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Aqueous solutions of lithium and calcium chlorides: – Property formulations for use in air conditioning equipment design

Manuel R. Conde-Petit
 M. CONDE ENGINEERING
 Zurich - Switzerland

Abstract

The dehydration of air, for air conditioning purposes, either for human comfort or for industrial processes, is done most of the times by making it contact a surface at a temperature below its dew point. In this process not only is it necessary to cool that surface continuously, but also the air is cooled beyond the temperature necessary to the process, thus requiring reheating after dehumidification. Although the equipment for this purpose is standard and mostly low-cost, the running costs are high and high grade energy is dissipated at very low efficiency. Alternative sorption-based processes require only low grade energy for regeneration of the sorbent materials, thus incurring lower running costs. On the other hand, sorption technology equipment is usually more expensive than standard mechanical refrigeration equipment, which is essentially due to their too small market share. This report describes the development of calculation models for the thermophysical properties of aqueous solutions of the chlorides of lithium and calcium, particularly suited for use as desiccants in sorption-based air conditioning equipment. This development has been undertaken in order to create consistent methods suitable for use in the industrial design of liquid desiccant-based air conditioning equipment. We have reviewed sources of measured data from 1850 onwards, and propose calculation models for the following properties of those aqueous solutions: Solubility boundary, vapour pressure, density, surface tension, dynamic viscosity, thermal conductivity, specific thermal capacity, and differential enthalpy of dilution.

Keywords: liquid desiccants/properties/air conditioning/lithium chloride/calcium chloride/calculation models

Nomenclature

C_p	specific thermal capacity	$\text{kJ.kg}^{-1}.\text{K}^{-1}$	ρ	density	kg.m^{-3}
p	pressure	kPa	σ	surface tension	mN.m^{-1}
T	temperature (absolute)	K	ϑ	temperature (centigrade)	$^{\circ}\text{C}$
h_d	enthalpy of dilution	$\text{kJ.kg}^{-1}_{\text{H}_2\text{O}}$	Δ	difference, differential	
M	molar mass				
<i>Greek Symbols</i>			<i>Subscripts</i>		
η	dynamic viscosity	mPa.s	c	at the critical point	
θ	reduced temperature (with critical temperature of water, except when defined otherwise)		H_2O	for water	
λ	thermal conductivity	$\text{mW.m}^{-1}.\text{K}^{-1}$	$\text{H}_2\text{O},0$	for water at 0 $^{\circ}\text{C}$	
ζ	mass fraction of solute		$\text{H}_2\text{O},20$	for water at 20 $^{\circ}\text{C}$	
π	relative pressure		sol	for the solution	

Introduction

Aqueous solutions of alkali halides have a set of very useful characteristics for applications in refrigeration and air conditioning. While they were first studied and characterized as freezing point depressors and used as brines in refrigeration applications, other of their properties, such as the high water affinity, were later recognized as very interesting for the dehydration of gases, in particular of air. Dehydration (dehumidification) of air is an important operation in many processes, especially in air conditioning, either for human comfort or for industrial processes. The important point here is that the air does not have to be cooled below its dew-point, as is typical of surface dehumidification. It may be sufficiently dehumidified at temperatures well above its dew-point. This may have a significant impact in the energy requirements and on the size and capacity of the cooling equipment necessary.

The R&D effort in this field has increased significantly in the last twenty years, in particular because of the perceived need to replace the more conventional technologies that use mechanical refrigeration equipment. Uncertainties regarding the availability of safe and suitable working fluids for mechanical refrigeration systems, as well as the effort to reduce greenhouse gases emitted in power generation, are pressing manufacturers, designers and users to search for alternative solutions, naturally without any penalty in the perceived quality of life and in the quality of manufacturing facilities.

On the other hand, systems using sorption processes to dehydrate gases require only low grade thermal driving energy for the regeneration of the sorbent materials, besides some electric power for the prime movers in the system, mostly electric motors. Low grade thermal energy for the regeneration process, may be obtained from effluents in many production processes including CHP, or from solar thermal collectors. Theoretically, at least, such low grade energy should be much cheaper than the electric power required to drive conventional mechanical refrigeration equipment. However, as in many situations in life, the newcomer must overdo the incumbent by a large advantage to be seriously considered.

Basic materials used in sorption based dehydration of air and other gases, are mostly naturally occurring substances. However, besides having to overdo the incumbent technology, sorption based technologies for air conditioning seem to get much less R&D effort than that invested in the development of new, completely artificial substances, suitable to replace those working fluids that had to be banned, due to their hazardous effects on the environment. It is perhaps a signal of our times that a larger effort is invested in the development of non-natural working fluids than on the development of the processes and equipment that may use natural substances to the same effect.

In this communication we report on the properties of the aqueous solutions of lithium and calcium chlorides, particularly on empirical formulations of their thermophysical properties required in the industrial design of sorption based air conditioning equipment. To that end, we have reviewed the literature spanning the period from 1850 onwards. Special care has been taken in order for the formulations to reproduce the measured data sets with good accuracy in their range of validity, and that they remain congruent at the limits of concentration. Formulations for the calculation of the following properties are described herein:

- Solubility boundary,
- Vapour pressure,
- Density,
- Surface tension,
- Dynamic viscosity,
- Thermal conductivity,
- Specific thermal capacity,
- Differential enthalpy of dilution, and
- Diffusion coefficient of water into aqueous solutions.

Furthermore, Othmer and Dühring diagrams and a diagram giving the relative humidity of air in equilibrium with solutions of both chlorides are also discussed.

We expect that this work will contribute to ease the efforts of the few R&D groups and manufacturers active in the development of sorption based technologies for air conditioning applications.

Solubility boundary

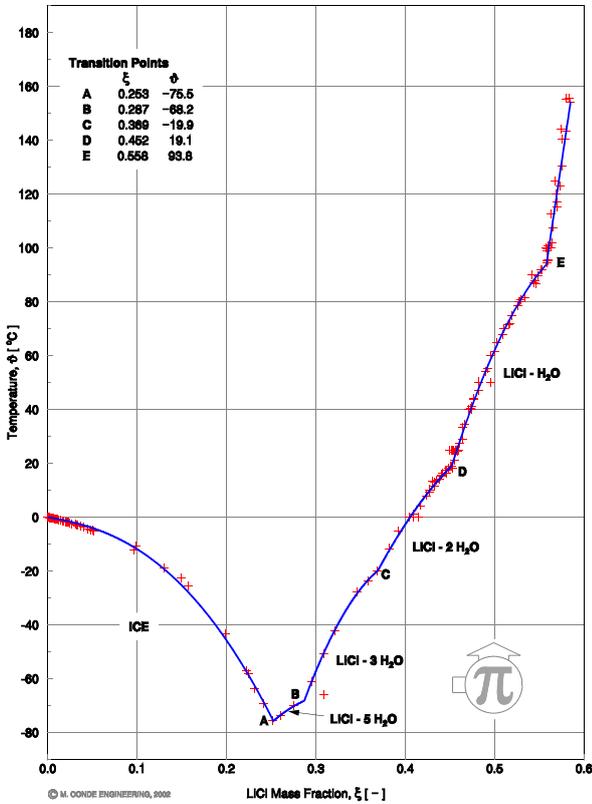


Figure 1 - Solubility boundary of aqueous solutions of lithium chloride.

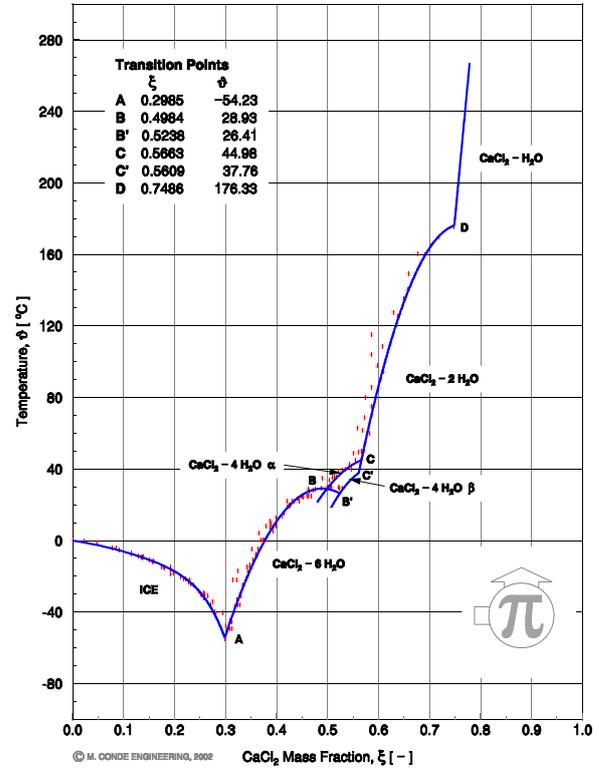


Figure 2 - Solubility boundary of aqueous solutions of calcium chloride.

The solubility boundaries of these two salt solutions are defined by several lines. For salt concentrations lower than that at the eutectic point, the solubility line defines the conditions at which ice crystals start to form. This is the ice line. For higher concentrations, the solubility boundary defines the conditions at which salt hydrates or anhydrous salt crystallize from the solution. This is the crystallization line.

For LiCl-H₂O solutions, the crystallization line, A-B-C-D-E in Figure 1, defines also the transition points separating the ranges of formation of the various hydrates, as indicated in the Figure. Equations for each range were adjusted to experimental data from the literature [1-14] and have the general form for the crystallization line:

$$\theta = \sum_{i=0}^2 A_i \xi^i \quad \theta \equiv \frac{T}{T_{c,H_2O}}$$

where ξ is the mass fraction of the salt in the solution. For the ice line, the equation is slightly different:

$$\theta = A_0 + A_1 \xi + A_2 \xi^{2.5}$$

The parameters A_i are included in Table I, for each range of the boundary.

