

**State Variables  
for Modelling  
Thermohaline Flow  
in Rocks**





Gesellschaft für Anlagen-  
und Reaktorsicherheit  
(GRS) mbH

## State Variables for Modelling Thermohaline Flow in Rocks

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## **Abstract**

Modelling thermohaline flow can easily involve complex physical interactions even if only the basic processes occurring in density-driven flow and heat transport are considered. In the light of these complexities it is of vital importance to know the thermal and hydraulic parameters required for the model and their dependencies as precise as possible. But also for designing a numerical simulator it is useful to know the dependencies of the parameters on the primary variables temperature, pressure and salinity in order to select an appropriate underlying mathematical model.

The present report thus compiles the mathematical formulations for the fluid parameters from the literature. For each parameter the origin, at least one meaningful figure, a comment where necessary and conclusions about the influence of each primary variable on the thermo-hydraulic parameters are given. All required coefficients and auxiliary functions including dimensions are listed, too.

Simulation of heat transport requires also information about some properties of the porous medium. Thus some complementary information about the properties of rocks is also given. In contrast to the properties for pure substances that are considered for the fluid the porous medium cannot be characterised as easily. Usually, the solids are a mixture of different materials with locally varying composition. Thus rather hints than exact values are provided for the rocks considered here.

This compilation represents a complete set of mathematical formulations for fluid and solid properties to be used for thermohaline modelling that can directly be used in the composing of a numerical simulator.



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# 1 Introduction

Modelling density-driven flow in a solution of water and NaCl under non-isothermal conditions generally requires formulations for the material parameters that depend on the primary variables pressure, temperature and salinity<sup>1</sup>. However, not all properties depend on all three primary variables. In some cases some dependencies do not exist, in other cases some dependencies can be neglected within the bandwidths considered for the primary variables. It is thus that not only the dependencies in general but also a specification of the ranges of validity becomes important for the definition of a specific mathematical formulation. It is assumed here that the value ranges of the primary variables are restricted to the following bandwidths:

- pressure from 0.1 MPa to 30 MPa,
- temperature from 0 °C to 200 °C, and
- salinity from 0 to saturation concentration.

In principle, also state variables can exert a direct or an indirect influence on other properties. This concerns mainly the solubility of salt in water which varies according to pressure and temperature and thereby extends the range of possible salt concentrations. Thus all properties that depend on salinity can be affected by a change of solubility. Variations of solubility may also result in dissolution and precipitation of salt which in turn alter porosity and permeability.

Also to be considered is the phenomenon that high temperatures and low pressures may lead to a phase change from liquid water to water vapour<sup>2</sup>. This effect limits the range of admissible combinations of the primary variables. If a flow simulator is not designed to

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<sup>1</sup> Some terms used in this report need to be clarified: liquid and solid materials in general can be characterized by **material parameters** (like density or thermal conductivity) that describe the state of the material, either as physical constants or as dependencies on independent quantities (like temperature). Such a dependency which describes a **material property** is generally called a **relation**. A specific mathematical approach for the relation is also referred to as **formulation** or **equation-of-state (EOS)**.

In numerical modelling the above mentioned independent quantities are calculated and are thus referred to as **primary variables**. Depending material parameters are then called **secondary variables** or **state variables**.

<sup>2</sup> In order to differentiate the phase state of H<sub>2</sub>O the term 'water' will be used for liquid H<sub>2</sub>O and vapour for a H<sub>2</sub>O-rich gas-phase.

handle multi-phase flow there is a physical constraint to be monitored in the whole domain and at all times.

The following compilation of graphs visualizing the dependencies in question is intended to give an insight into the extent to which the referring material parameters depend on the primary variables. The compilation not only provides the basis for the mathematical model but also allows simplifying the formulations in order to reduce the complexity of the model where possible. However, a precise formulation of the equations of state is indispensable if physically unstable conditions are modeled. All formulations used in this report are either given in the text or in Appendix A. Appendix B contains the additionally required constants.

First, the properties of the pure components – water, salt, and rock – are discussed. Later, the properties of salt solution are given to identify the additional influence of salinity. Finally, matrix properties have to be combined with solution properties for the modeling of heat transport.

The influence of a primary variable on the investigated material property is also evaluated. On the basis of the variations that are caused by the primary variables within the specified range of interest, the influence is defined to fall into one of the following four influence classes: strong, moderate, little or negligible/none. These classes are defined in Tab. 1.1.

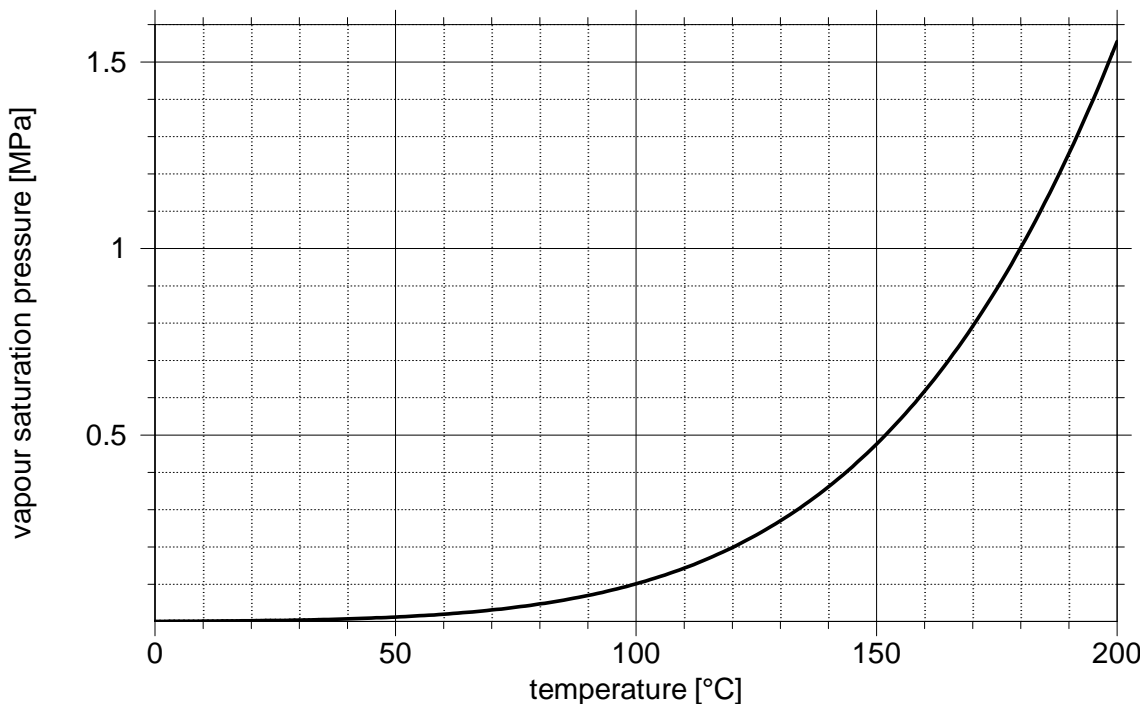
**Tab. 1.1** Definition of influence classes

