconsistencies. The model proposed by Filippov (1955)²⁸ when applied to these experimental would also not yield coherent parameters. For this reason a formulation for a quasi-ideal solution is proposed here on the basis of the corresponding values of the thermal conductivity of the pure substances. This formulation is described with the following equations:

$$\lambda_m = x \lambda_{NH_3, T_{NH_3}^*} + (1 - x) \lambda_{H_2O, T_{H_2O}^*}$$

The thermal conductivity of the pure substances is determined at the corresponding temperatures $T_{NH_3}^*$, $T_{H_2O}^*$ calculated as explained above. The equation

$$\lambda = \sum_{i=0}^3 A_i T^i$$

²⁵ Lees, Ch. E. 1898. On the thermal conductivities of single and mixed solids and liquids and their variation with temperature, Philosophical Transactions of the Royal Society of London, Series A, Vol 191, 399-440.

²⁶ Braune, B. 1937. Dissertation Universität Leipzig.

²⁷ Baranov A. N. et al. 1997. The investigation of ammonia-water gas and liquid mixture properties, Report on the Workshop on Thermophysical Properties of Ammonia/Water Mixtures, NISTIR 5059, D. G. Friend, W. M. Haynes Ed.s, Boulder, Colorado.

²⁸ Filippov, L. P. 1955. Chem. Abstr., 50 : 8276, 1956. Descrito em The Properties of Gases and Liquids, R.C. Reid, J. M. Prausnitz, B. E. Poling, McGraw-Hill, Inc., 4th Ed., 1987.

with the parameters

	A_0	A_1	A_2	A_3	$\bar{\Delta}$	Δ_{\max}
NH ₃	$8.902\,275 \times 10^2$	-0.692 35	$-2.401\,0 \times 10^{-3}$	0.0	0.527 %	6.630 %

allows for the calculation of the thermal conductivity of saturated liquid ammonia between the triple and critical points. The parameters $A_{0..3}$ were obtained from the experimental data of Richter & Sage (1964)²⁹ and Needham & Ziebland (1965)³⁰. The IAPWS (1998)³¹ formulation for industrial use is considered to calculate the thermal conductivity water (see Appendix A for details).

Figure 8 shows a comparison between the model adopted here and the experimental data from the literature for ammonia. The graph in Figure 9 shows the values calculated for saturated liquid water. Finally, Figure 10 depicts a comparison between literature data and calculated data for the solution thermal conductivity.

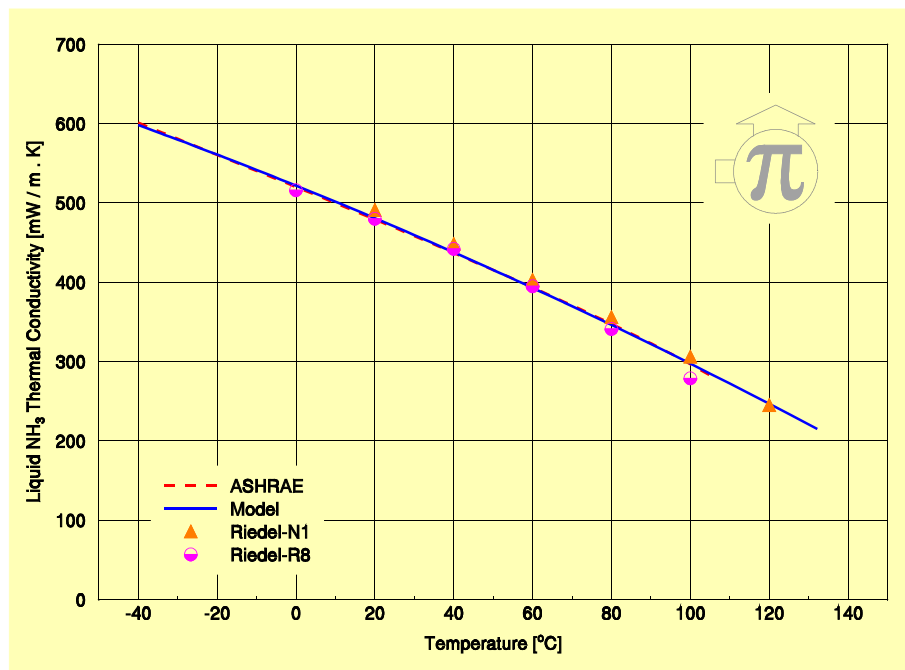


Fig. 8 - Thermal conductivity of saturated liquid ammonia.

²⁹ Richter, G. N., B. H. Sage 1964. J. Chem. Eng. Data, 9(1964):75.

³⁰ Needham, D. P., H. Ziebland 1965. Int. J. Heat Mass Transfer, 8(1965), 1387.

³¹ The International Association for the Properties of Water and Steam, 1998. Revised Release on the IAPWS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance, IAPWS London.

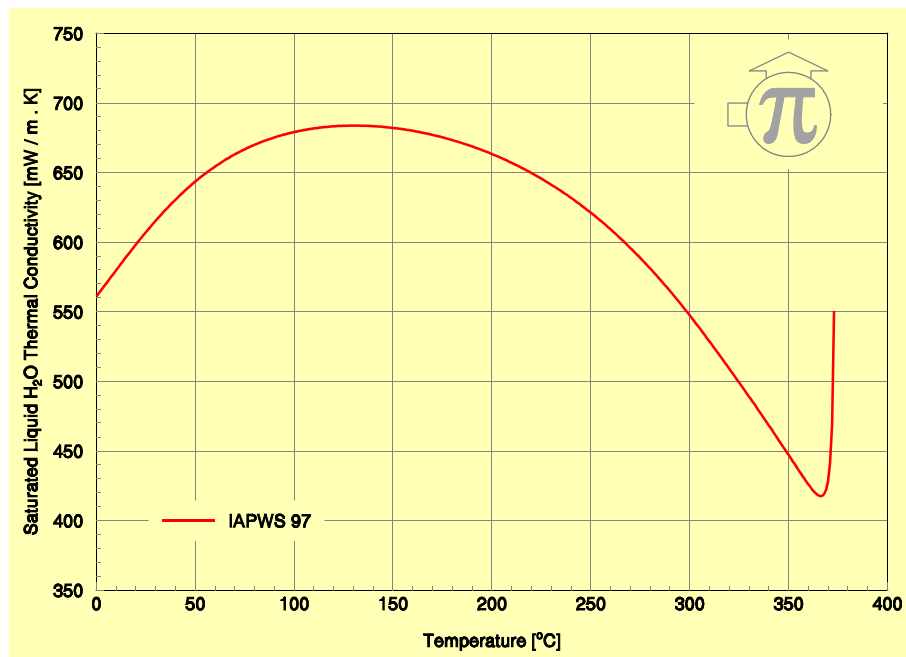


Fig. 9 - Thermal conductivity of saturated liquid water.

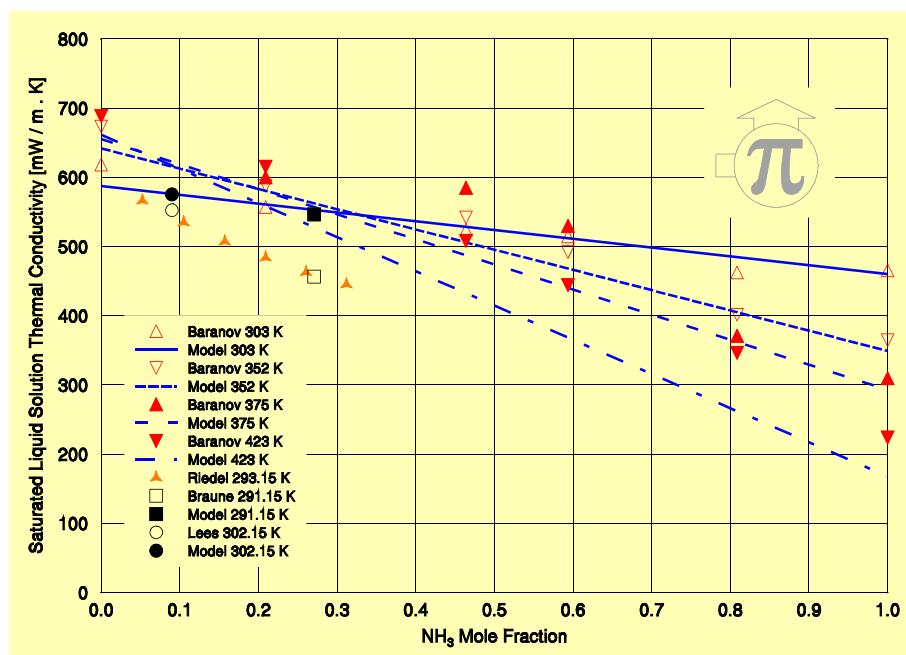


Fig. 10 - Thermal conductivity of saturated liquid solution: – Comparison of literature data with the model proposed (ideal solution).

8. DYNAMIC VISCOSITY OF LIQUID SOLUTIONS

Experimental data for the dynamic viscosity of liquid ammonia + water solutions are quite sparse. Kanitz (1897)³² made the first known measurements at 25 °C, followed by a few other points, also at 25 °C, measured by Blanchard & Pushee (1904, 1912)^{33,34}. Pleskov & Igamberdyev (1939)³⁵ made measurements at 20 °C, but the largest set of experimental data known is that published by Pinevic (1948)³⁶. Recently Frank et al. (1996)³⁷ carried out a few measurements in a limited range of temperatures and concentrations, that complement well the Pinevic and Pleskov sets. Research on cryomagmatism for planetary applications has also led to the study of the viscosity of {ammonia + water} liquid solutions and crystal-liquid slurries at rather low temperatures, Kargel et al., (1991)³⁸. Due to the large uncertainties reported for the measurements, these data were not considered here. There is at present a large effort under way, by institutions linked with the IAPWS, to fill in the existing gap in terms of experimental data on this extremely important property. In terms of predicting models, El-Sayed (1988)³⁹ reported an equation based on the Pinevic data, that reproduces them rather poorly, even after some corrections introduced by Thorin (2000)⁴⁰ (see Figure 13). The same applies to the approximation proposed by Stokar (1986)⁴¹. Frank et al. (1996), proposed as well an approximating equation, based on their experimental data alone, that naturally misses the behaviour of the solution viscosity at higher ammonia concentrations and at higher temperatures. In face of this, it was decided to establish a new approximative equation that should reproduce better the sets of experimental data, if possible. The data and models are compared in the graph of Figure 13. It may be concluded from this Figure that the model proposed in the following is better at reproducing the experimental data than any previous equation.