Boundary	A_0	A_1	A_2
Ice Line	0.422 088	-0.090 410	-2.936 350
LiCl-5H ₂ O	-0.005 340	2.015 890	-3.114 590
LiCl-3H ₂ O	-0.560 360	4.723 080	-5.811 050
LiCl-2H ₂ O	-0.315 220	2.882 480	-2.624 330
LiCl-H ₂ O	-1.312 310	6.177 670	-5.034 790
LiCl	-1.356 800	3.448 540	0.0

Figure I - Parameters of the equations describing the solubility boundary of LiCl-H₂O solutions.

For CaCl₂-H₂O solutions, the crystallization line is more complex, particularly due to the formation of various tetrahydrates. Some of those are metastable. In the boundary represented in *Figure 2* we decided to show only those generally reported as stable in the literature, i.e. the α and β tetrahydrates, with the boundaries described below.

The equations adjusted to measured data from the literature [9,15-25] have the general form given above, with the exception of the ice line, which is described by the equation

$$\theta = \sum_{i=0}^2 A_i \xi^i + A_3 \xi^{7.5}$$

with θ as defined before. The parameters of this equation and those for the various ranges of the crystallization line are given in Table II.

The transition points between the boundaries are shown in *Figure 2*.

Boundary	A_0	A_1	A_2	A_3
Ice Line	0.422 088	-0.066 933	-0.282 395	-355.514 247
CaCl ₂ -6H ₂ O	-0.378 950	3.456 900	-3.531 310	0.0
CaCl ₂ -4H ₂ O α	-0.519 970	3.400 970	-2.851 290	0.0
CaCl ₂ -4H ₂ O β	-1.149 044	5.509 111	-4.642 544	0.0
CaCl ₂ -2H ₂ O	-2.385 836	8.084 829	-5.303 476	0.0
CaCl ₂ -H ₂ O	-2.807 560	4.678 250	0.0	0.0

Figure II - Parameters of equations describing the solubility boundary of CaCl₂-H₂O solutions.

Vapour Pressure

The equilibrium pressure of saturated water vapour above aqueous solutions of the salts here considered is perhaps their best studied property. Despite the amount of experimental data, spanning almost a century of research, no consistent formulation for the accurate prediction of this property has yet been published. Most attempts made are limited to short ranges either on concentration or temperature. Formulations derived from basic principles have not done better than the empirical ones and are confined to very dilute solutions. The formulations we report in the following reproduce quite accurately the known experimental data and default to congruent values at the boundaries.

We formulate it in terms of the relative vapour pressure π (to water at the same temperature, Appendix A). In fact we established an accurate formula for a single temperature, for which accurate measured data are known, as function of the mass fraction, and derived a correction function for other temperatures in the available range of data.

The general equation is

$$\pi \equiv \frac{p_{sol}(\xi, T)}{p_{H_2O}(T)} = \pi_{25} f(\xi, \theta)$$

where

$$f(\xi, \theta) = A + B \theta$$

$$A = 2 - \left[1 + \left(\frac{\xi}{\pi_0} \right)^{\pi_1} \right]^{\pi_2}$$

$$B = \left[1 + \left(\frac{\xi}{\pi_3} \right)^{\pi_4} \right]^{\pi_5} - 1$$

$$\pi_{25} = 1 - \left[1 + \left(\frac{\xi}{\pi_6} \right)^{\pi_7} \right]^{\pi_8} - \pi_9 e^{-\frac{(\xi - 0.1)^2}{0.005}}$$

	LiCl - H ₂ O	CaCl ₂ - H ₂ O
π_0	0.28	0.31
π_1	4.30	3.698
π_2	0.60	0.60
π_3	0.21	0.231
π_4	5.10	4.584
π_5	0.49	0.49
π_6	0.362	0.478
π_7	-4.75	-5.20
π_8	-0.40	-0.40
π_9	0.03	0.018

and the parameters are given in Table III for both salt solutions.

The parameters for $f(\xi, \theta)$ were derived from the data of Gibbard [26] for LiCl-H₂O and from the data of Baker and Waite [27] for CaCl₂-H₂O. The graphs depicted in *Figures 3 and 4*, for LiCl-H₂O and CaCl₂-H₂O, respectively, show plots of the vapour pressure along isotherms calculated with the equations adjusted, against the data from the literature.

The literature sources are, for LiCl-H₂O [1,2,22,28-42], and for CaCl₂-H₂O [17,18, 22,28,30,43-52].

Figure III - Parameters for the vapour pressure equation.

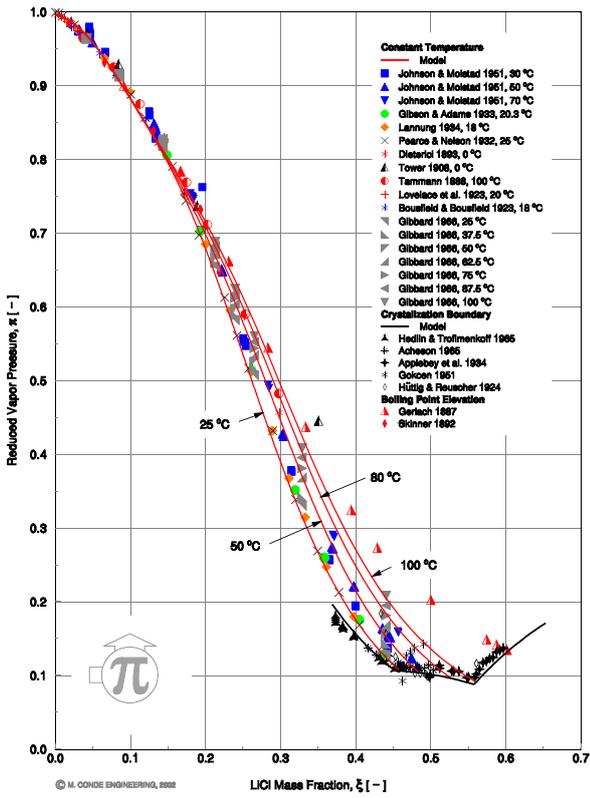


Figure 3 - Relative vapour pressure of aqueous solutions of lithium chloride.

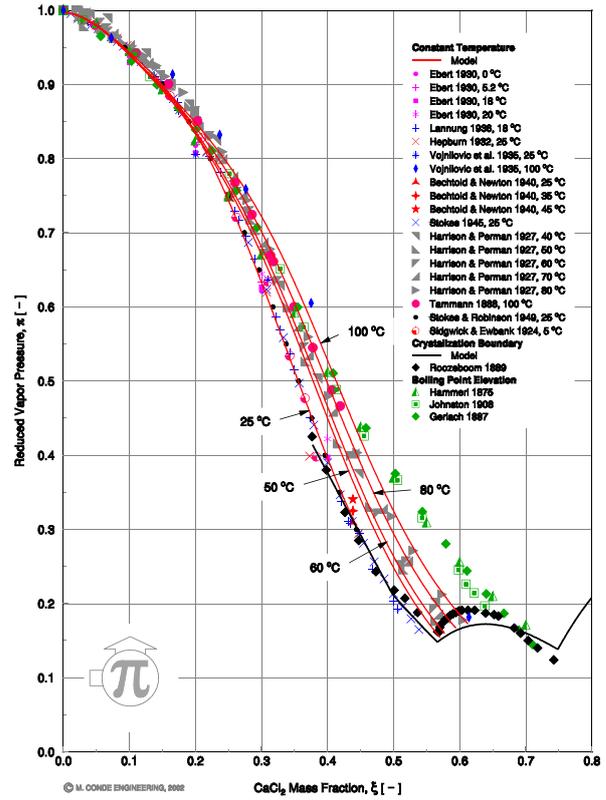


Figure 4 - Relative vapour pressure of aqueous solutions of calcium chloride.

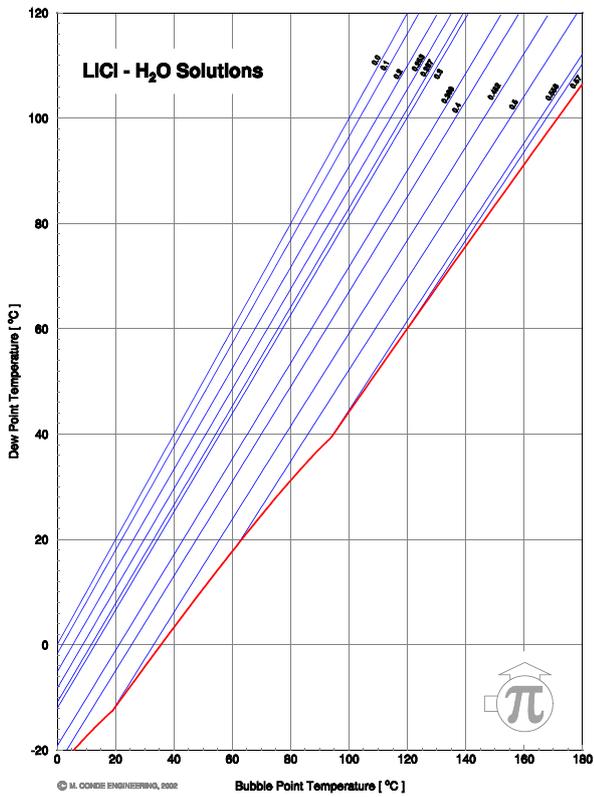


Figure 5 - Dühring diagram for aqueous solutions of lithium chloride.