Influence Class	Variation Range
strong	> 50 %
moderate	5 % – 50 %
little	1 % – 5 %
none (or negligible)	< 1 %

## 2 Properties of pure water

### 2.1 Vapour pressure

Vapour pressure of pure water is only dependent on temperature. It rises comparatively slowly with temperature up to of 100 °C but significantly faster above this value up to nearly 1.6 MPa at 200 °C. The pressure of 1.6 MPa corresponds to a pure water column of about 150 m. Fluid pressure does not enter the mathematical formulation.



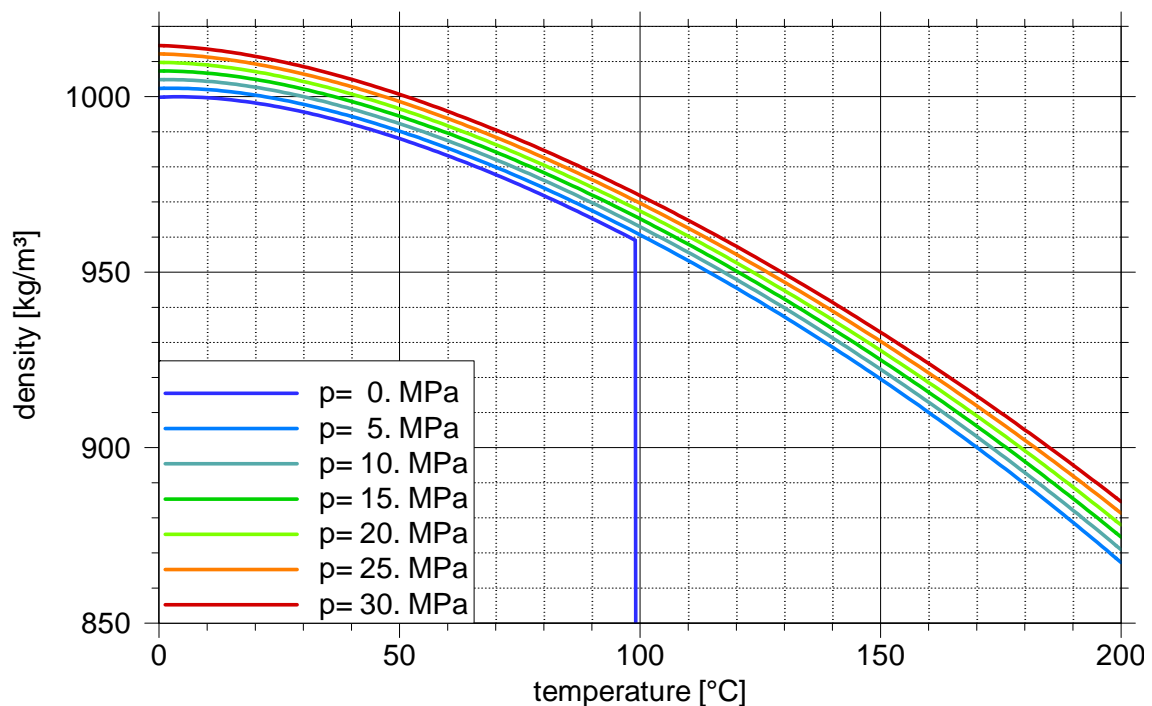
**Fig. 2.1** Vapour pressure of pure water

Conclusions:

- Influence
  - of temperature is high,
  - of pressure is none.
- A phase change from liquid to vaporous water at temperatures up to 200 °C can be excluded for depths significantly below 150 m below the water table.
- At a depth of less than 150 m the allowable maximum temperature decreases.
- Atmospheric pressure prevents boiling of pure water at temperatures below 100 °C.

## 2.2 Density

A pressure increase from 0.1 MPa to 30 MPa – the latter relating roughly to the hydrostatic pressure of a pure water column of 3000 m height – results in an increase of density of about 15 kg/m<sup>3</sup> at 0 °C and in an increase of about 18 kg/m<sup>3</sup> at 200 °C. The decrease in density due to a temperature increase from 0 °C to 200 °C amounts approximately to 130 kg/m<sup>3</sup> while an increase up to 100 °C only leads to a decrease of about 40 kg/m<sup>3</sup>. Note that the blue curve for atmospheric pressure drops down to the value for vapour density at 100 °C due to a phase change (boiling).