The model proposed is described by the following equations:

$$\ln \eta_m = x \ln \eta_{NH_3, T_{NH_3}^*} + (1 - x) \ln \eta_{H_2O, T_{H_2O}^*} + \Delta \eta_{T_{sol}, x}$$

$$\Delta \eta_{T_{sol}, x} = \left(0.534 - 0.815 \frac{T_{sol}}{T_{c, H_2O}} \right) F(x)$$

$$F(x) = 6.38 (1 - x)^{1.125 x} \left(1 - e^{-0.585 x (1 - x)^{0.18}} \right) \ln \left(\eta_{NH_3, T_{NH_3}^*}^{0.5} \eta_{H_2O, T_{H_2O}^*}^{0.5} \right)$$

³² Kanitz, A. 1897. Ueber die innere Reibung von Salzlösungen und ihren Gemischen, Zeitschrift für physikalische Chemie, 22(3), 336-357.

³³ Blanchard, A. A. 1904. The viscosity of solutions in relation to the constitution of the dissolved substance, J. American Chemical Society, 26, 1315-1339.

³⁴ Blanchard, A. A., H. B. Pushee, 1912. Viscosity of solutions of the metal ammonia salts, J. American Chemical Society, 34, 28-32.

³⁵ Pleskov, V. A., I. Igamberdyev 1939. Viscosity of mixtures of ammonia and water at 20 °C, J. Physical Chemistry (USSR), 13(5), 701-702.

³⁶ Pinevic, G. 1948. Kholodilnaya Tekhnika, 20(3), 30. Reproduced in Kältetechnik, 1950(1), 29-30.

³⁷ Frank, M. J. W., et al. 1996. Diffusion coefficients and viscosities of CO₂ + H₂O, CO₂ + CH₃OH, NH₃ + H₂O, and NH₃ + CH₃OH Liquid Mixtures, J. Chemical and Engineering Data, 41, 297-302

³⁸ Kargel, J. S., et al. 1991. Rheological properties of ammonia-water liquids and crystal-liquid slurries: Planetological applications, Icarus, 89, 93-112.

³⁹ El-Sayed, Y. M. 1988. On exergy and surface requirements for heat transfer processes involving binary mixtures, ASME-AES - Vol. 6, HTD - Vol. 97, 19-24.

⁴⁰ Thorin, E. 2000. On thermophysical properties of ammonia-water mixtures for prediction of heat transfer areas in power cycles, 14th Symposium on Thermophysical Properties, June 25-30, Boulder, Colorado.

⁴¹ Stokar von Neuforn, M. R. 1986. Kompressionswärmepumpe mit Lösungskreislauf, Diss. ETHZ Nr. 8101.

For the pure substances the liquid dynamic viscosities are calculated at saturation. For water the formulation for industrial use proposed by the IAPWS⁴² is adopted, and is reproduced in Appendix B. For saturated liquid ammonia we propose the use of the method presented by Fenghour et al. (1995)⁴³. The method is described in full in Appendix C.

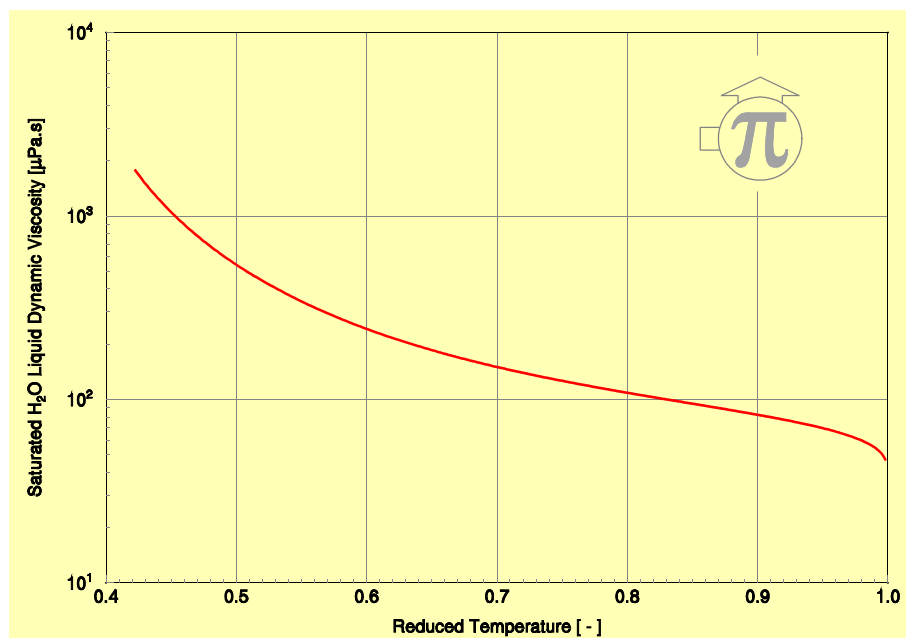


Fig. 11 - Dynamic viscosity of saturated liquid water between the triple and the critical points.

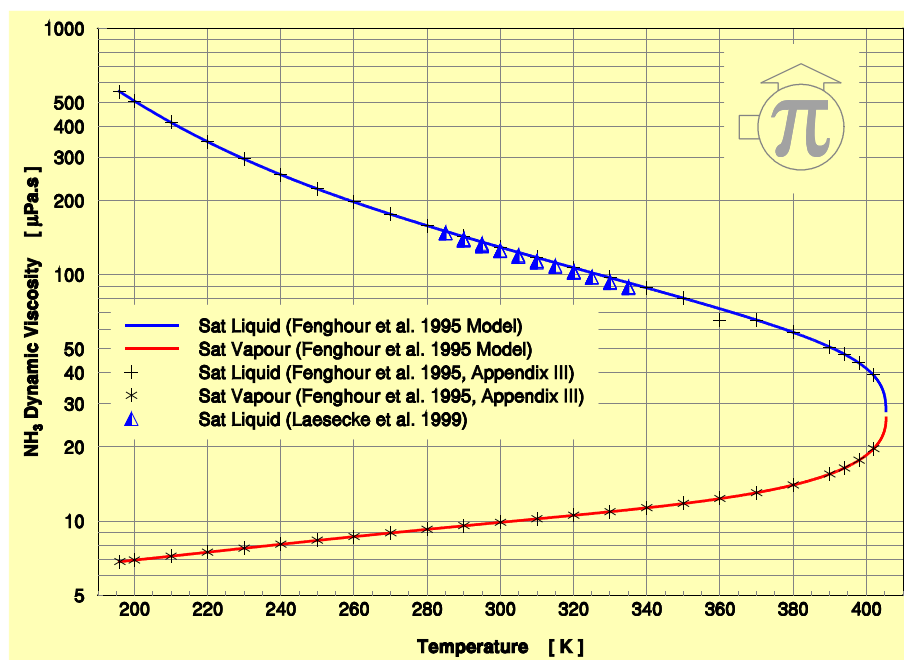


Fig. 12 - Dynamic viscosity of ammonia at saturation.

⁴² The International Association for the Properties of Water and Steam 1997. Revised Release on the IAPWS Formulation 1985 for the Viscosity of Ordinary Water Substance, IAPWS, London.

⁴³ Fenghour, A., et al. 1995. The Viscosity of Ammonia, J. Phys. Chem. Ref. Data, 24(5), 1649-1667.

Figure 11 shows the evolution of the dynamic viscosity of saturated liquid water vs reduced temperature, as obtained with the IAPWS⁴² formulation for industrial use. Figure 12 depicts the dynamic viscosity of saturated liquid and vapour of ammonia, calculated according to Fenghour et al., (1995)⁴³ and compares it with the measurements of Laesecke et al. (1999)⁴⁴.