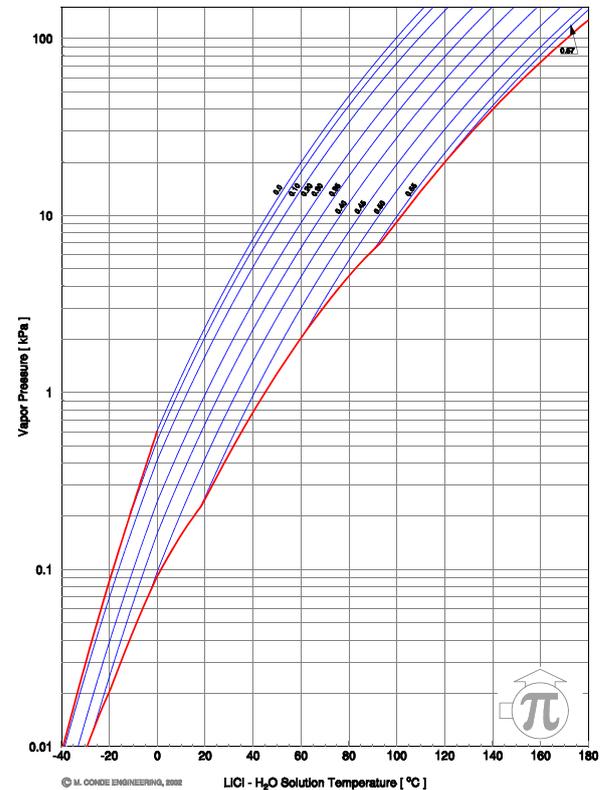


Figure 6 - Othmer diagram for aqueous solutions of lithium chloride.

Two types of charts are commonly used to represent the vapour pressure of solutions, namely Dühring [53] and Othmer [54,55] charts. The Dühring chart represents the dew-point temperature of the vapour phase against the bubble point temperature of the solution, while the Othmer chart represents the vapour pressure against the solution temperature. *Figures 5 and 6* show Dühring and Othmer charts for aqueous solutions of lithium chloride with several isosterics. *Figures 7 and 8* depict the same kind of charts for aqueous solutions of calcium chloride.

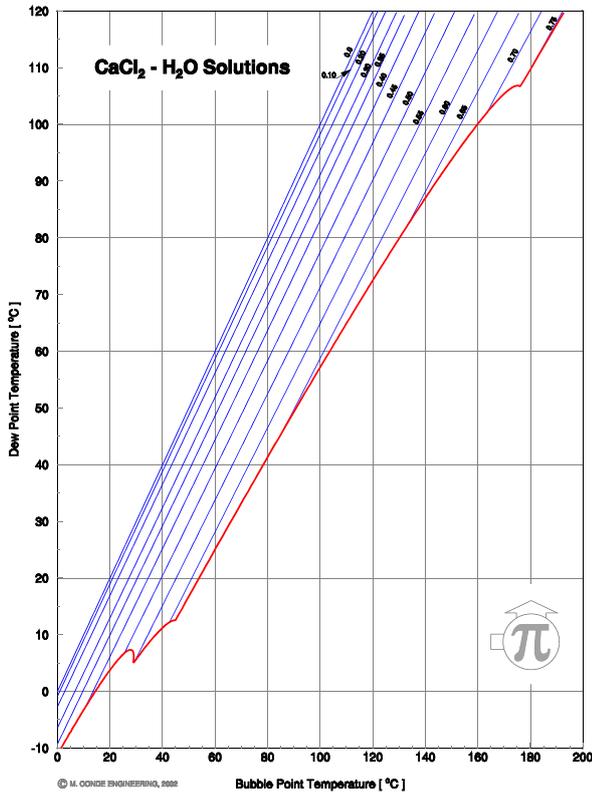


Figure 7 - Dühring chart for aqueous solutions of calcium chloride.

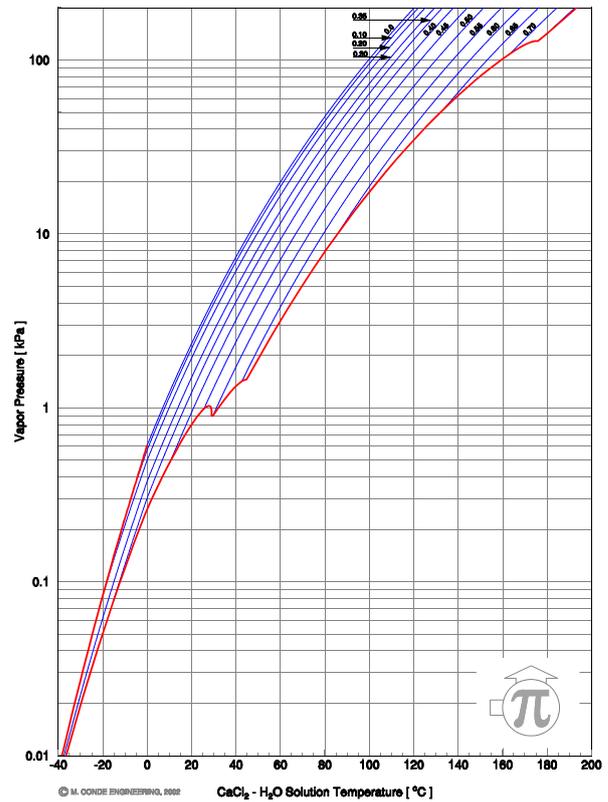


Figure 8 - Othmer chart for aqueous solutions of calcium chloride.

For the particular application of these solutions as desiccants in air conditioning, it was thought useful to develop a new type of chart showing lines of equilibrium of solution vapour pressure with the partial pressure of water vapour in the air. The charts depicted in *Figures 9 and 10* are of this new type for aqueous solutions of lithium and calcium chlorides, respectively, at an atmospheric pressure of 101.325 kPa (sea level atmospheric pressure). Shown in the charts are the corresponding relative humidity lines. This type of chart permits the visualization of the required dilution of the solution for a given dehydration of the air, when the efficiency of the dehumidification system is known.

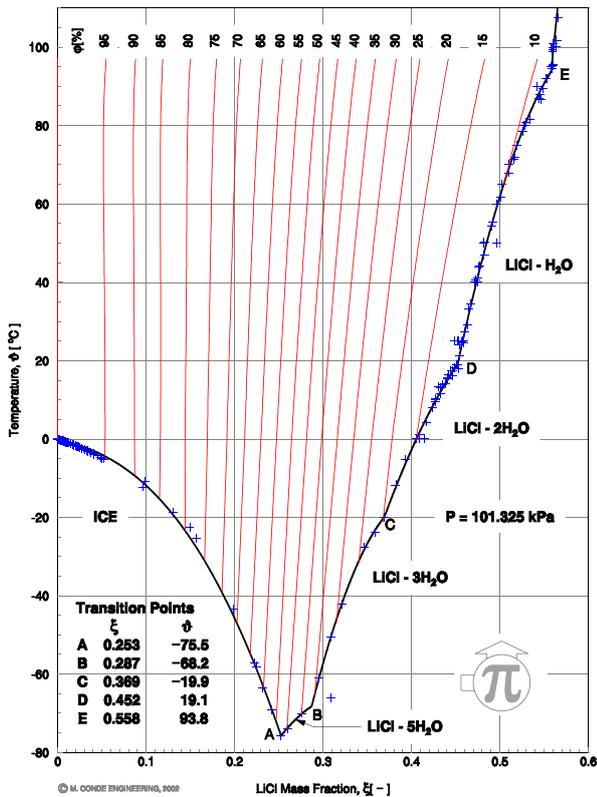


Figure 9 - Chart of equilibrium between the vapour pressure of aqueous solutions of lithium chloride and the partial pressure of water vapour in the air, at the normal sea level atmospheric pressure.

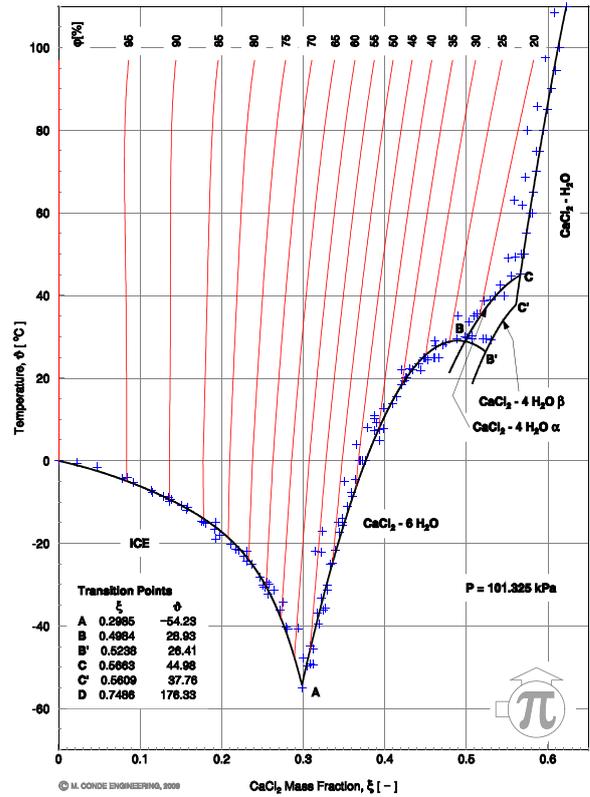


Figure 10 - Chart of equilibrium between the vapour pressure of aqueous solutions of calcium chloride and the partial pressure of water vapour in the air, at the normal sea level atmospheric pressure.