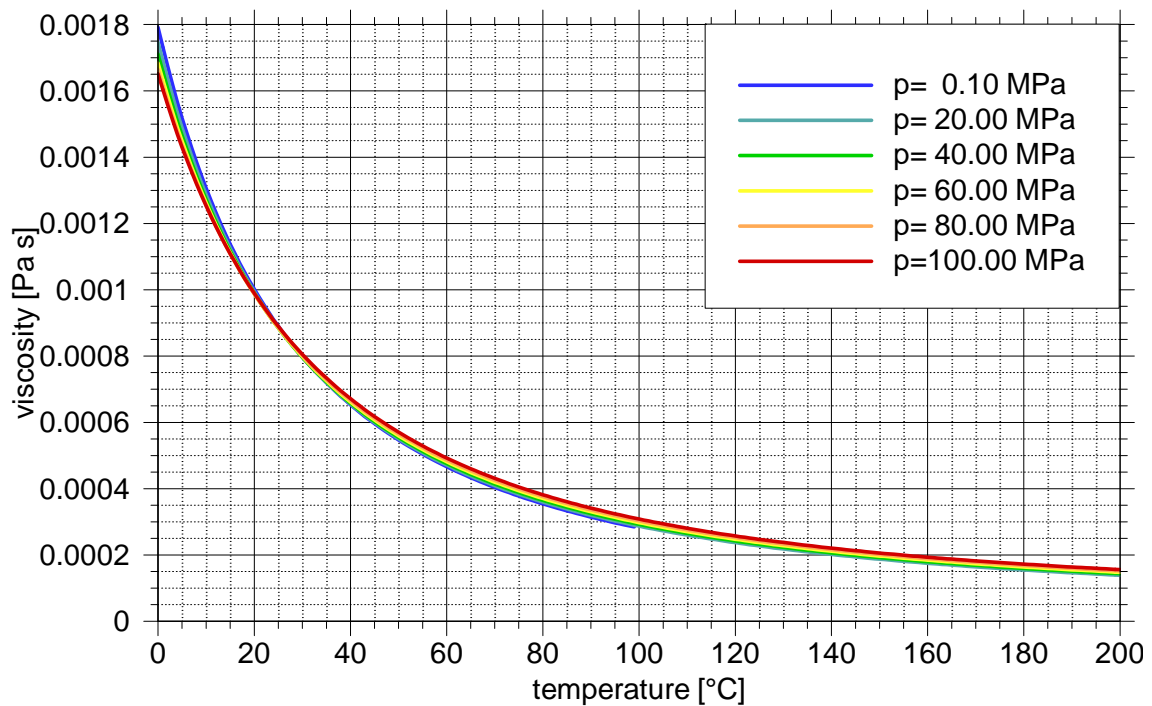
**Fig. 2.2** Density of pure water

Conclusions:

- Influence
  - of temperature is moderate,
  - of pressure is little.
- Density can be affected by phase changes.

## 2.3 Viscosity

The viscosity of pure water at 100 °C is less than a third of that at 20 °C. Decrease with temperature is slower for temperatures above 100 °C. In contrast, viscosity does not change significantly with pressure in the temperature range between 0 °C and 200 °C. At almost 100 °C the maximum difference due to pressure amounts to 2.8 %.



**Fig. 2.3** Viscosity of pure water

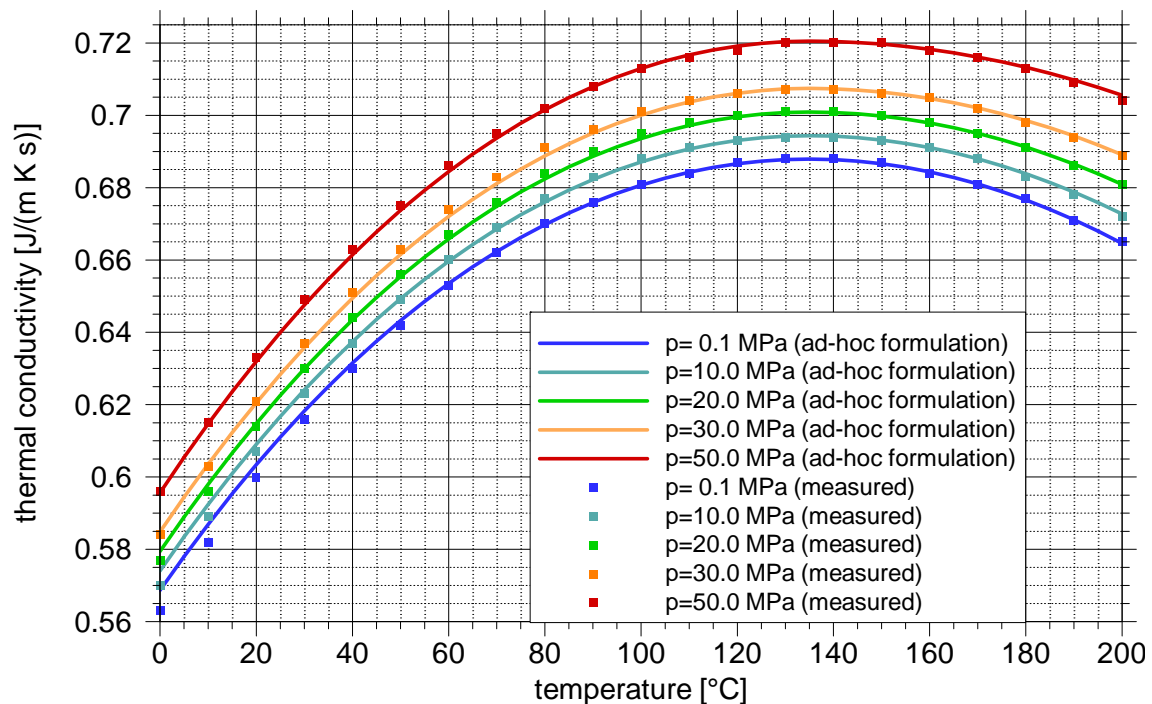
Conclusions:

- Influence
  - of temperature is high,
  - of pressure is little.