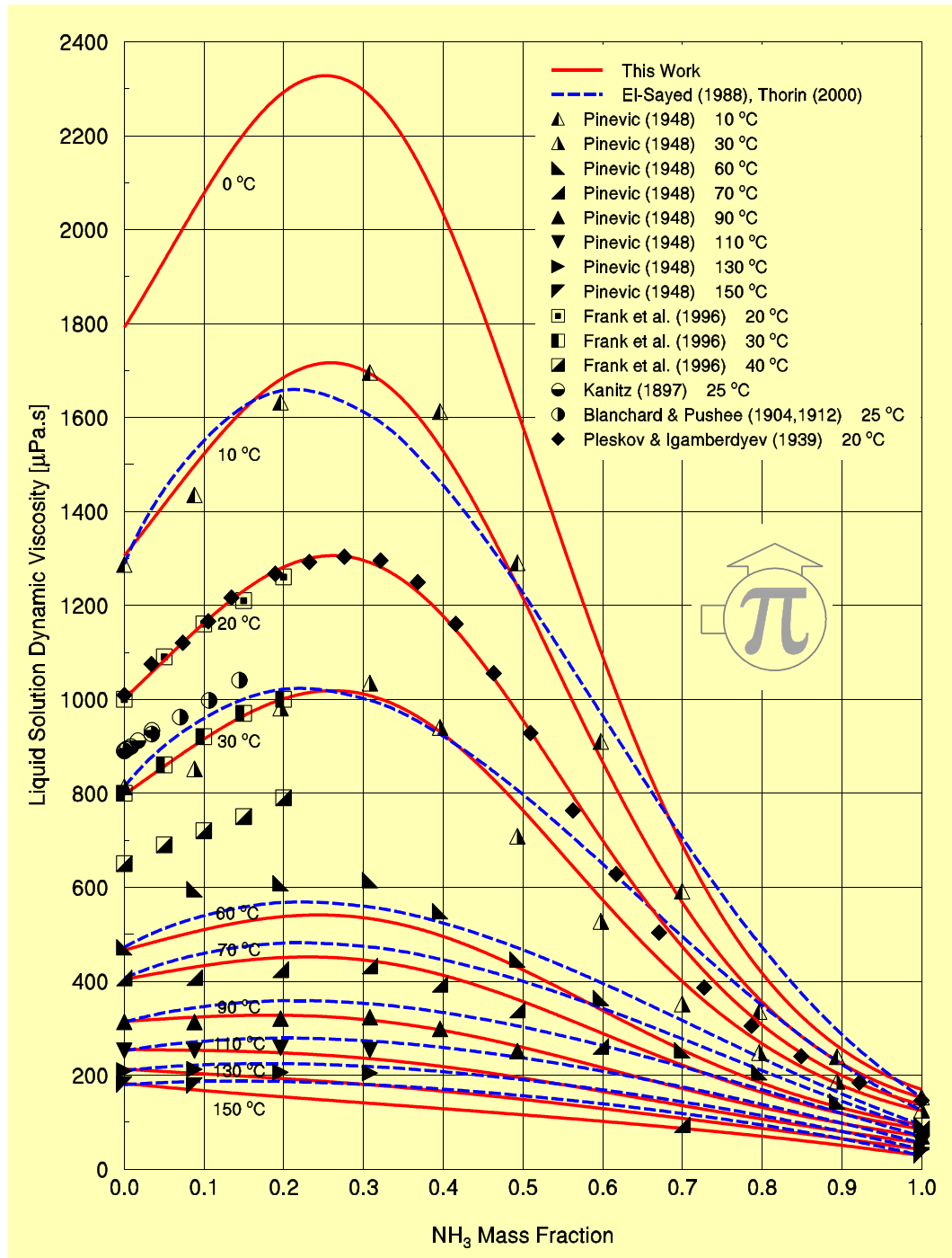


Fig. 13 - Dynamic viscosity of the saturated liquid solution: – Comparison of literature data with the model proposed by El-Sayed & Tribus (1985) with the corrections introduced by Thorin (2000) and with the model proposed here.

⁴⁴ Laesecke, A., et al. 1999. Viscosity measurements of Ammonia, R32, and R134a. Vapor Buoyancy and Radial Acceleration in Capillary Viscometers, Int. J. Thermophysics, 20(2), 401-434.

9. SURFACE TENSION OF THE SOLUTIONS

Only one set of experimental data on the surface tension of ammonia water solutions, dating back to de 1930, King & Hall & Ware⁴⁵ has been found. The model proposed below, assuming a quasi-ideal solution, is based upon these data, and is described with the following equations:

$$\sigma_m = x\sigma_{NH_3, T_{NH_3}}^* + (1 - x)\sigma_{H_2O, T_{H_2O}}^* + \Delta\sigma_{T_{sol}, x}$$

$$\Delta\sigma_{T_{sol}, x} = -\left(\sigma_{H_2O, T_{H_2O}}^* - \sigma_{NH_3, T_{NH_3}}^*\right) F(x)$$

$$F(x) = 1.442(1 - x)\left[1 - e^{-2.5x^4}\right] + 1.106x\left[1 - e^{-2.5(1-x)^6}\right]$$

The surface tension of the pure substances is described by the formulation proposed by Straub & Rosner & Grigull (1980)⁴⁶ and also adopted by the IAPWS for water(IAPWS 1994)⁴⁷

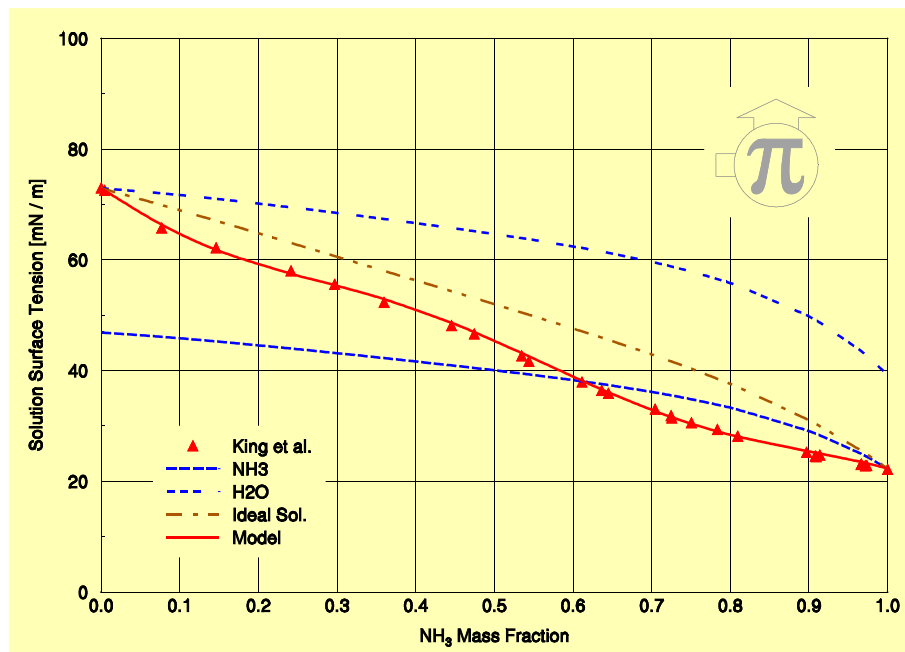
$$\sigma = \sigma_0(1 + b\tau)\tau^\mu.$$


Fig. 14 - Surface tension of the solution at 20 °C. Comparison of the model with experimental data.

The parameters of this equation are:

	σ_0	μ	b
NH ₃	91.2	1.102 8	0.0
H ₂ O	235.8	1.256	-0.625

⁴⁵ King, H. H., J. L. Hall, G. C. Ware 1930. A study of the density, surface tension and adsorption in the water-ammonia system at 20 °C, J. Amer. Chem. Soc., 52, 5128-5135.

⁴⁶ Straub, J., N. Rosner, U. Grigull 1980. Oberflächenspannung von leichten und schweren Wasser, Wärme-und Stoffübertragung, 13, 241-252.

⁴⁷ The International Association for the Properties of Water and Steam 1994. IAPWS Release on Surface Tension of Ordinary Water Substance, Sept. 1994, IAPWS, London.

Figure 14 shows values of the surface tension of the solution at 20 °C, and compares the results obtained with the experimental data of King et al. Depicted are the curves of the surface tension of the pure substances at the equivalent temperature (function of the solution temperature and concentration, see definitions in 6., above).

10. LIQUID SOLUTION DENSITY

The density of the liquid solution is calculated as for a quasi-ideal solution with the equation

$$\rho_m = x\rho_{NH_3, T_{NH_3}^*} + (1 - x)\rho_{H_2O, T_{H_2O}^*} + \Delta\rho_{T_{sol}^*, x}$$

where the 'excess' density in relation to the ideal solution is approximated with the function

$$\Delta\rho_{T_{sol}^*, x} = [x(1 - x) - Ax^2(1 - x)] \rho_{NH_3, T_{NH_3}^*}^{0.5} \rho_{H_2O, T_{H_2O}^*}^{0.5}$$

and the A parameter, which is a function of the solution temperature,

$$T_{sol}^* \equiv \frac{T_{sol}}{T_{c, H_2O}}$$

that is made dimensionless with the critical temperature of water. The A parameter is defined by the equation

$$A = \sum_{i=0}^2 A_{1,i} T_{sol}^{*i} + \frac{\sum_{i=0}^2 A_{2,i} T_{sol}^{*i}}{x}$$

where the A₁ and A₂ have the following components

	i = 0	i = 1	i = 2
A ₁	-2.410	8.310	-6.924
A ₂	2.118	-4.050	4.443

The calculation of the solution density by this process has been validated for the temperature range 0 °C ... 250 °C with the values obtained by Tillner-Roth & Friend (1998)⁷, and reproduce them with a maximum deviation of 5,5 %.

The density of the pure substances is calculated with the equation

$$\frac{\rho_L}{\rho_c} = \sum_{i=0}^6 A_i \tau^{b_i}$$

with the parameters

i	H ₂ O		NH ₃	
	A	b	A	b
0	1.0	0	1.0	0
1	1.993 771 843 0	1/3	2.024 912 83	1/3
2	1.098 521 160 4	2/3	0.840 496 67	2/3
3	-0.509 449 299 6	5/3	0.301 558 52	5/3
4	-1.761 912 427 0	16/3	-0.209 266 19	16/3
5	-44.900 548 026 7	43/3	-74.602 501 77	43/3
6	-723 692.261 863 2	110/3	4 089.792 775 06	70/3

This equation is valid for both ammonia and water in the saturated liquid phase between the tripiple to the critical points. It reproduces the density of water recommended by IAPWS (1994)⁴⁸ with a mean deviation of 0.003% and a maximum deviation of 0.044%, while for ammonia the data by Haar & Gallagher (1978)²² are reproduced with a mean deviation of 0.126% and a maximum of 4.7%.