Density

The densities of aqueous solutions of lithium and calcium chlorides have been extensively studied and reported upon in the literature (for LiCl-H₂O [1,33,38,56-70] and for CaCl₂-H₂O [46,58,62,70-78]). As shown in *Figures 11 and 12*, for LiCl-H₂O and CaCl₂-H₂O, respectively, the relative (to saturated liquid water at the same temperature) densities may be represented by a single cubic function of the mass fraction ratio solute solvent $\xi/(1 - \xi)$. This function has the form

$$\rho_{sol}(\xi, T) = \rho_{H_2O}(T) \sum_{i=0}^3 \rho_i \left(\frac{\xi}{1 - \xi} \right)^i$$

where the ρ_i are given in Table IV for the solutions of both chlorides. $\rho_{H_2O}(T)$ is the density of saturated liquid water at the temperature T . It is calculated from

$$\rho_{H_2O}(\tau) = \rho_{c,H_2O} \left(1 + B_0 \tau^{\frac{1}{3}} + B_1 \tau^{\frac{2}{3}} + B_2 \tau^{\frac{5}{3}} + B_3 \tau^{\frac{16}{3}} + B_4 \tau^{\frac{43}{3}} + B_5 \tau^{\frac{110}{3}} \right)$$

where $\tau \equiv 1 - \theta$ and the B_i are given in Table V. ρ_{c,H_2O} is the density of water at the critical point (322 kg.m⁻³).

	LiCl-H ₂ O	CaCl ₂ -H ₂ O
ρ_0	1.0	1.0
ρ_1	0.540 966	0.836 014
ρ_2	-0.303 792	-0.436 300
ρ_3	0.100 791	0.105 642

Figure IV - Parameters of the density equation.

i	B _i
0	1.993 771 843 0
1	1.098 521 160 4
2	-0.509 449 299 6
3	-1.761 912 427 0
4	-44.900 548 026 7
5	-723 692.261 863 2

Figure V - Parameters for the liquid water density equation.

For solutions of LiCl, the scatter is almost negligible. The break point defined on the base of the data Applebey et al. [1] for the crystallization boundary, does not exactly match the corresponding transition point in Figure 1. This is due to the scarce density data for concentrations higher than that at that transition point.

For solutions of CaCl₂, the scatter is somewhat larger, although the prediction of a single function remains excellent. The range of application of the equation is $0 \leq \xi \leq 0.56$ and $0 \leq \xi \leq 0.60$ for solutions of LiCl and CaCl₂, respectively.

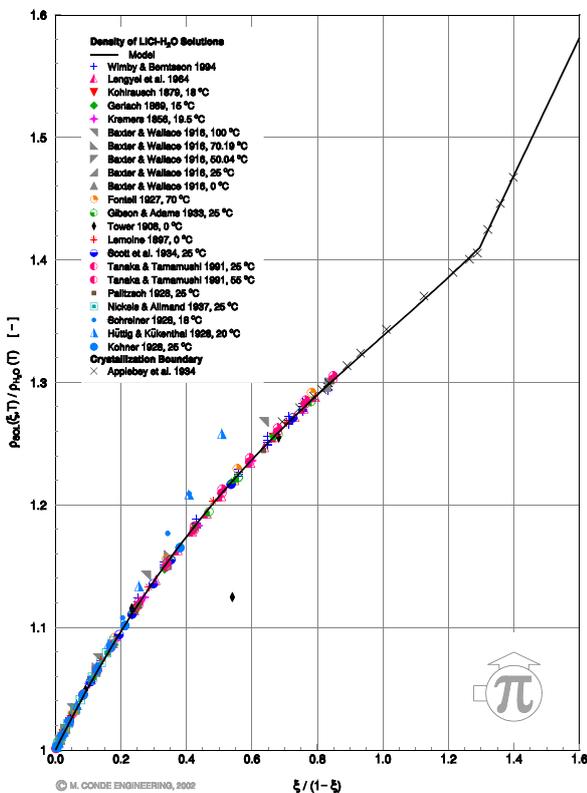


Figure 11 - Relative densities of aqueous solutions of lithium chloride.

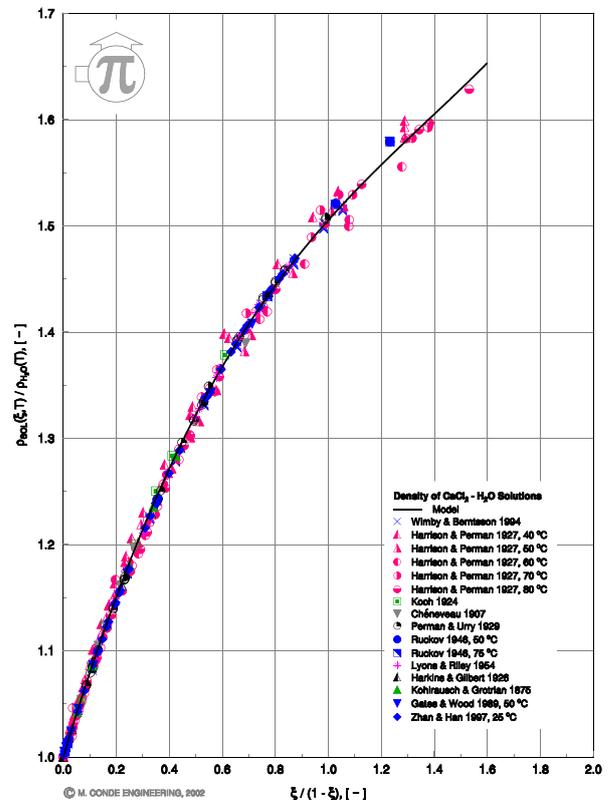


Figure 12 - Relative densities of aqueous solutions of calcium chloride.

Surface Tension

The values of the surface tension of aqueous solutions of the lithium and calcium chlorides reported in the literature (for LiCl-H₂O [65,79-86], and for CaCl₂-H₂O [74,87-91]) are well reproduced by a function of the reduced temperature and mass fraction of the form

$$\sigma_{sol}(\xi, \theta) = \sigma_{H_2O}(\theta) \left(1 + \sigma_1 \xi + \sigma_2 \xi \theta + \sigma_3 \xi \theta^2 + \sigma_4 \xi^2 + \sigma_5 \xi^3 \right)$$

where θ is, as defined before, the reduced temperature of water $\frac{T}{T_{c,H_2O}}$.

The parameters σ_i are given in Table VI for the solutions of both chlorides. Figures 13 and 14 show comparisons of values calculated with the model proposed with data from the literature cited above.

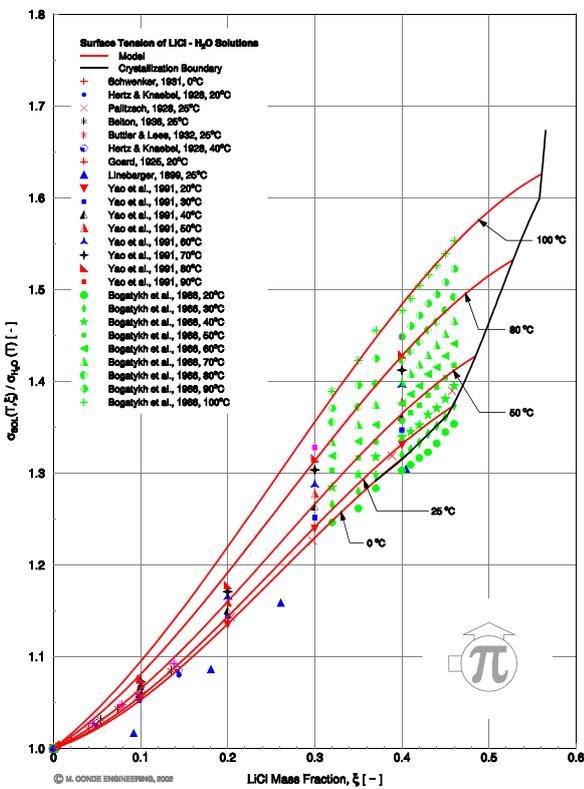


Figure 13 - Relative values of the surface tension of aqueous solutions of lithium chloride. Model plotted against literature data.

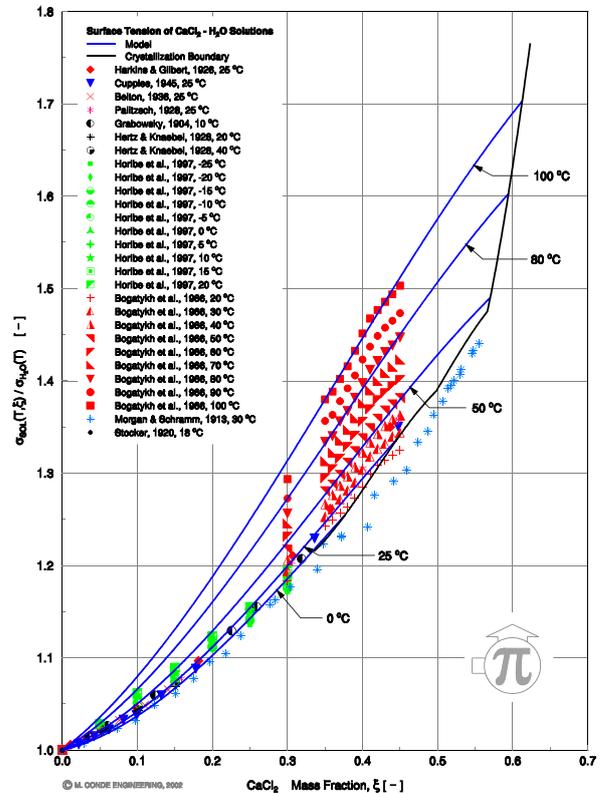


Figure 14 - Relative values of the surface tension of aqueous solutions of calcium chloride. Model plotted against literature data.