## 2.4 Thermal conductivity

As shown in Fig. 2.4 thermal conductivity at atmospheric pressure rises from 0.57 J/(m K s) at 0 °C up to 0.68 J/(m K s) at 100 °C. Data above 100 °C is measured under increased pressure, namely the vapour saturation pressure (see section 2.1). At 135 °C a maximum can be seen with a thermal conductivity of about 0.69 J/(m K s) after which it decreases to 0.665 J/(m K s) at 200 °C. Maximum deviation of the thermal conductivity is 3.8 % for a pressure difference of 30 MPa.

The approach from /YUS75/ as presented in /KRÖ08/ does not include a pressure dependency. Data from /LAN72/, however, shows a pressure dependency. An ad-hoc correction for the pressure assuming that the effects of pressure and temperature on the thermal conductivity are independent of each other is given in Appendix A. A comparison of this formulation with measured data is shown in Fig. 2.4.



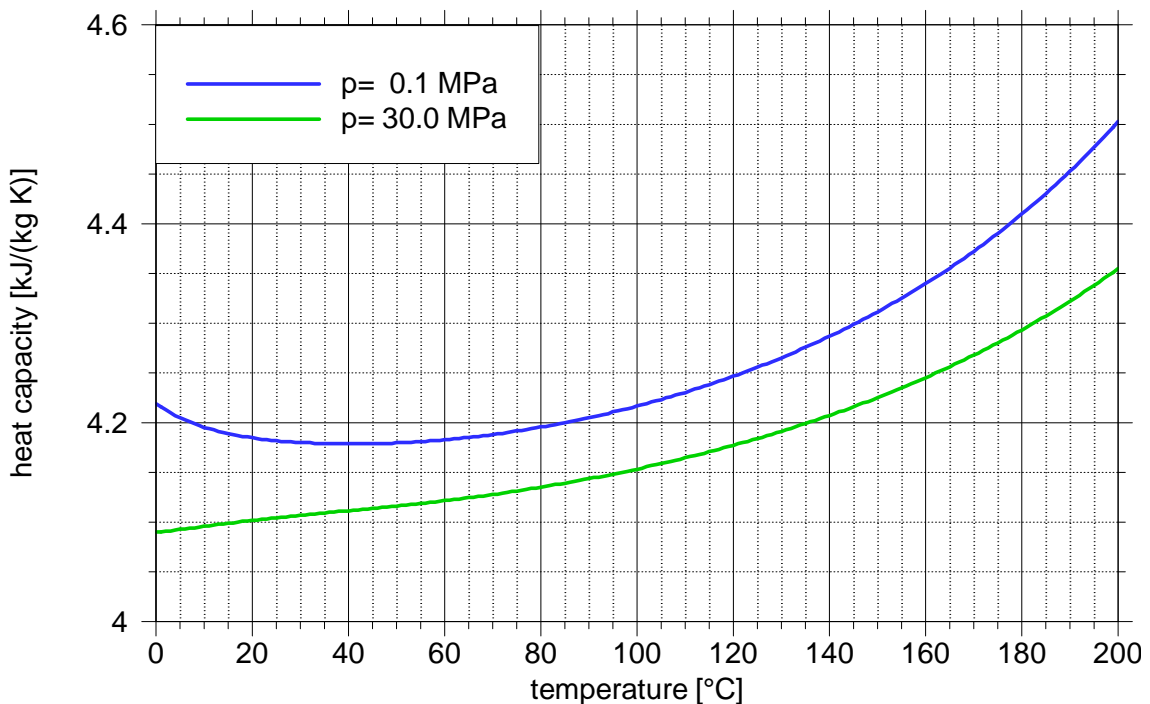
**Fig. 2.4** Thermal conductivity of pure water

Conclusions:

- Influence
  - of temperature is moderate,
  - of pressure is little.

## 2.5 Heat capacity

In the temperature range up to 100 °C the heat capacity of pure water varies between 4.18 and 4.21 kJ/(kg K) under atmospheric pressure and between 4.1 and 4.15 kJ/(kg K) at a pressure of 30 MPa. Above 100 °C the values increase up to 4.5 and 4.35 kJ/(kg K), respectively. Over the whole temperature range this results in a variation of 7.1 % and 4.8 %, respectively. Depending on the temperature a pressure increase of 30 MPa causes a drop of up to 0.15 kJ/(kg K) which means a variation of about 3 %.



**Fig. 2.5** Heat capacity of pure water

Conclusions:

- Influence
  - of temperature is moderate,
  - of pressure is little.
- Between 20 °C and 100 °C and up to 30 MPa influences of temperature and pressure are below 2 %. In this temperature range a characteristic value is therefore sufficient for modelling purposes.