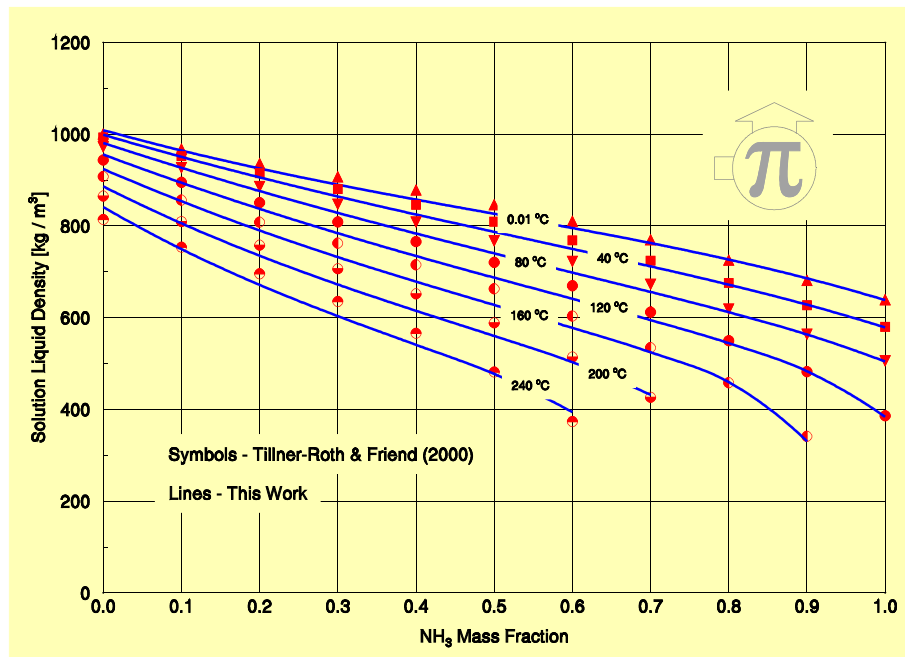


Fig. 15 - Density of the saturated liquid solution at various temperatures.

Figure 15 depicts a graph of the density of the saturated liquid solution vs mass fraction of NH₃ at various temperatures, while the densities of the pure substances are shown in the graphs of Figures 16 and 17, for water and ammonia, respectively.

⁴⁸ IAPWS 1994. IAPWS Release on the Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance, IAPWS, London.

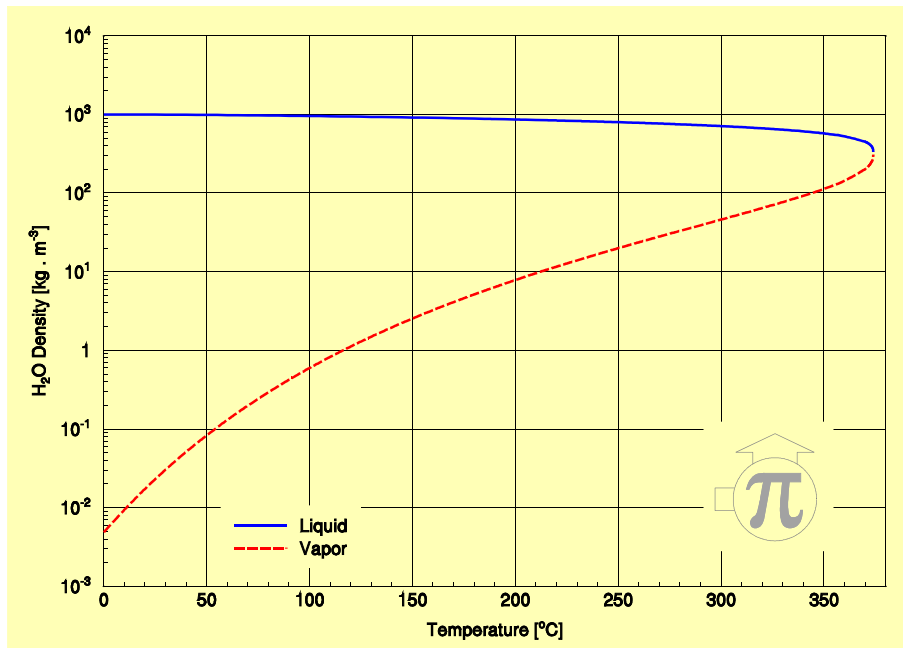


Fig. 16 - Densities of saturated water in the liquid and vapour phases.

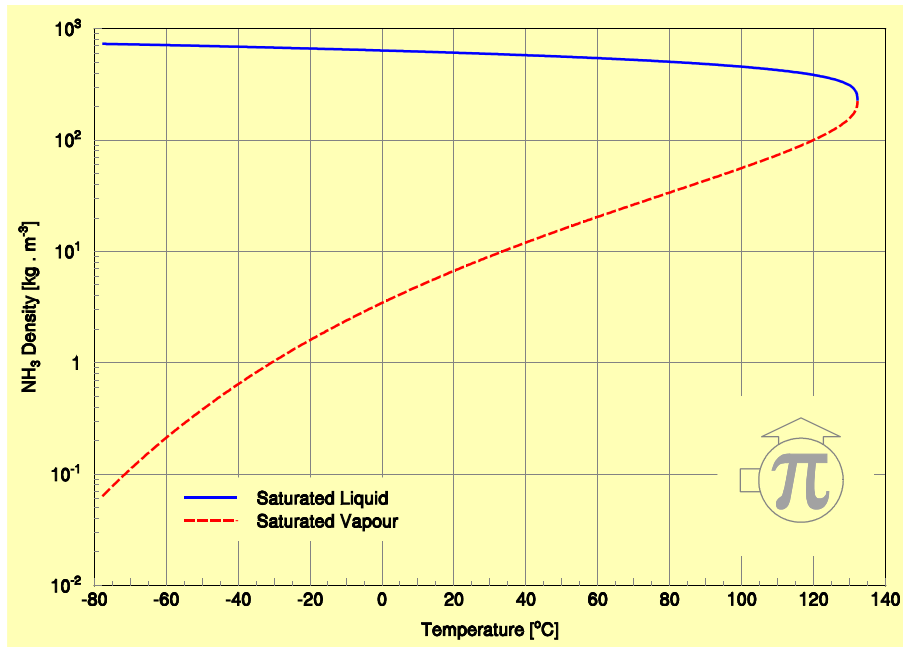


Fig. 17 - Densities of saturated ammonia in the liquid and vapour phases.

11. MASS DIFFUSIVITY (AMMONIA VAPOUR INTO AQUEOUS SOLUTIONS OF AMMONIA)

The diffusion coefficient (mass diffusivity) is the proportionality constant defined by the general equation

$$n_A = -D \frac{dx_A}{dz}$$

where A is the diffusing substance, n the number of transferred moles and dx_A/dz the molar concentration gradient.

For strongly associative liquids, such as water and its solutions with ammonia, Wilke & Chang (1955)⁴⁹ proposed an equation for the calculation of D , that has given good results in practice (Niederhauser 1991⁵⁰, 1994⁵¹). The Wilke & Chang equation

$$D = 7.4 \times 10^{-8} T_{sol} \frac{\sqrt{\psi_{sol} M_{sol}}}{\eta_{sol} \tilde{V}_{diff}^{0.6}} \quad [cm^2 s^{-1}]$$

in laboratory units, was obtained for diluted solutions. It contains the parameter ψ_{sol} , which must be estimated from experimental data. In strongly diluted solutions, meaning a very high concentration of solvent, ψ_{sol} , M_{sol} and η_{sol} may be considered as those for the solvent at the temperature T_{sol} . On the other hand, the molar volume of the solute \tilde{V}_{diff} may be considered at the normal boiling point ($p = 101\,325$ Pa).

For concentrated solutions it is required to consider the respective properties at the conditions the diffusion is taking place.

The basic equation of Wilke & Chang is adapted here for application in the design of absorbers in absorption refrigeration equipment. The experimental data of Kashiwagi & Okajima (1987)⁵² are used to obtain an equation for the calculation of the *associative factor* ψ of ammonia. The *associative factor* ψ of water has been obtained by Wilke & Chang. The adapted equation, transformed to SI units, is

$$D = 117.282 \times 10^{-18} T_{sol} \frac{\sqrt{\psi_{sol} M_{sol}}}{\eta_{sol} \tilde{V}_{diff}^{0.6}} \quad [m^2 s^{-1}]$$

with

$$\psi_{sol} \equiv x \psi_{NH_3} + (1 - x) \psi_{H_2O}$$

$$M_{sol} \equiv x M_{NH_3} + (1 - x) M_{H_2O}$$

$$\tilde{V}_{diff} \equiv \frac{M_{NH_3}}{\rho_{NH_3, T_{sol}}}$$

⁴⁹ Wilke, C. R., P. Chang 1955. Correlation of Diffusion Coefficients in Dilute Solutions, AIChE Journal, 1(2), 264-270.

⁵⁰ Niederhauser, Th. 1991. Desorptionsvorgänge in Wasser - Ammoniak Rieselfilm - Entgasern, Diss. ETHZ Nr. 9576.

⁵¹ Niederhauser, Th., C. Trepp 1994. Wärme- und Stoffübertragung in Wasser/Ammoniak-Riselfilm an glatten und rauhen Rohroberflächen, Wärme- und Stoffübertragung, 29(4), 251-264.

⁵² Kashiwagi, T., J. Okajima 1987. Mass Diffusion in the Process of Ammonia Vapor Absorption in NH₃ - H₂O - LiBr ternary System, Proc. 17th Int. Congress of Refrigeration, Vol. B, 1010-1017.

The characteristic parameters for the pure substances are:

	ψ	M
NH ₃	1.7	17.03
H ₂ O	2.6	18.0152

η_{sol} is determined as described in 8 above. The units to use are SI, (Pa.s), for η_{sol} as well.

Figure 18 depicts the variation of mass diffusivity vs the mass fraction of ammonia in solution for the pressures of 5 and 18 bar.