	σ_1	σ_2	σ_3	σ_4	σ_5
LiCl - H ₂ O	2.757 115	-12.011 299	14.751 818	2.443 204	-3.147 739
CaCl ₂ - H ₂ O	2.330 67	-10.787 79	13.566 11	1.950 17	-1.779 90

Figure VI - Parameters of the equation to calculate the surface tension of aqueous solutions of lithium and calcium chlorides.

The surface tension of water $\sigma_{H_2O}(\theta)$ is calculated with the equation

$$\sigma_{H_2O}(\theta) = \sigma_0 [1 - b(1 - \theta)](1 - \theta)^\mu$$

proposed by the IAPWS [92] where $\sigma_0 = 235.8 \text{ mN.m}^{-1}$, $b = -0.625$ and $\mu = 1.256$.

Dynamic Viscosity

The dynamic viscosity of aqueous solutions of the lithium and calcium chlorides may be calculated with the equation

$$\eta_{sol}(\zeta, \theta) = \eta_{H_2O}(\theta) e^{\eta_1 \zeta^{3.6} + \eta_2 \zeta + \eta_3 \frac{\zeta}{\theta} + \eta_4 \zeta^2}$$

where ζ is defined as $\zeta \equiv \frac{\xi}{(1 - \xi)^{0.6}}$

The parameters η_i are those in Table VII for the solutions of both chlorides.

	LiCl-H ₂ O	CaCl ₂ -H ₂ O
η_1	0.090 481	-0.169 310
η_2	1.390 262	0.817 350
η_3	0.675 875	0.574 230
η_4	-0.583 517	0.398 750

Figure VII - Parameters of viscosity equation for solutions of lithium and calcium chlorides.

Figures 15 and 16 show comparisons of calculated values with measured data from the literature. For aqueous LiCl solutions, the data available [67-70,93,94,95,96] agree very well with those calculated, while for the solutions of CaCl₂ [70,78,94,95,97,98,] some of the older data, in particular the data of Stakelbeck and Plank [109] at -20 °C, show noticeable deviations.

The dynamic viscosity of water η_{H_2O} , considered here at liquid saturation conditions, is calculated from the formulation recommended by the IAPWS [99] for industrial use, for temperatures above 0 °C, Appendix A.

For subcooled water ($\vartheta < 0$ °C), although the IAPWS formulation would be satisfactory down to approximately -20 °C, we have fitted an equation to the few data available in the literature [100-102], that reproduces those data with excellent accuracy, as shown in *Figure 17*.

The equation is

$$\eta_{H_2O} = \eta_{H_2O,0} \times (A + B\theta^{0.02} + C\theta^{0.04} + D\theta^{0.08} + E\theta^{2.85} + F\theta^8)$$

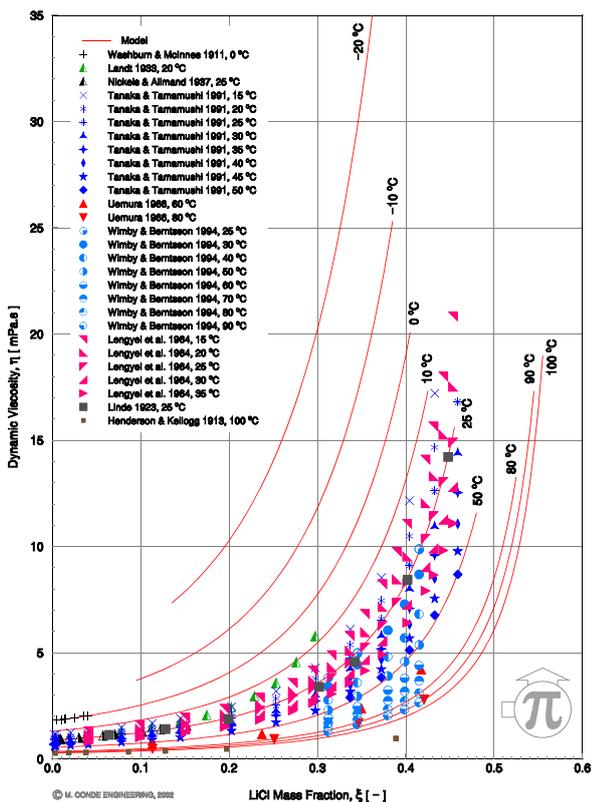


Figure 15 - Dynamic viscosity of aqueous solutions of lithium chloride. Comparison of model with literature data.

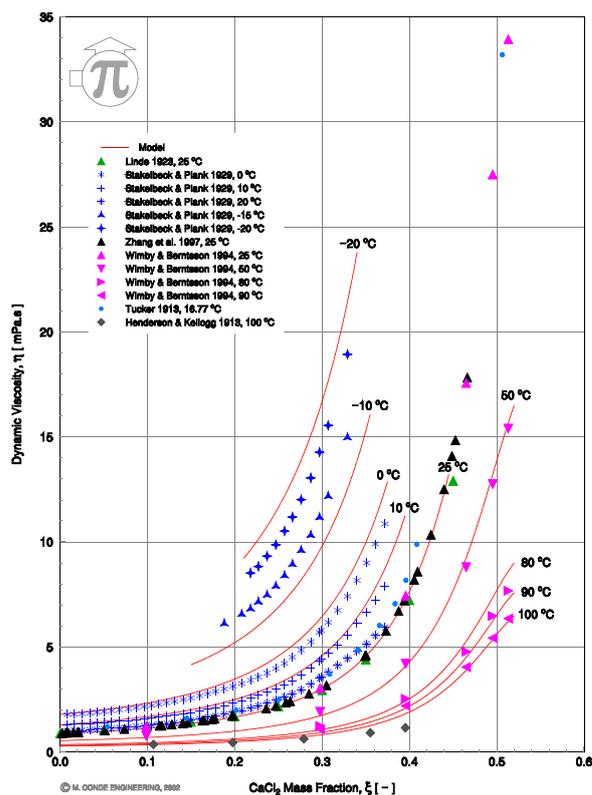


Figure 16 - Dynamic viscosity of aqueous solutions of calcium chloride. Comparison of model with literature data.

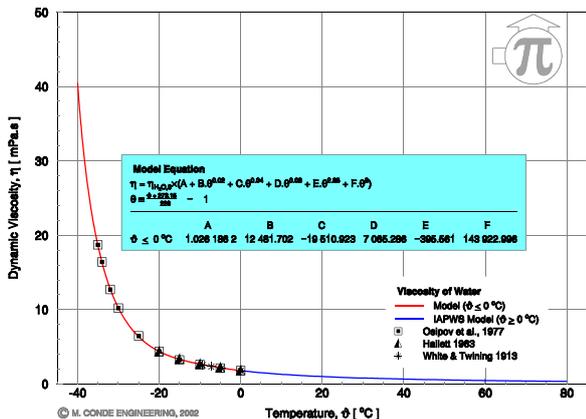


Figure 17 - Dynamic viscosity of subcooled water. Model and literature data.

with θ for this particular case defined as

$$\theta \equiv \frac{T}{228} - 1$$

$\eta_{H_2O,0}$ is the viscosity of liquid water at 0 °C, calculated from the IAPWS formulation.

The parameters A ... F are given in Table VIII.

A	B	C	D	E	F
1.026 186 2	12 481.702	-19 510.923	7 065.286	-395.561	143 922.996

Figure VIII - Parameters of the equation for the dynamic viscosity of subcooled water.

Thermal Conductivity

The thermal conductivity of aqueous solutions of lithium and calcium chlorides are, perhaps, their less well known property. In fact, literature is sparse and the measured data reported seems not to be always beyond doubts regarding accuracy (see for instance, the discussion by Riedel [103] of the results of Meyer [104] and Rau [105] and the answer by Meißner [106]). Even new data, such as those by Assael et al. [107], for calcium chloride and by Takeuchi et al. [108], for lithium chloride, seem to suffer from large uncertainties. This may eventually be due to the very nature of the solutions to be measured and the methods used.

We have considered the data of Riedel [109] and Uemura [96] for lithium chloride, and of Riedel [103,109] for calcium chloride, to obtain the parameters of a model proposed by Riedel [109] and described in the following.

Riedel defined a characteristic value called ‘*equivalent thermal conductivity depression*’ and understood it as a value constant for each salt in aqueous solution, at least for diluted solutions:

$$\alpha_R \equiv \frac{\lambda_{H_2O}(T) - \lambda_{sol}(T, \xi)}{\zeta_{eq}}$$

In this equation, ζ_{eq} is the ‘*equivalent ionic concentration*’ as named by Riedel,

$$\zeta_{eq} = \frac{\xi \times \rho_{sol}(T, \xi) \times I_s}{M}$$

I_s is the ionic strength of the species in solution (1 for LiCl, 2 for CaCl₂), and M the molar mass of the salt in solution.

Riedel also noted that α_R would tend to decrease at the higher concentrations in his measurements. We found that α_R shows a linear dependence upon concentration, for solutions of both lithium and calcium chlorides, decreasing with concentration. Equations for α_R were fitted to the data of Riedel at 20 °C.

$$\alpha_R = \alpha_0 + \alpha_1 \xi$$

Their parameters are given in Table IX for both chlorides.

	LiCl	CaCl ₂
α_0	10.8958x10 ⁻³	5.9473x10 ⁻³
α_1	-11.7882x10 ⁻³	-1.3988x10 ⁻³

Figure IX - Parameters of the α_R equations.