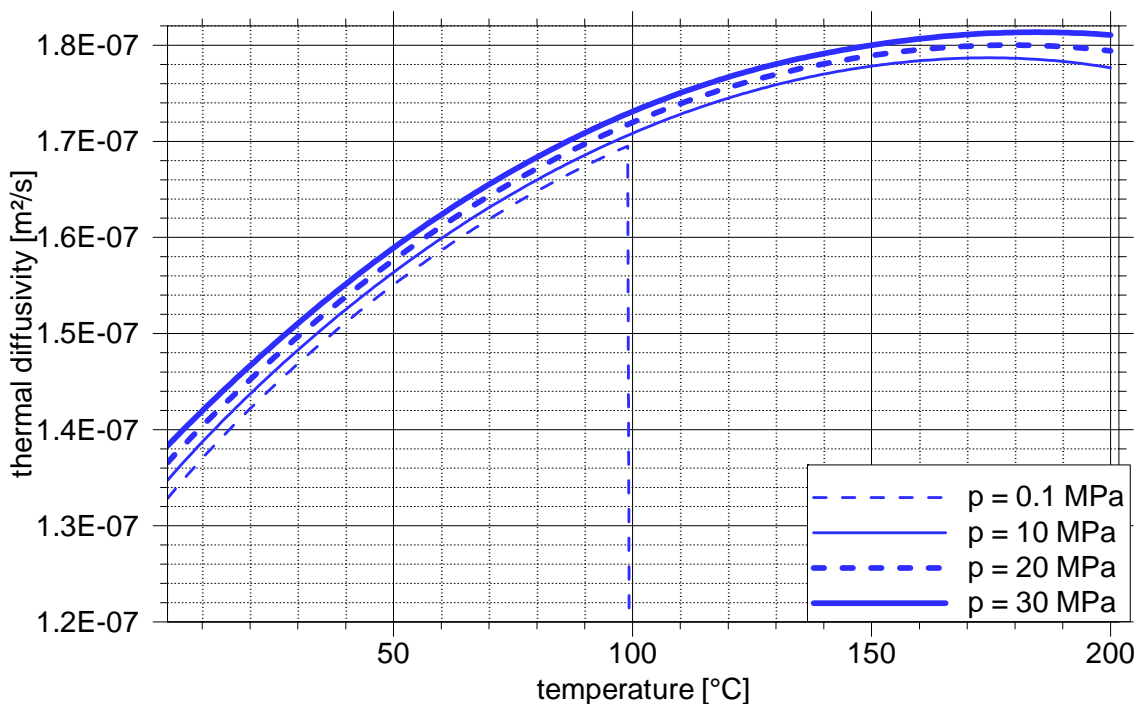
## 2.6 Thermal diffusivity

In a strict sense thermal diffusivity is not a basic property of water but a derived quantity. It is defined as:

$$\kappa = \frac{\lambda}{\rho c} \quad (2.1)$$

- $\kappa$  - thermal diffusivity [m<sup>2</sup>/s]
- $\lambda$  - thermal conductivity [W/(m K)]
- $\rho$  - density [kg/m<sup>3</sup>]
- $c$  - specific heat capacity [J/(kg K)]

Thermal diffusivity controls the velocity of a heat transport by conduction. It increases approx. from  $1.3 \cdot 10^{-7}$  m<sup>2</sup>/s at 0 °C up to  $1.8 \cdot 10^{-7}$  m<sup>2</sup>/s at 180 °C. It decreases up to  $0.6 \cdot 10^{-7}$  m<sup>2</sup>/s with a pressure increase of 30 MPa.



**Fig. 2.6** Thermal diffusivity of pure water

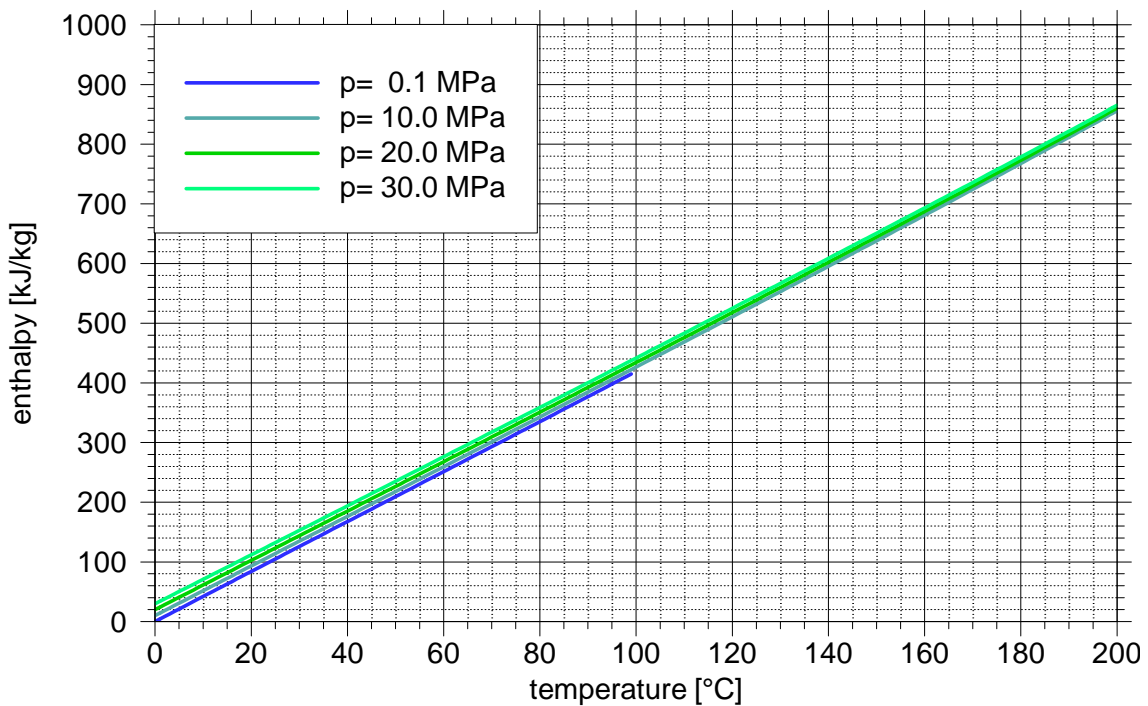
Conclusions:

- Influence
  - of temperature is moderate,
  - of pressure is little.



## 2.7 Enthalpy

The enthalpy of pure water changes almost linearly with temperature and thereby changes for several hundred percent. The differences introduced by pressure decrease slightly with temperature. The increase from 10 MPa to 30 MPa amounts to approx. 17 kJ/kg at 20 °C and approx. 10 kJ/kg at 200 °C. The related relative changes, however, are significantly higher for low temperatures than for high temperatures, namely about 16.5 % at 20 °C, about 3.5 % at 100 °C, and 1 % at 200 °C.



**Fig. 2.7** Enthalpy of pure water

Conclusions:

- Influence
  - of temperature is strong,
  - of pressure is little for high temperatures and moderate for low temperatures.