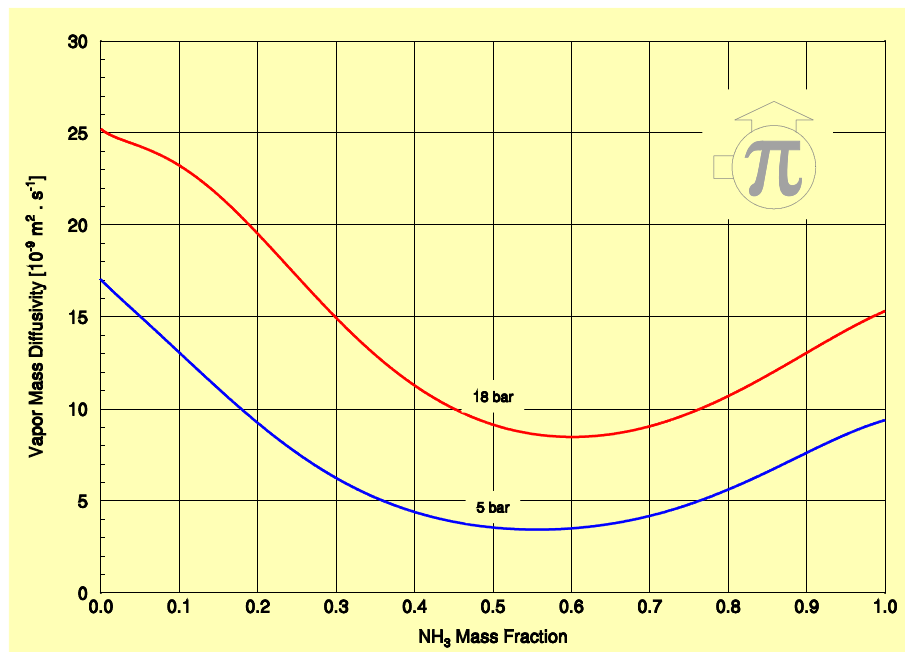


Fig. 18 - Mass diffusivity of ammonia vapour into ammonia + water solutions at 5 and 18 bar.

12. THERMAL CONDUCTIVITY OF SOLUTIONS IN THE VAPOUR PHASE

The thermal conductivity of the solution in the vapour phase, shall be calculated with the equation of Wassiljewa (1904)⁵³, considering the modifications introduced by Mason & Saxena (1958)⁵⁴, as applied to binary solutions, ammonia + water in this case:

$$\lambda_m = \frac{y \lambda_{NH_3}}{y + (1 - y) \phi_{12}} + \frac{(1 - y) \lambda_{H_2O}}{(1 - y) + y \phi_{21}}$$

⁵³ Wassiljewa, A. 1904.: Physik Zeitschrift, 5, pp. 737.

⁵⁴ Mason, E. A., C. S. Saxena 1958: Physics of Fluids, 1, pp. 361.

with

$$\phi_{12} = \frac{\left[1 + \left(\frac{\eta_{NH_3}}{\eta_{H_2O}} \right)^{0.5} \left(\frac{M_{H_2O}}{M_{NH_3}} \right)^{0.25} \right]^2}{\left[8 \left(1 + \frac{M_{NH_3}}{M_{H_2O}} \right) \right]^{0.5}}$$

$$\phi_{21} = \phi_{12} \frac{\eta_{H_2O}}{\eta_{NH_3}} \frac{M_{NH_3}}{M_{H_2O}}$$

The thermal conductivity of ammonia vapour is calculated with the equation

$$\lambda = \sum_{i=0}^3 A_i \left[\ln \left(\frac{1}{\tau} \right) \right]^i$$

where τ is calculated from the temperature of the saturated solution, at the actual pressure and concentration of the solution. The parameters for this equation are

	A_0	A_1	A_2	A_3	M
NH ₃	-0.481 73	20.043 83	0.0	0.0	17.03

The equation for the thermal conductivity of ammonia is valid between the triple and critical points. For water vapour the thermal conductivity is calculated according to the IAPWS by the method described in Appendix B. Figures 19 and 20 depict graphs of the thermal conductivity of saturated vapour of ammonia and water, respectively. Figure 21 shows values of the thermal conductivity of saturated solution vapour at various pressures.

The required dynamic viscosities of the vapours of the pure substances are calculated by the methods described in 13., below.

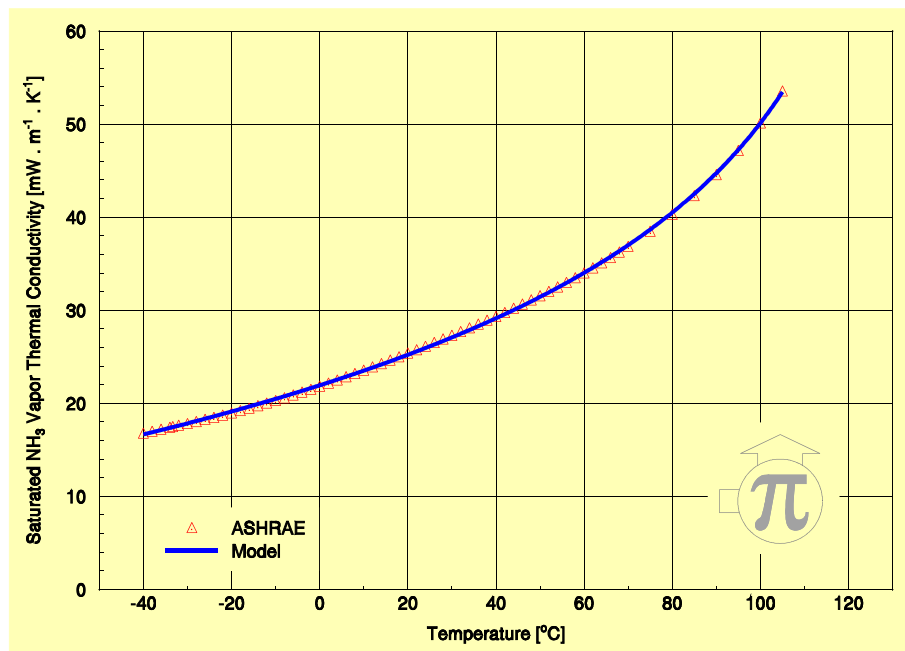


Fig. 19 - Thermal conductivity of saturated ammonia vapour.

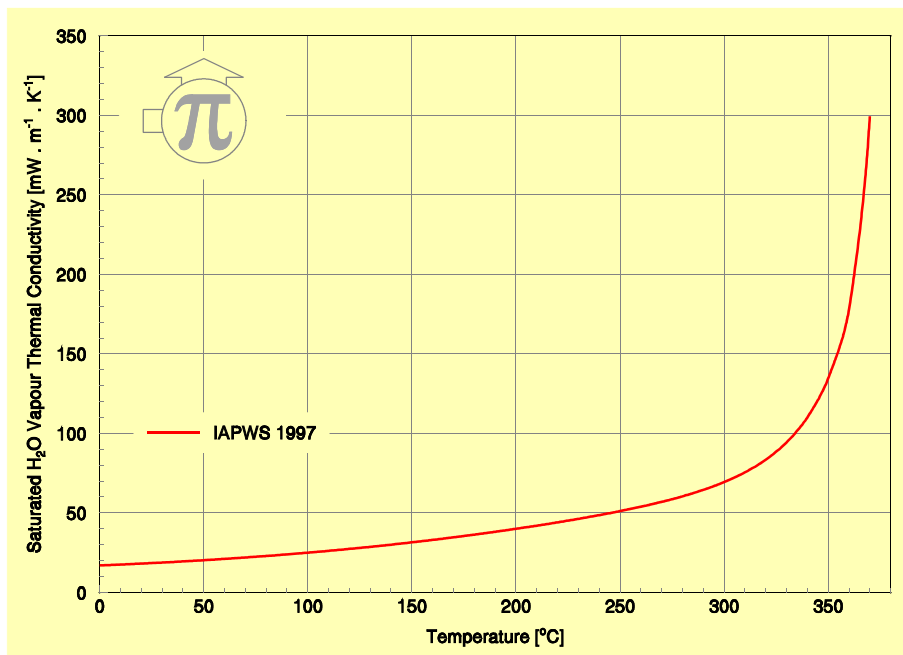


Fig. 20 - Thermal conductivity of saturated water vapour.

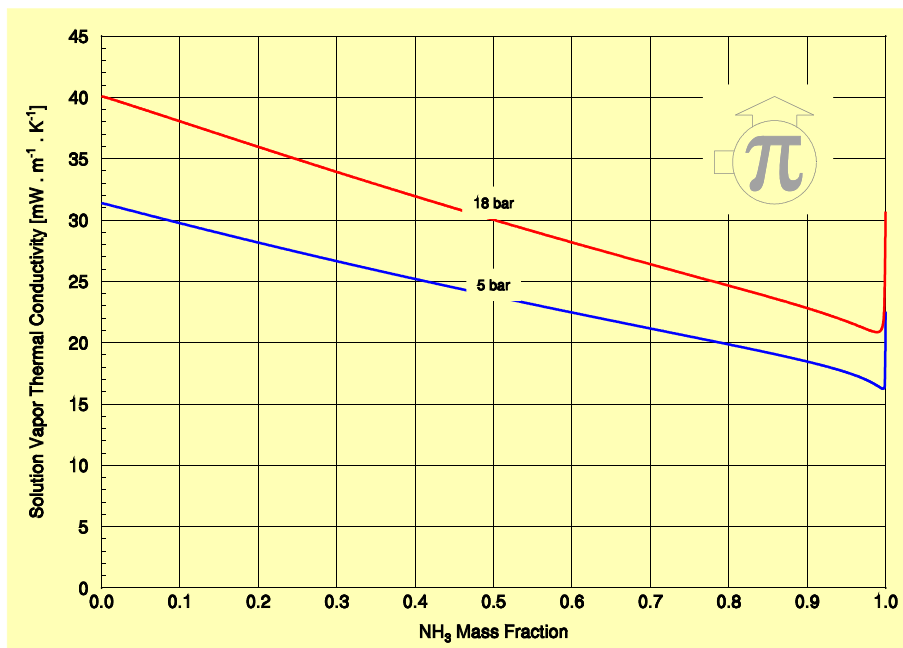


Fig. 21 - Thermal conductivity of the saturated vapour of the solution at 5 and 18 bar.