As may be seen in *Figure 18*, the data of Uemura [96], for lithium chloride at temperatures from 10 to 90 °C, are predicted with good accuracy on this basis.

For calcium chloride the values measured at 20 °C are as well predicted with good accuracy, *Figure 19*. All other data, as already mentioned, seem to suffer from poor accuracy, and above all

from inconsistency. This was discussed by Riedel [103] for the data of Meyer [104] and Rau [105]. On the other hand, Assael et al. [107] data for calcium chloride show an almost linear behaviour with temperature and a relation to water values that does not conform to Riedel’s ‘*equivalent thermal conductivity depression*’ model, *Figure 20*. Although those last authors suggest that Riedel’s model would not explain the dependency of the thermal conductivity of the solution upon temperature, we believe that the behaviour shown by their data has essentially to do with their method of measurement and the very nature of the solution to be measured.

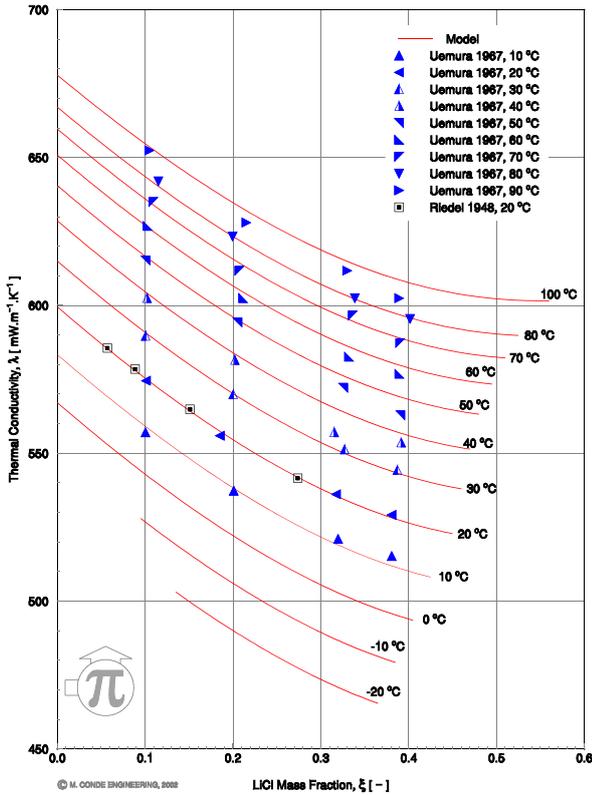


Figure 18 - Thermal conductivity of aqueous solutions of lithium chloride. Comparison of model

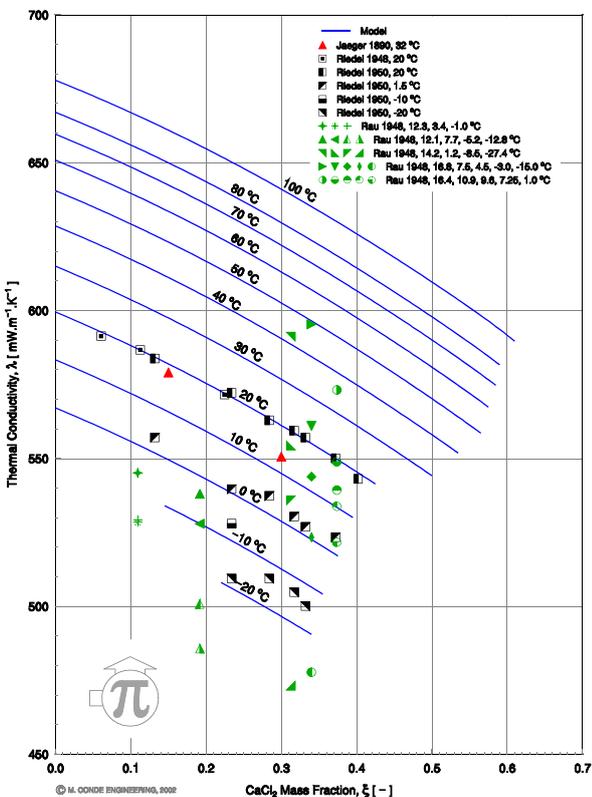


Figure 19 - Thermal conductivity of aqueous solutions of calcium chloride. Comparison of model with measured data.

$\lambda_{H_2O}(T)$ is the thermal conductivity of pure liquid water. For temperatures $\vartheta \geq 20$ °C, it is calculated using the IAPWS formulation for industrial applications as described in Appendix B.

For subcooled water we follow the recommendation of Riedel [103] also adopted by McLaughlin [121], which gives a linear variation of the thermal conductivity with temperature:

$$\lambda_{H_2O}(\theta) = \lambda_{H_2O,20} \times (\lambda_0 + \lambda_1 \theta)$$

$\lambda_{H_2O,20}$ is the thermal conductivity at 20 °C, calculated with the IAPWS formulation.

λ_0 is 0.208 496, λ_1 is 1.747 278, and θ is the water reduced temperature.

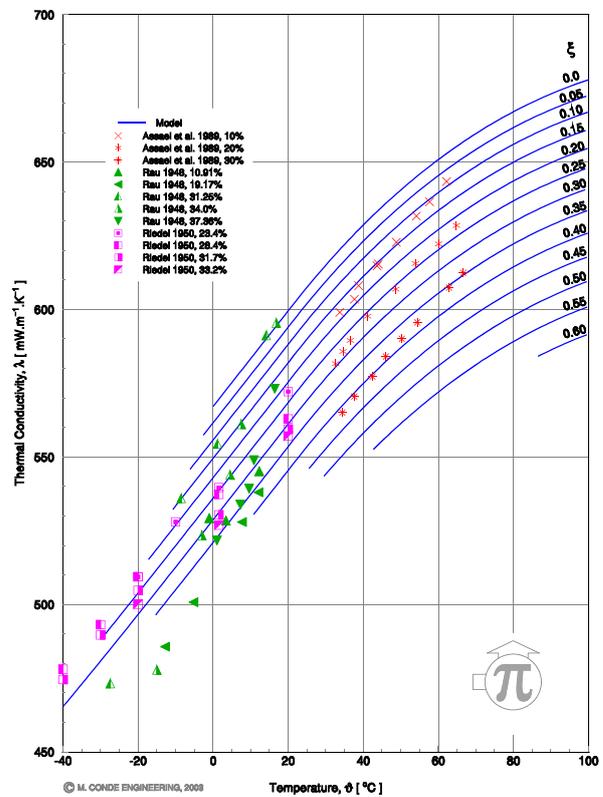


Figure 20 - Thermal conductivity of aqueous solutions of calcium chloride. Temperature dependence.

Specific Thermal Capacity

The specific thermal capacities of aqueous solutions of lithium and calcium chlorides were extensively studied due to their earlier use as a brines in refrigeration systems. The range of temperatures considered was that mostly suitable for this application. Measurements have been reported for lithium chloride by Richards and Rowe [110] Jauch [111] Lange and Dürr [112] Gucker and Schminke [113] and Bennewitz and Kratz [114]. Rüterjans et al. [115] carried out measurements for temperatures up to 90 °C, albeit for low concentrations of the salt, *Figure 23*. For calcium chloride the measurements reported by Dickinson et al. [24], Koch [116], Richards and Dole [117] all cover the range of applications as a refrigeration brine. Ruckov [75] extended the range of measurements up to 75 °C, *Figure 24*. Tucker [120] reports measurements of the specific thermal capacity for solutions of both chlorides. As may be observed from *Figure 23* for lithium chloride, and *Figure 24* for calcium chloride, those measurements do not fit together with the measurements of other authors.

The equation we propose for the calculation of the specific thermal capacity of the solutions of both chlorides, has the following general form:

$$Cp_{sol}(T, \xi) = Cp_{H_2O}(T) \times (1 - f_1(\xi) \times f_2(T))$$

The specific thermal capacity of liquid water is calculated with a modified Sato [118] equation fitted to the data of Angell et al. [119] as

$$Cp_{H_2O}(\theta) = A + B\theta^{0.02} + C\theta^{0.04} + D\theta^{0.06} + E\theta^{1.8} + F\theta^8$$

$$\theta \equiv \frac{T}{228} - 1$$

Figure 21 depicts a graph of this equation comparing it with the data and includes its parameters for the two ranges of validity.

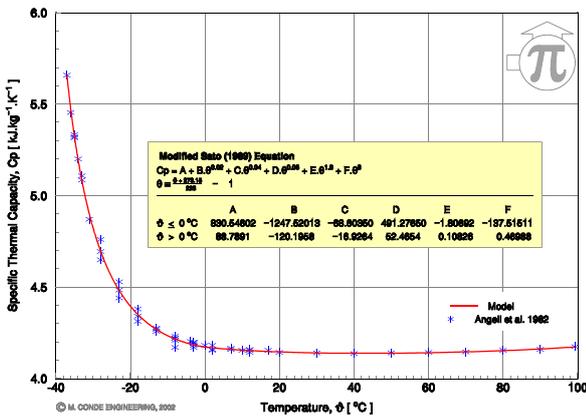


Figure 21 - Specific thermal capacity of liquid water for temperatures down to -35 °C.

The function $f_1(\xi)$

$$f_1(\xi) = A\xi + B\xi^2 + C\xi^3$$

describes the effects of salt concentration upon the specific thermal capacity for the whole range for the solutions of calcium chloride and the up to $\xi \leq 0.31$ for those of lithium chloride. For larger concentrations, it is linear on mass fraction

$$f_1(\xi) = D + E\xi$$

$f_2(T)$ is,

$$f_2(\theta) = F\theta^{0.02} + G\theta^{0.04} + H\theta^{0.06}$$

$$\theta \equiv \frac{T}{228} - 1$$

for both chlorides, with the parameters given in Table X.