## 2.8 Diffusion

Self-diffusion in pure water is depicted in Fig. 2.8 as a function of pressure and temperature and as a function of temperature with extended temperature range in Fig. 2.9.

Fig. 2.8 shows no significant changes of the coefficient of self-diffusion with pressure up to 45 °C and even up to 100 MPa. One measurement at 50 °C suggests a decrease with pressure. However, one of the measurements at 25 °C shows just the opposite behaviour even if this trend is not as pronounced as at 50 °C.

The data shown in Fig. 2.9 is probably measured at atmospheric pressure. Here, a clear trend can be seen in the diffusion coefficient rising slightly exponentially from  $2 \cdot 10^{-9} \text{ m}^2/\text{s}$  to  $8.7 \cdot 10^{-9} \text{ m}^2/\text{s}$  in the temperature range from 20 °C to 100 °C. Data reaching into the temperature range above 200 °C were not found. The black curve represents an ad-hoc approach given in /KRÖ08/ to provide a realistic mathematical formulation.

It has to be noted that the source for data for the diffusion coefficient is rather old so that a deeper knowledge than given here can be expected.

Conclusions:

- Influence
  - of temperature is strong,
  - of pressure is none.
- Presently there are gaps in the knowledge
  - Independence from pressure is shown only for temperatures up to 45 °C. It remains to be investigated whether the measurement at 50 °C indicates a dependency on pressure at higher temperature since not further data was available.
  - It remains to be investigated whether the dependency on temperature continues above 100 °C the identified trend since no further data was available.

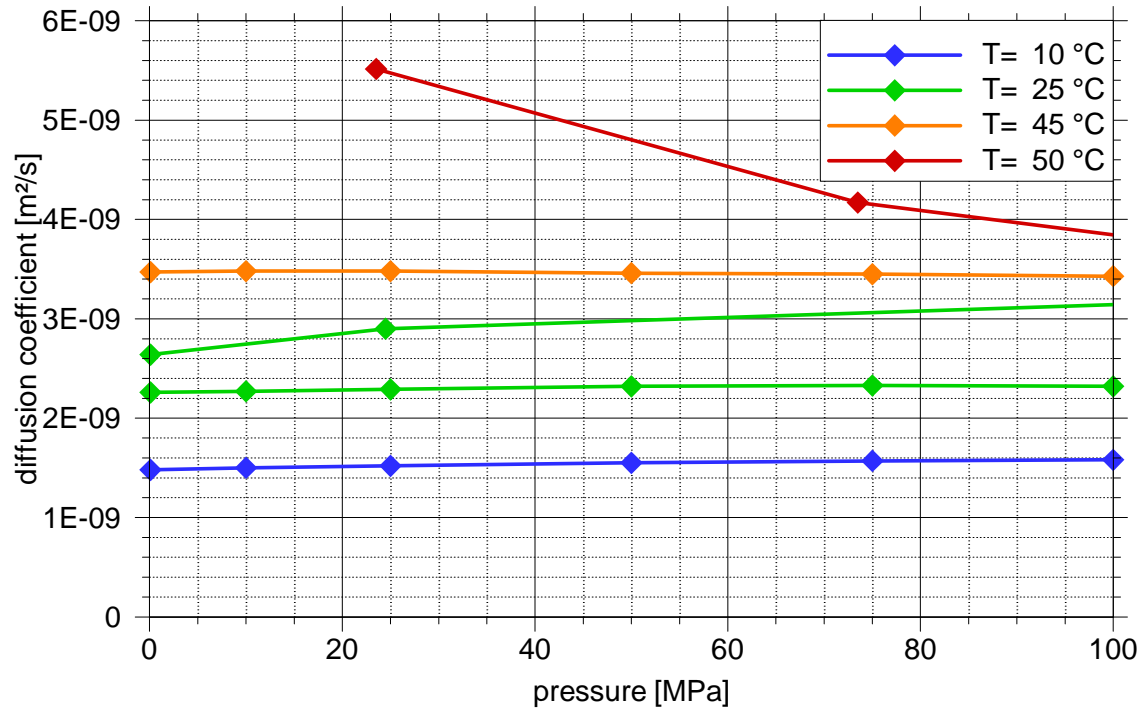


Fig. 2.8 Diffusion coefficient of pure water as a function of temperature and pressure