13. DYNAMIC VISCOSITY OF SOLUTIONS IN THE VAPOUR PHASE

As for the thermal conductivity of solution vapour, the dynamic viscosity of the solution vapour shall be calculated with an equation similar to the Wassiljewa, as proposed by Wilke (1950)⁵⁵

$$\eta_m = \frac{y \eta_{NH_3}}{y + (1 - y) \phi_{12}} + \frac{(1 - y) \eta_{H_2O}}{(1 - y) + y \phi_{21}}$$

with the following auxiliary equations

$$\phi_{12} = \frac{\left[1 + \left(\frac{\eta_{NH_3}}{\eta_{H_2O}} \right)^{0.5} \left(\frac{M_{H_2O}}{M_{NH_3}} \right)^{0.25} \right]^2}{\left[8 \left(1 + \frac{M_{NH_3}}{M_{H_2O}} \right) \right]^{0.5}} \quad \phi_{21} = \phi_{12} \frac{\eta_{H_2O}}{\eta_{NH_3}} \frac{M_{NH_3}}{M_{H_2O}}$$

The dynamic viscosity of saturated ammonia vapour is calculated according to Fenghour et al. (1995)⁷⁷, (see Figure 12). The method is described in full in Appendix C. For saturated vapour of pure water the dynamic viscosity is calculated by the method proposed by the IAPWS, described in Appendix A.

Figure 22 shows a graph of the dynamic viscosity of saturated water vapour, while Figure 23 depicts values of the dynamic viscosity of solution vapour at the pressures of 5 and 18 bar.

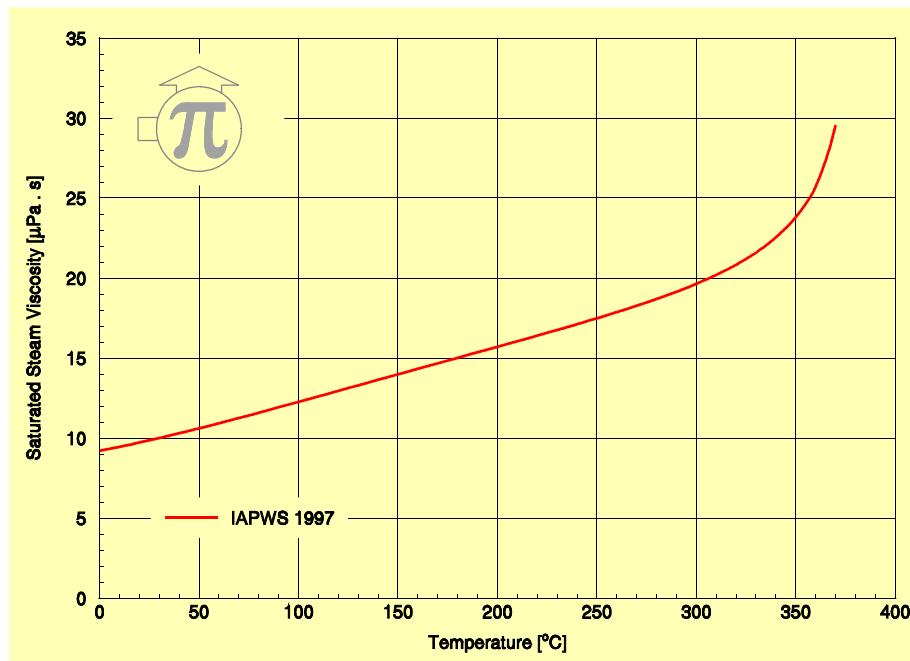


Fig. 22 - Dynamic viscosity of saturated water vapour.

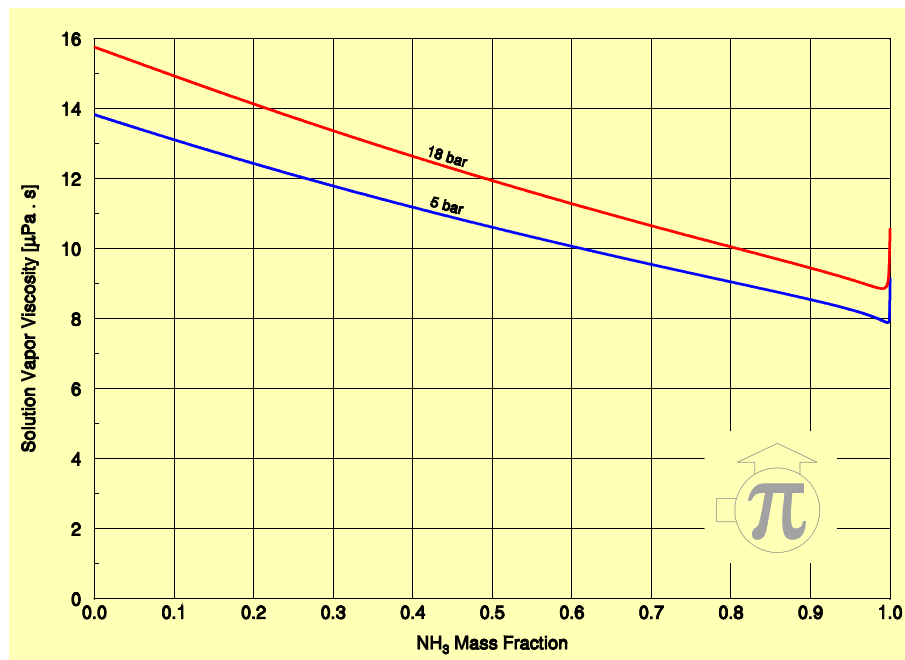


Fig. 23 - Dynamic viscosity of saturated solution vapour at 5 and 18 bar.

14. DENSITY OF SATURATED SOLUTIONS IN THE VAPOUR PHASE

The density of saturated solution vapour is calculated as for a quasi-ideal solution of real gases with the equation

$$\rho_m = y\rho_{NH_3, T_{NH_3}^*} + (1 - y)\rho_{H_2O, T_{H_2O}^*} + \Delta\rho_{T_{sol}^*, y}$$

The 'excess' density in relation to the ideal solution is approximated with the function

$$\Delta\rho_{T_{sol}^*, y} = A(1 - y)^B(1 - e^{Cy^D})\Delta\rho_{max, T_{sol}^*}$$

$$\Delta\rho_{max, T_{sol}^*} = e^{J - K/T_{sol}^*}$$

with

$$T_{sol}^* \equiv \frac{T_{sol}}{T_{c, H_2O}}$$

The parameters of these equations are

$A =$	82.0	$D =$	2.75
$B =$	0.5	$J =$	9.952
$C =$	-0.05	$K =$	3.884

The densities of the saturated vapour of the pure substances are calculated from the equation

$$LN\left(\frac{\rho_G}{\rho_c}\right) = \sum_{i=1}^6 A_i \tau^{b_i}$$

with the parameters

	H ₂ O		NH ₃	
i	A	b	A	b
1	-2.025 450 113	1/3	-1.430 974 26	1/3
2	-2.701 314 216	2/3	-3.312 736 38	2/3
3	-5.359 161 836	4/3	-4.444 257 69	4/3
4	-17.343 964 539	3	-16.844 664 19	3
5	-44.618 326 953	37/6	-37.797 135 47	37/6
6	-64.869 052 901	71/6	-97.828 538 34	71/6

Curves for the densities of saturated vapour are shown in Figures 16 and 17 for saturated vapours of ammonia and water, respectively. Figure 24 depicts curves of the density of saturated solution vapour at the pressures of 5 and 18 bar.

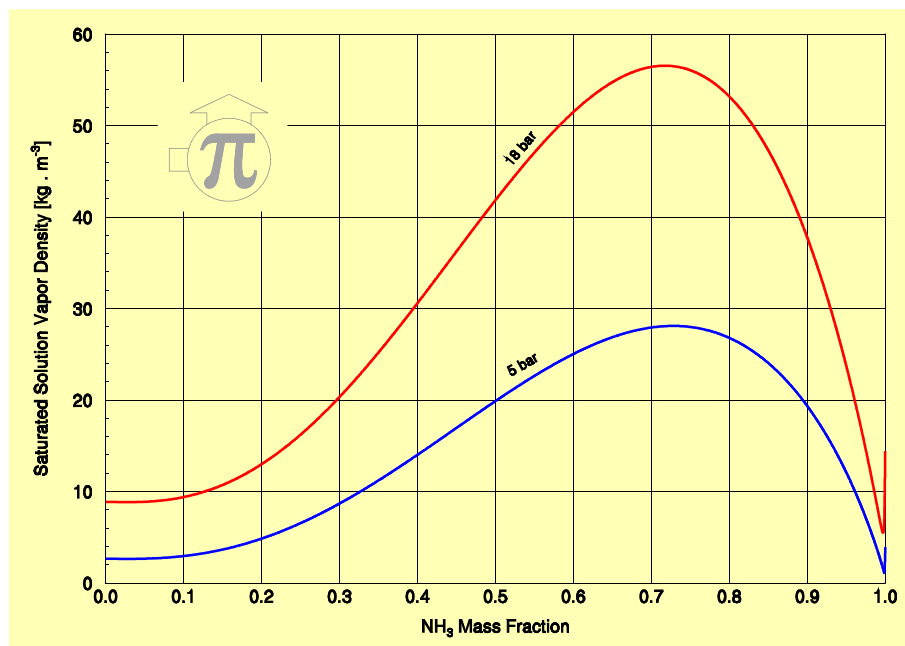


Fig. 24 - Density of saturated solution vapour at 5 and 18 bar.

15. SPECIFIC THERMAL CAPACITY OF SATURATED SOLUTIONS IN THE VAPOUR PHASE

The specific thermal capacity of saturated solution vapour is calculated as for an ideal solution of real gases, i.e., as the molar concentration weighted mean y of the saturated vapour specific thermal capacities of the individual components:

$$Cp_m = y Cp_{NH_3, T_{NH_3}^*} + (1 - y) Cp_{H_2O, T_{H_2O}^*}$$

The specific thermal capacities of the saturated vapour of the two components is calculated with the equation

$$Cp(\tau) = A + B\tau^{-\frac{1}{3}} + C\tau^{-\frac{2}{3}} + D\tau^{-\frac{5}{3}} + E\tau^{-\frac{7.5}{3}}$$

τ is determined from the solution vapour temperature as

$$\tau \equiv 1 - \theta_{sol} \equiv 1 - \frac{T_{sol}}{T_{c,sol}}$$

The parameters $A \dots E$ were obtained on the basis of IAPWS (IAPWS 1997)²⁴ data, for water vapour, and from Haar & Gallagher (1978)²² data for ammonia. This equation is valid between the triple and critical points for the pure substances.