	A	B	C	D	E	F	G	H
LiCl-H ₂ O	1.439 80	-1.243 17	-0.120 70	0.128 25	0.629 34	58.522 5	-105.634 3	47.794 8
CaCl ₂ -H ₂ O	1.637 99	-1.690 02	1.051 24	0.0	0.0	58.522 5	-105.634 3	47.794 8

Figure X - Parameters of the equations for the specific thermal capacity of the aqueous solutions of lithium and calcium chlorides.

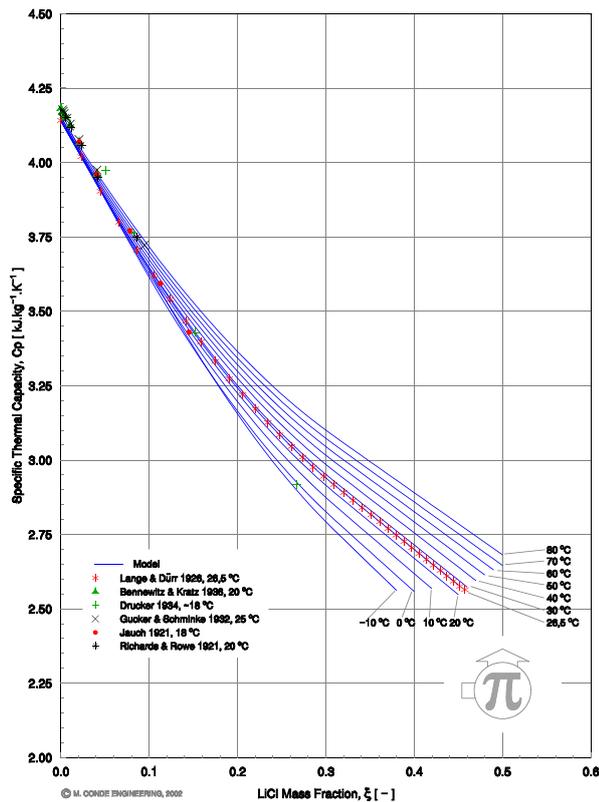


Figure 22 - Specific thermal capacity of aqueous solutions of lithium chloride. Data measured at constant temperature compared with model.

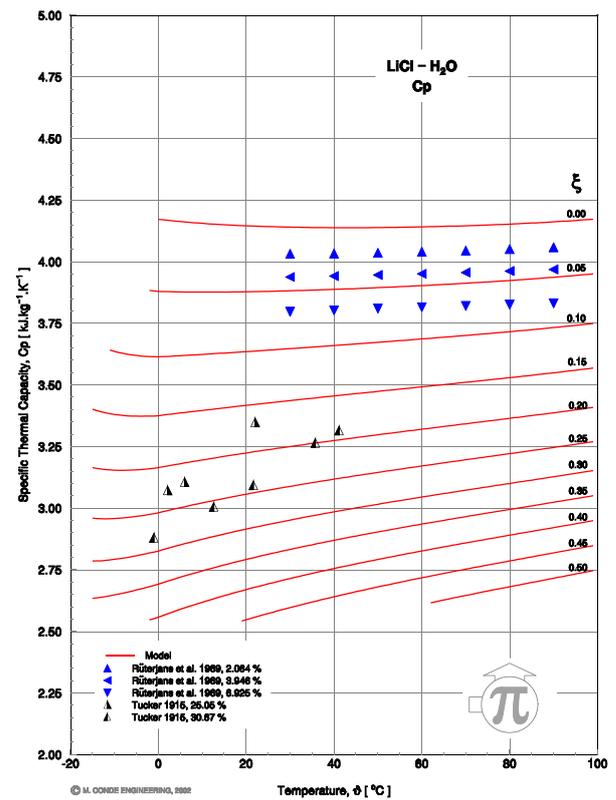


Figure 23 - Specific thermal capacity of aqueous solutions of lithium chloride. Data measured at constant concentration compared with model.

Figures 22 and 23 show comparisons of the model with measured data at constant temperature and concentration, respectively, for aqueous solutions of lithium chloride. *Figures 24 and 25* depict the same comparisons for aqueous solutions of calcium chloride.

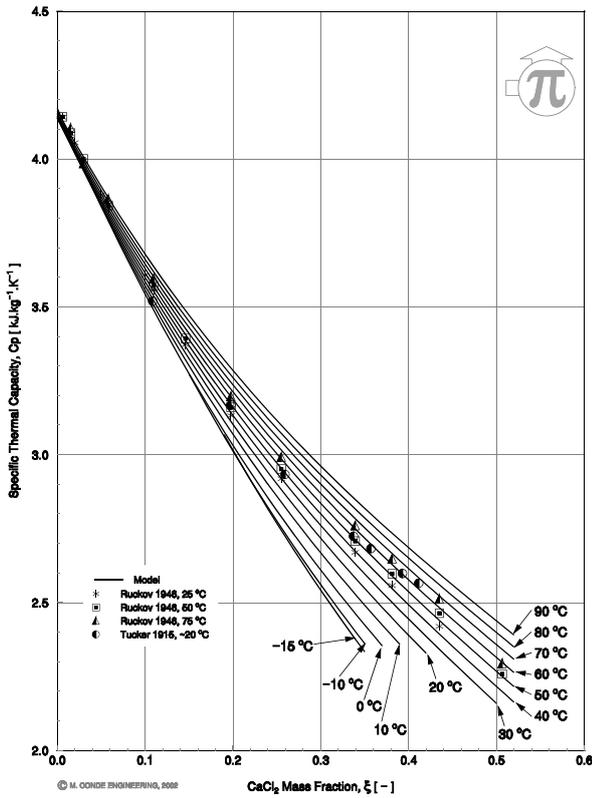


Figure 24 - Specific thermal capacity of aqueous solutions of calcium chloride. Data measured at constant temperature compared with model.

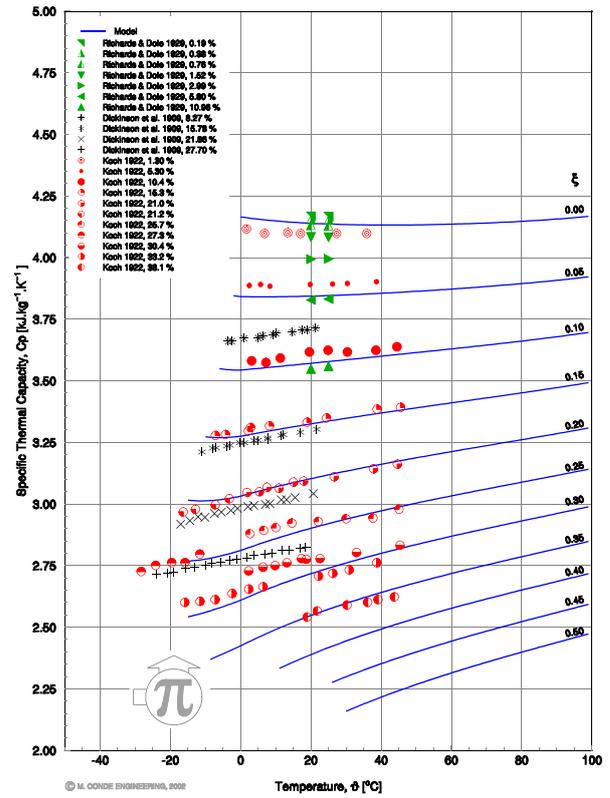


Figure 25 - Specific thermal capacity of aqueous solutions of calcium chloride. Data measured at constant concentration compared with model.

Differential enthalpy of dilution

In the dehydration of gases (e.g. moist air) with aqueous salt solutions, the water vapour is absorbed by the solution in the conditioner, to be later desorbed in the regenerator. For the salt solutions considered here, the absorption (dilution) is an exothermic process, while the desorption (regeneration) requires the supply of thermal energy to the solution. This thermal energy required (or liberated) is larger than that corresponding to the vaporization (or condensation) of pure water. This difference constitutes the energy of dilution, and when referred to the unit mass of water is named *differential enthalpy of dilution*.

We used data from the literature to establish interpolating equations for the differential enthalpy of dilution of aqueous solutions of lithium chloride [40,112] and calcium chloride [46,124]. The equations have the general form:

$$\Delta h_d = \Delta h_{d,0} \left[1 + \left(\frac{\zeta}{H_1} \right)^{H_2} \right]^{H_3}$$

where ζ is defined from the salt mass fraction as

$$\zeta = \frac{\xi}{H_4 - \xi}$$

The reference $\Delta h_{d,0}$ is related to the temperature as

$$\Delta h_{d,0} = H_5 + H_6 \theta$$

The parameters H_i for these equations are given in Table XI:

	LiCl - H ₂ O	CaCl ₂ - H ₂ O
H ₁	0.845	0.855
H ₂	-1.965	-1.965
H ₃	-2.265	-2.265
H ₄	0.6	0.8
H ₅	169.105	-955.690
H ₆	457.850	3011.974

Figure XI - Parameters of the differential enthalpy of dilution equations for solutions of lithium and calcium chlorides.

The graphs of Figures 26 and 27 show comparisons of the literature data with calculations with the models described, for aqueous solutions of lithium and calcium chlorides, respectively.