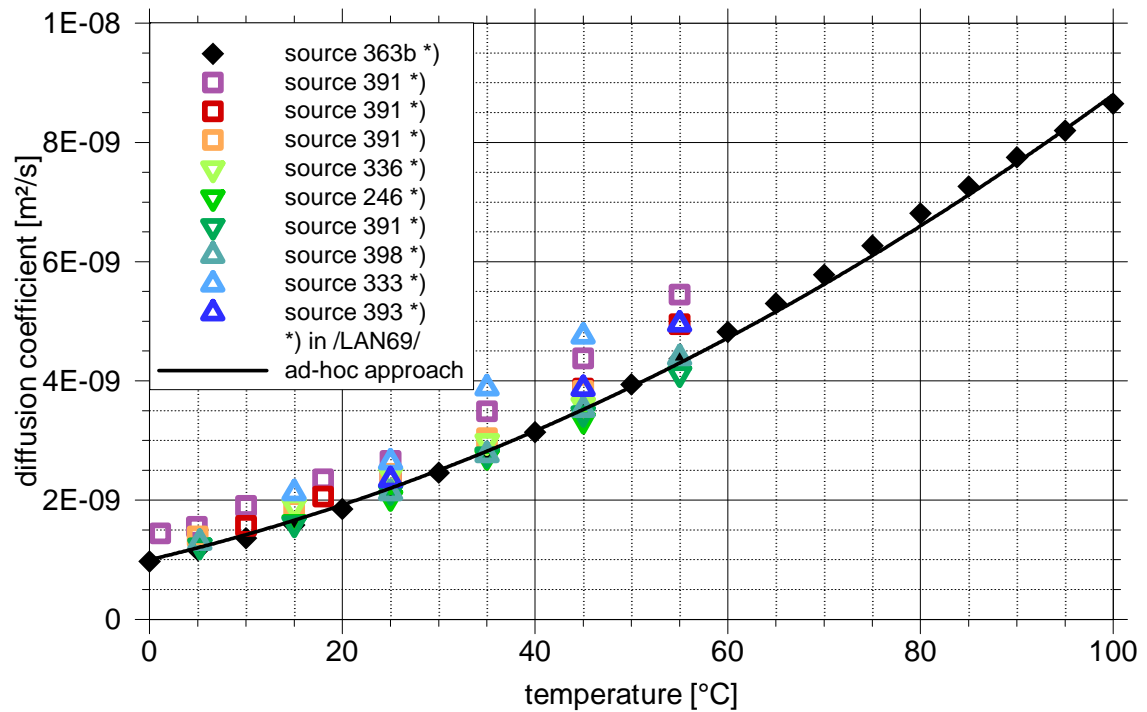


Fig. 2.9 Diffusion coefficient of pure water at atmospheric pressure as a function of temperature



### 3 Properties of pure NaCl

#### 3.1 Density

The density of NaCl at 20 °C amounts to 2165 kg/m<sup>3</sup>. The linear thermal expansion coefficient of NaCl is given as  $\alpha_L = 4.2 \cdot 10^{-5} \text{ 1/T}$  (e. g. /BGR89/). For isotropic materials, the linear thermal expansion coefficient is one third of the volumetric coefficient  $\alpha_V$ . The volume of NaCl thus changes about 2.5 % over the considered temperature range.

The bulk modulus  $K$  of rock salt relates pressure and relative volumetric expansion. Based on data from /LUX86/ (Young's modulus  $E = 25 \text{ MPa}$  and Poisson's ratio  $\nu = 0.27$ ) it amounts to 18.12 GPa. Relative volumetric change and thus change in density for a pressure of 30 MPa results in 0.16 %.

Conclusions:

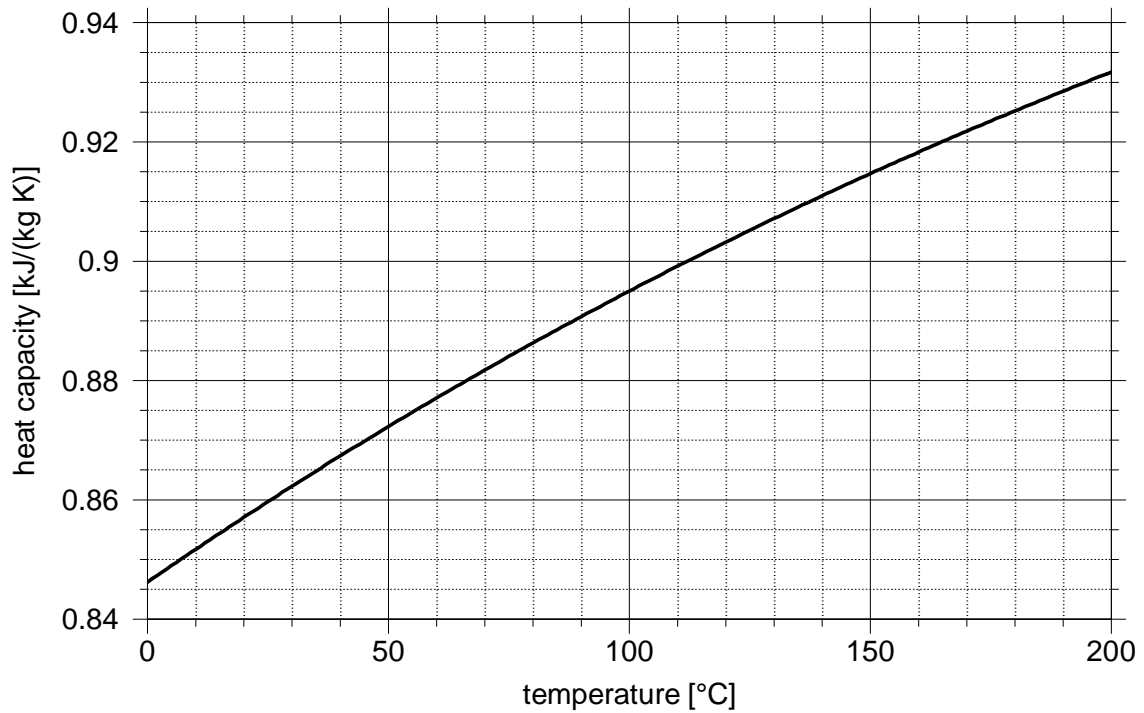
- Influence
  - of temperature is little,
  - of pressure is none.

#### 3.2 Heat capacity

The heat capacity of pure NaCl rises slightly non-linearly from 0.857 kJ/(kg K) at 20 °C up to 0.895 kJ/(kg K) at 100 °C. The corresponding maximum variation amounts to less than 4 %. At 200 °C the value further increases to 0.932 kJ/(kg K) so that over the whole temperature range variations can reach 8 %. Fluid pressure does not enter the mathematical formulation.

Conclusions:

- Influence
  - of temperature is moderate,
  - of pressure is none.