	A	B	C	D	E	$\bar{\Delta}$	Δ_{max}
NH ₃	-1.199 197 086	1.240 129 495	0.924 818 752	0.018 199 633	-0.245 034 E-3	0.124 %	0.737 %
H ₂ O	3.461 825 651	-4.987 788 063	2.994 381 770	6.259 308 E-3	-8.262 961 E-6	1.919 %	4.397 %

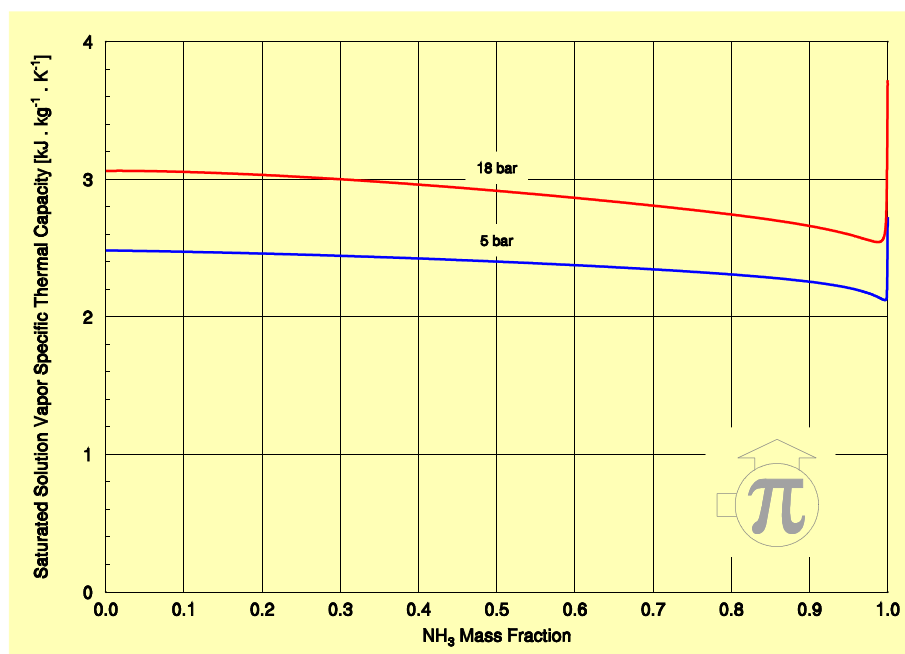


Fig. 25 - Capacidade térmica isobárica do vapor saturado de solução a 5 e a 18 bar.

Figure 25 shows curves of the specific thermal capacity of the saturated solution vapour at 5 and 18 bar.

APPENDIX A - THE IAPWS FORMULATION FOR THE THERMAL CONDUCTIVITY OF ORDINARY WATER SUBSTANCE FOR INDUSTRIAL USE

This formulation is included here for the sake of completeness.

The IAPWS formulation for industrial use consists of the following interpolating equation

$$\bar{\lambda} = \bar{\lambda}_0(\bar{T}) \times \bar{\lambda}_1(\bar{\rho}) \times \bar{\lambda}_2(\bar{T}, \bar{\rho})$$

The first term, $\bar{\lambda}_0(\bar{T})$, represents the thermal conductivity of steam in the ideal-gas limit, and is

$$\bar{\lambda}_0(\bar{T}) = \bar{T}^{0.5} \left(\sum_{i=0}^3 L_{0,i} \bar{T}^i \right)$$

The term $\bar{\lambda}_1(\bar{\rho})$ is defined by

$$\bar{\lambda}_1(\bar{\rho}) = L_{1,0} + L_{1,1} \bar{\rho} + L_{1,2} e^{L_{1,3}(\bar{\rho} + L_{1,4})^2}$$

and $\bar{\lambda}_2(\bar{T}, \bar{\rho})$ is defined by the equation

$$\begin{aligned} \bar{\lambda}_2(\bar{T}, \bar{\rho}) = & \left(\frac{L_{2,0}}{\bar{T}^{10}} + L_{2,1} \right) \bar{\rho}^{\frac{9}{5}} e^{L_{3,0} \left(1 - \bar{\rho}^{\frac{14}{5}} \right)} \\ & + L_{2,2} \Lambda_0 \bar{\rho}^{\Lambda_1} e^{\left(\frac{\Lambda_1}{1 + \Lambda_1} \right) (1 - \bar{\rho}^{1 + \Lambda_1})} + L_{2,3} e^{L_{3,1} \bar{T}^{\frac{3}{2}} + \frac{L_{3,2}}{\bar{\rho}^5}} \end{aligned}$$

Λ_0 and Λ_1 are functions of

$$\Delta \bar{T} = |\bar{T} - 1| + L_{3,3}$$

Defined as

$$\Lambda_0 = \begin{cases} \frac{1}{\Delta \bar{T}} \leftarrow \bar{T} \geq 1 \\ \frac{L_{3,5}}{\Delta \bar{T}^{\frac{3}{5}}} \leftarrow \bar{T} < 1 \end{cases}$$

$$\Lambda_1 = 2 + \frac{L_{3,4}}{\Delta \bar{T}^{\frac{3}{5}}}$$

The parameters of these equations are given in Table 1. The variables with the bar above represent reduced values. These are reduced as follows: $\bar{T} = T/T^*$, $\bar{\rho} = \rho/\rho^*$, $\bar{\lambda} = \lambda/\lambda^*$, with the reference values: $T^* = 647.26$ K, $\rho^* = 317.7$ kg.m⁻³, $\lambda^* = 1.0$ W.m⁻¹.K⁻¹.

Table 1 - Parameters for the thermal conductivity equation of normal water.

L_{ij}	$i = 0$	$i = 1$	$i = 2$	$i = 3$
$j = 0$	0.010 281 1	-0.397 070	0.070 130 9	0.642 857
$j = 1$	0.029 962 1	0.400 302	0.011 852 0	-4.117 17
$j = 2$	0.015 614 6	1.060 000	0.001 699 37	-6.179 37
$j = 3$	-0.004 224 64	-0.171 587	-1.020 0	0.003 089 76
$j = 4$	0.0	2.392 190	0.0	0.082 299 4
$j = 5$	0.0	0.0	0.0	10.093 2

APPENDIX B - THE IAPWS FORMULATION FOR THE DYNAMIC VISCOSITY OF ORDINARY WATER SUBSTANCE FOR INDUSTRIAL USE

The dynamic viscosity of liquid water at temperatures above 0 °C is calculated with the IAPWS formulation for industrial use as follows:

$$\bar{\eta} = \bar{\eta}_0(\bar{T}) \times \bar{\eta}_1(\bar{T}, \bar{\rho}) \times \bar{\eta}_2(\bar{T}, \bar{\rho})$$

The term

$$\bar{\eta}_0(\bar{T}) = \bar{T}^{0.5} \left(\sum_{i=0}^3 H_i \bar{T}^{-i} \right)^{-1}$$

represents the viscosity of steam in the ideal gas limit with the parameters H_i given in Table 2.

Table 2 - H_i parameters for the water viscosity equation.

i	H_i
0	1.000
1	0.978 197
2	0.579 829
3	-0.202 354

The second term is

$$\bar{\eta}_1(\bar{T}, \bar{\rho}) = e^{\bar{\rho} \sum_{i=0}^5 \sum_{j=0}^6 G_{i,j} (\bar{T}^{-1} - 1)^i (\bar{\rho} - 1)^j}$$

with the parameters $G_{i,j}$ as given in Table 3.

The term $\bar{\eta}_2(\bar{T}, \bar{\rho})$ may be taken as unity for industrial applications, since it concerns only a narrow region around the critical point. The variables with the bar above represent reduced values. These are reduced as follows: $\bar{T} = T/T^*$, $\bar{\rho} = \rho/\rho^*$, $\bar{\eta} = \eta/\eta^*$, with the reference values: $T^* = 647.226$ K, $\rho^* = 317.763$ kg.m⁻³, $\eta^* = 55.071 \times 10^{-6}$ Pa.s.

Table 3 - G_{ij} parameters for the water viscosity equation.

i \ j	0	1	2	3	4	5	6
0	0.513 204 7	0.215 177 8	-0.281 810 7	0.177 806 4	-0.041 766 1	0.0	0.0
1	0.320 565 6	0.731 788 3	-1.070 786	0.460 504 0	0.0	-0.015 783 86	0.0
2	0.0	1.241 044	-1.263 184	0.234 037 9	0.0	0.0	0.0
3	0.0	1.476 783	0.0	-0.492 417 9	0.160 043 5	0.0	-0.003 629 481
4	-0.778 256 7	0.0	0.0	0.0	0.0	0.0	0.0
5	0.188 544 7	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX C - THE FENGHOUR ET AL. (1995)⁴² METHOD FOR THE CALCULATION OF THE VISCOSITY OF AMMONIA

According to Fenghour et al., the viscosity of a fluid may be calculated from

$$\eta(\rho, T) = \eta_0(T) + \Delta\eta(\rho, T) + \Delta\eta_c(\rho, T)$$

where $\eta_0(T)$ represents the viscosity at the zero-density limit, $\Delta\eta(\rho, T)$ represents the excess viscosity at higher density over that of the dilute gas at the same temperature, and $\Delta\eta_c(\rho, T)$ accounts for near critical point effects.