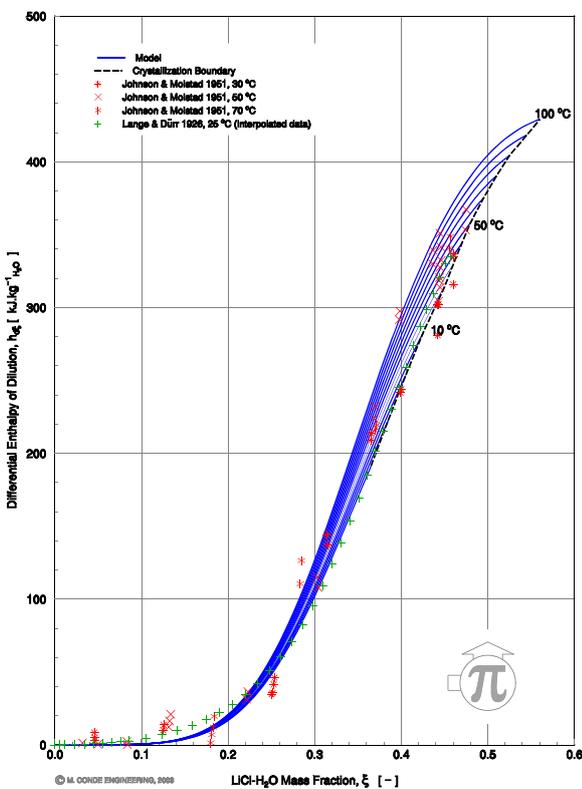


Figure 26 - Calculated and measured values of the differential enthalpy of dilution for aqueous solutions of lithium chloride.

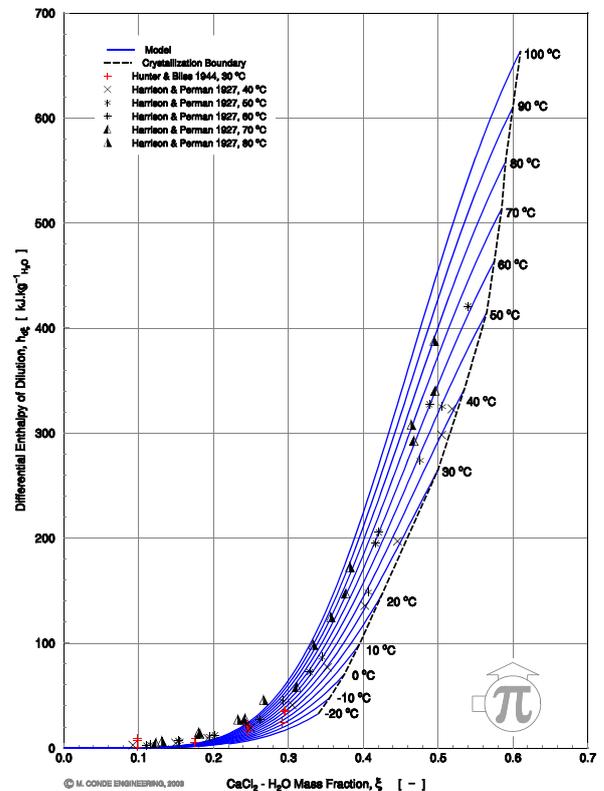


Figure 27 - Calculated and measured values of the differential enthalpy of dilution for aqueous solutions of calcium chloride.

Diffusion Coefficient of Water into Solutions of Lithium and Calcium Chlorides

The dehydration and hydration of gases by means of aqueous solutions of alkali halides involve the diffusion of water into the liquid solution. The diffusion of water into salt solutions may be seen as the self-diffusion of water *retarded* by the presence of the ions in solution. In the case of the chlorides discussed here, this is effectively so: The self-diffusion coefficient of water represents a maximum of the diffusion coefficient in the limit of extreme dilution and this tends to nil in the limit of the anhydrous salt. Dullien [125] proposes an equation for the prediction of the self diffusion coefficient of liquids that reproduces very well the known values of self-diffusion coefficient of water [126,127, 128].

Dullien’s equation is

$$\frac{\eta \tilde{V}_L D_0}{RT} = A \tilde{V}_C^{2/3}$$

where A takes the value 0.11353×10^{-16} for water. \tilde{V}_L is the molar volume of the liquid water at T , η is the dynamic viscosity of liquid water at T , R is the universal gas constant, D_0 is the self-diffusion coefficient, and \tilde{V}_C is the molar volume at the critical point.

The diffusion coefficient of water into the solution may be calculated with the equation

$$D = D_0 \left\{ 1 - \left[1 + \left(\frac{\sqrt{\xi}}{\delta_1} \right)^{\delta_2} \right]^{\delta_3} \right\}$$

The parameters δ_i are $\delta_1 = 0.52$, $\delta_2 = -4.92$, $\delta_3 = -0.56$ for solutions of lithium chloride and $\delta_1 = 0.55$, $\delta_2 = -5.52$, $\delta_3 = -0.56$ for those of calcium chloride.

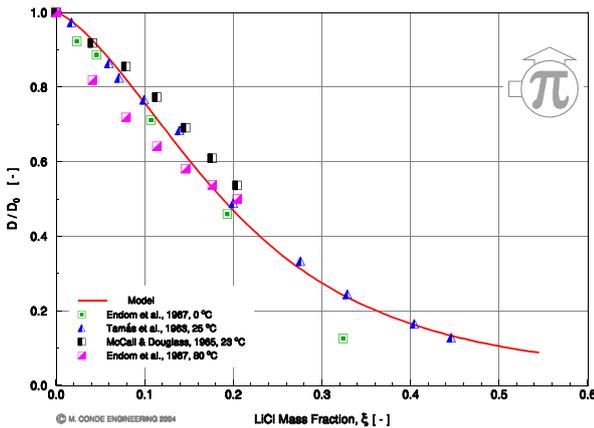


Figure 28 - Water diffusion coefficient into aqueous solutions of lithium chloride.

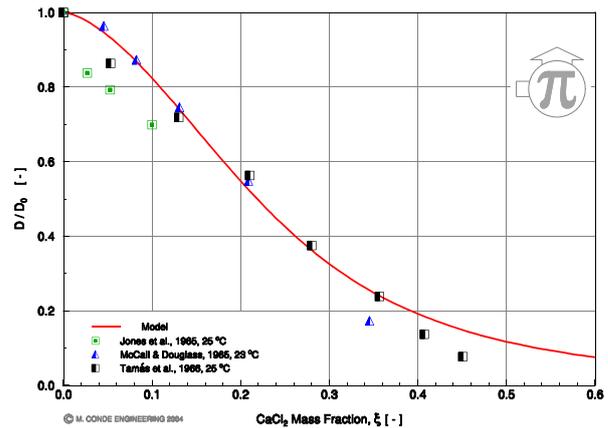


Figure 29 - Water diffusion coefficient into aqueous solutions of calcium chloride.

Figure 28 shows data from the literature [129, 130, 131] for solutions of lithium chloride compared with the above equation, and Figure 29 depicts data from [131, 132, 133] compared with the model for solutions of calcium chloride.

Discussion

This paper presents a complete collection of interpolating equations for the most important properties of aqueous solutions of the lithium and calcium chlorides, necessary in the design of absorption and air conditioning equipment, based on sorption processes with these salts. The data considered originate from a detailed research of old and new literature and concerns measurements by methods that evolved with time and the technologies available. This however, should not mean that newer measurements are more accurate than older ones. We have systematically given more weight to the data that represented best the data in the database for a given property, as is evident from the graphs. This means that although we have represented in the graphs all the data available in the literature, not all have been considered in the fitting process. The selection criteria is essentially based on the accuracy reported for the measurements, though this is not always available. In some cases, e.g. the crystallization line of aqueous solutions of calcium chloride, many experimental observations have been excluded. Some of the measurements of other properties seem to suffer from poor control of the concentration, given the strong hydrophilic characteristics of the solutions (e.g. some measurements of the surface tension). It also seems to us that the electrical conductivity of the solutions may have interfered with some of the most recent measurements of the thermal conductivity.

Although we would not like to give specific confidence limits for the values predicted by the equations proposed, we consider them well within the boundaries accepted in engineering calculations. We believe the equations proposed to represent a very significant contribution to the process of computer-assisted design of absorption and liquid desiccant based air conditioning systems. The equations were programmed into MathCad® calculation sheets that may be used as a base for process design and the design of parts of equipment.

Appendices

Appendix A - Vapour pressure of water over the liquid phase

The vapour pressure of ordinary water over the liquid phase is calculated with an equation due to Saul and Wagner [123] as follows. The parameters of this equation are given in Table XII.

$$\ln\left(\frac{p}{P_{c,H_2O}}\right) = \frac{A_0\tau + A_1\tau^{1.5} + A_2\tau^3 + A_3\tau^{3.5} + A_4\tau^4 + A_5\tau^{7.5}}{1 - \tau}$$

$$\tau = 1 - \frac{T}{T_{c,H_2O}}$$

i	A _i
0	-7.858 230
1	1.839 910
2	-11.781 100
3	22.670 500
4	-15.939 300
5	1.775 160

Figure XII - Parameters of the equation for the vapour pressure of water over the liquid phase.

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 [99] 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 XIII.

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 XIV.

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.

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

Figure XIV - $G_{i,j}$ parameters for the water viscosity equation.

Appendix C - The IAPWS formulation for the thermal conductivity of ordinary water substance for industrial use

This formulation [122], as the foregoing one, is included here for the sake of completeness.

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

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

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

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

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 XV. 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.

$L_{i,j}$	$i = 0$	$i = 1$	$i = 2$	$i = 3$
$j = 0$	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

Figure XV - Parameters for the thermal conductivity equation of normal water.

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