At the zero-density limit, a model based upon the kinetic theory of diluted gases is proposed by the authors:

$$\eta_0(T) = \frac{2.1357 \times T^{1/2} M^{1/2}}{\zeta^2 \zeta_\eta^*}$$

ζ is a length scaling parameter, M is the molecular mass of ammonia, and ζ_η^* is obtained from

$$\zeta_\eta^* = e^{\sum_{i=0}^4 a_{\eta_i} (\ln \theta^*)^i}$$

$$\text{with } \theta^* = \frac{\kappa}{\epsilon} T.$$

ζ and ϵ/κ were determined to have the values 0.2957 nm and 386 K , respectively. Since there are no experimental data for the viscosity of ammonia around the critical point, no specific effects for that region may be described independently. The excess viscosity $\Delta\eta(\rho, T)$ shall account for all effects, and is calculated as

$$\Delta\eta(\rho, T) = \rho b_1(T) + \sum_{i=2}^4 \left[\rho \sum_{j=0}^4 \frac{d\eta_{ij}}{\theta^{*j}} \right]$$

where the first viscosity coefficient $b_1(T)$, is calculated from

$$b_1(T) = 0.6022137 \times \eta_0(T) \zeta^3 \sum_{i=0}^{12} c\eta_i (\sqrt{\theta^*})^{-i}$$

In all these equations ρ is the molecular density in mol.l^{-1} . The coefficients $a\eta$, $c\eta$ and $d\eta$ are given in the following tables 4 and 5.

Table 4 - The coefficients $a\eta$ and $c\eta$ for the dynamic viscosity model.

i	$a\eta$	$c\eta$
0	4.993 182 20	-0.179 994 96x10 ¹
1	-0.611 223 64	0.466 926 21x10 ²
2	0.0	-0.534 607 94x10 ³
3	0.185 351 24	0.336 040 74x10 ⁴
4	-0.111 609 46	-0.130 191 64x10 ⁵
5		0.334 142 30x10 ⁵
6		-0.587 117 43x10 ⁵
7		0.714 266 86x10 ⁵
8		-0.598 34012x10 ⁵
9		0.336 527 41x10 ⁵
10		-0.120 273 50x10 ⁵
11		0.243 482 05x10 ⁴
12		-0.208 079 57x10 ³

Table 5 - The coefficients $d\eta$ for the dynamic viscosity model.

j	$d\eta_{2,j}$	$d\eta_{3,j}$	$d\eta_{4,j}$
0	0.0	$0.173\ 669\ 36 \times 10^{-2}$	0.0
1	0.0	$-0.642\ 503\ 59 \times 10^{-2}$	0.0
2	$2.196\ 642\ 85 \times 10^{-1}$	0.0	$1.676\ 686\ 49 \times 10^{-4}$
3	0.0	0.0	$-1.497\ 100\ 93 \times 10^{-4}$
4	$-0.836\ 511\ 07 \times 10^{-1}$	0.0	$0.770\ 122\ 74 \times 10^{-4}$

APPENDIX D - THE SIMPLE ABSORPTION CYCLE WITH THE MIXTURE {AMMONIA + WATER}

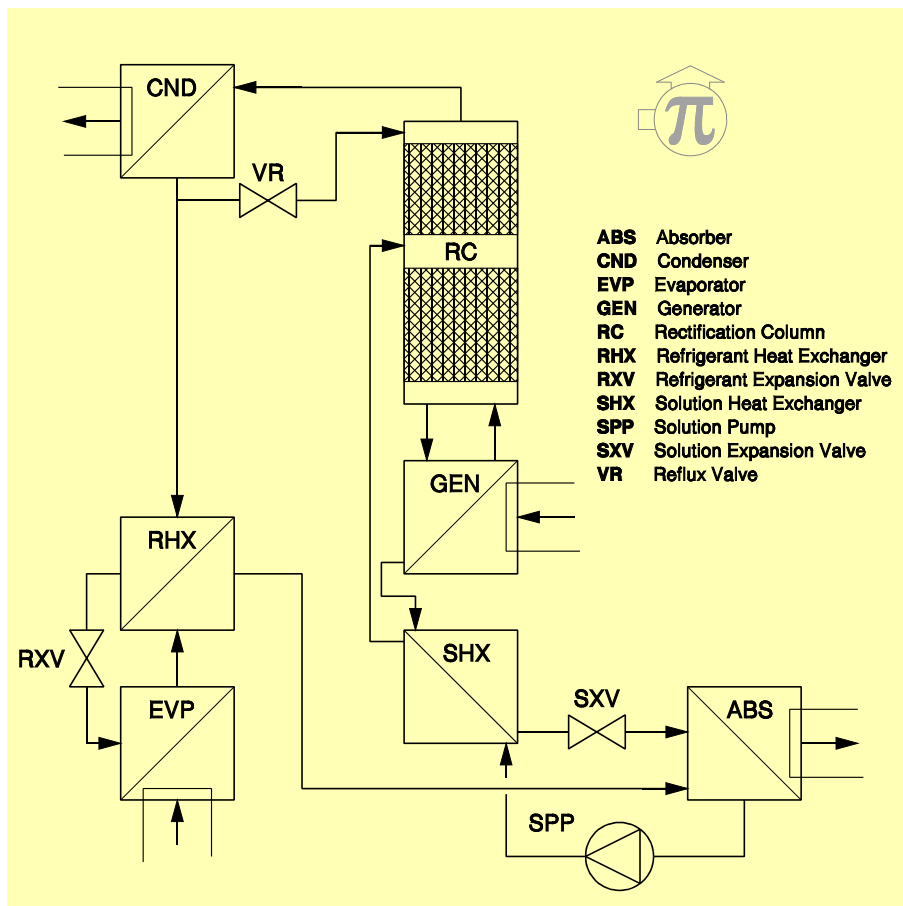


Fig. 26 - Schematic diagram of a simple absorption cycle, including internal heat recovery, operating with {ammonia + water}.

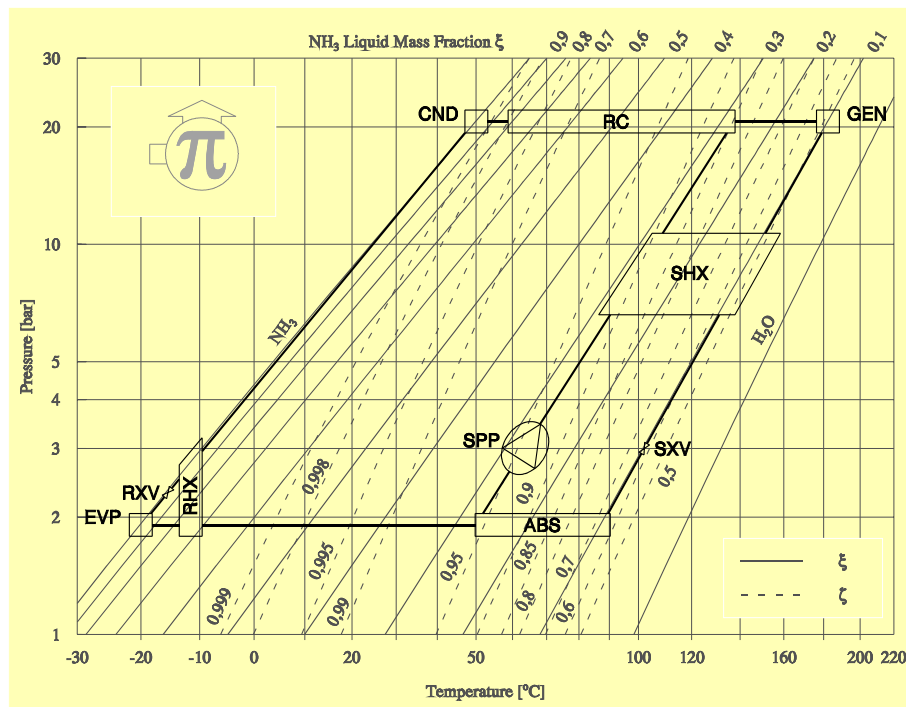


Fig. 27 - Representation of the simple absorption cycle on a PTX diagram of the mixture {ammonia + water}.

APPENDIX E - A GAX ABSORPTION CYCLE WITH THE MIXTURE {AMMONIA + WATER}

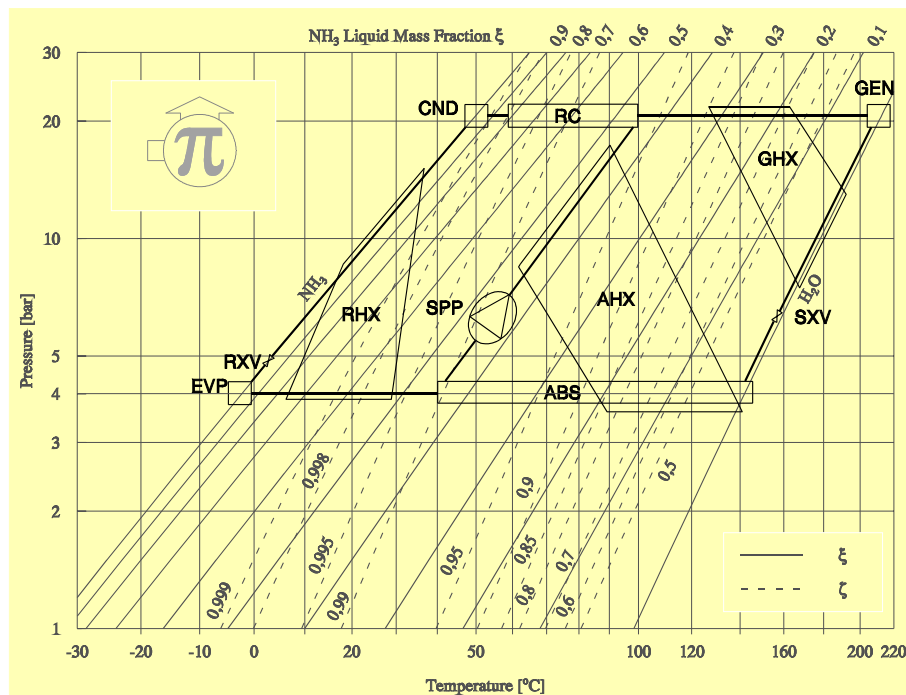


Fig. 28 - Representation of a GAX absorption cycle on a PTX diagram of the mixture {ammonia + water}.