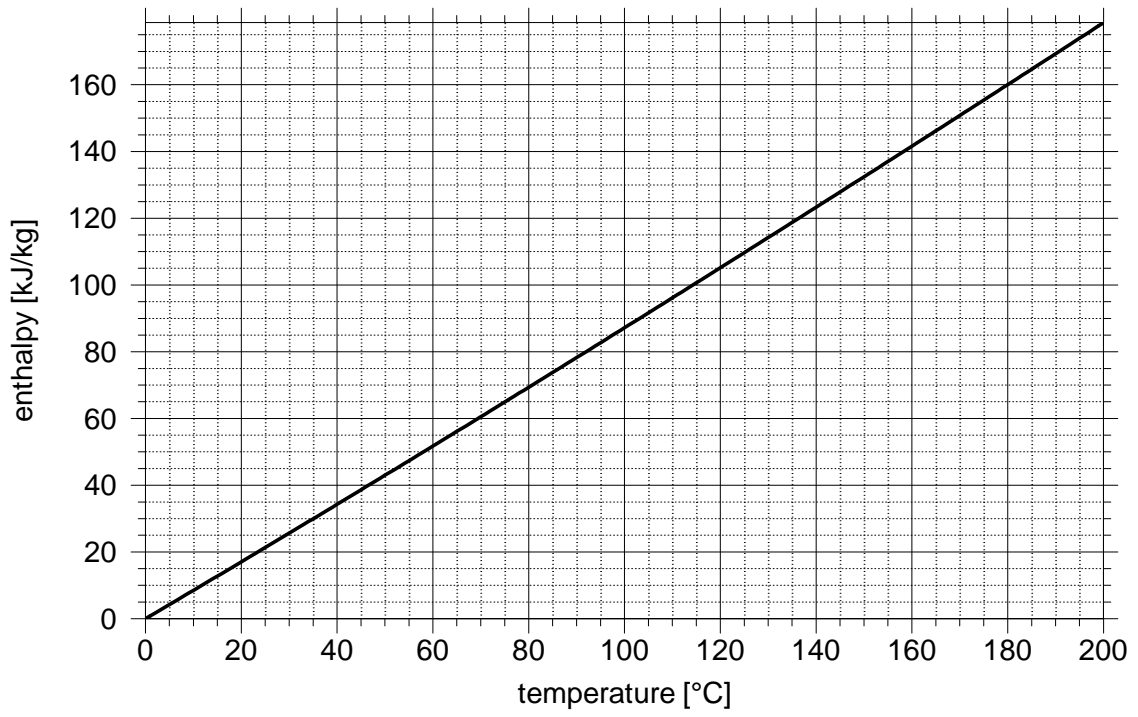
**Fig. 3.1** Heat capacity of pure NaCl

### 3.3 Enthalpy

As for the enthalpy of pure water the enthalpy of pure NaCl rises almost linearly over the temperature range considered. Fluid pressure does not enter the mathematical formulation.

Conclusions:

- Influence
  - of temperature is strong,
  - of pressure is none.



**Fig. 3.2** Enthalpy of pure NaCl

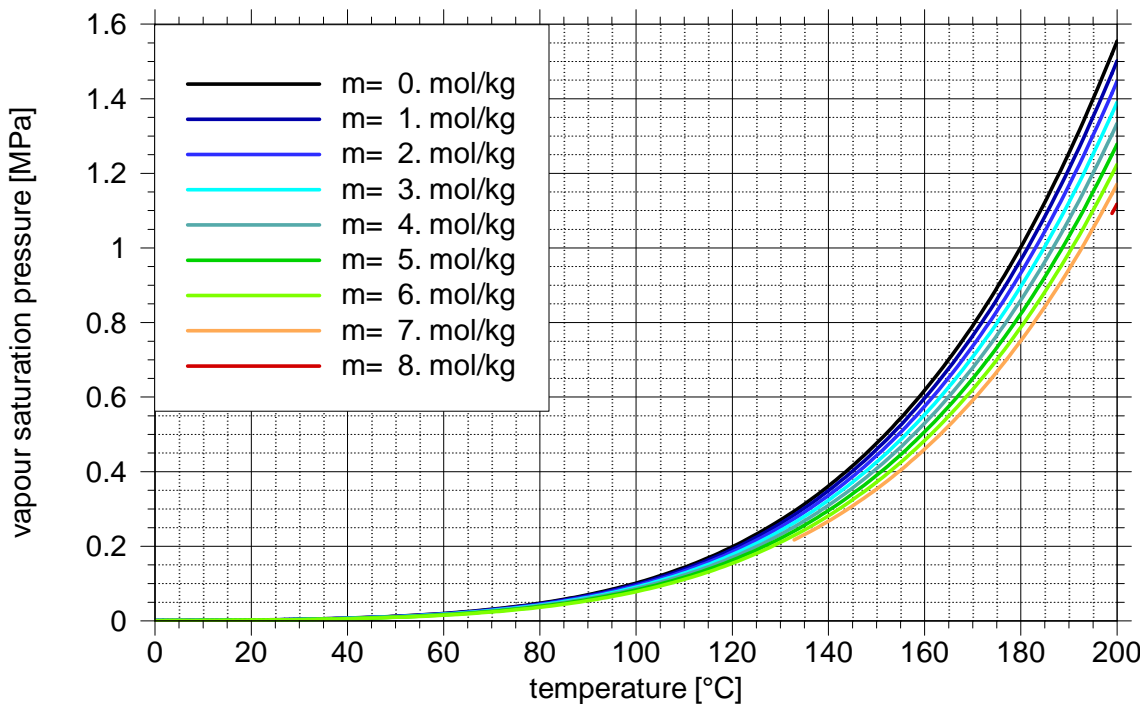




## 4 Properties of NaCl-solution

### 4.1 Vapour pressure

Vapour pressure over a NaCl-solution decreases with the salinity. An increase of salt concentration in the solution leads apparently to a decrease of the vapour pressure where the ratio of decrease to absolute value is constant. The difference or pure water compared to a solution of 6 mol/kg at 100 °C amounts approximately to 22 % which is the same at 200 °C. However, the temperature-dependent solubility shows a maximum salt content of 6.66 mol/kg at 100 °C and 8.03 mol/kg at 200 °C (q. v. section 2.1). With reference to vapour pressure at maximum salt concentration the influence increases with temperature. Fluid pressure does not enter the mathematical formulation.



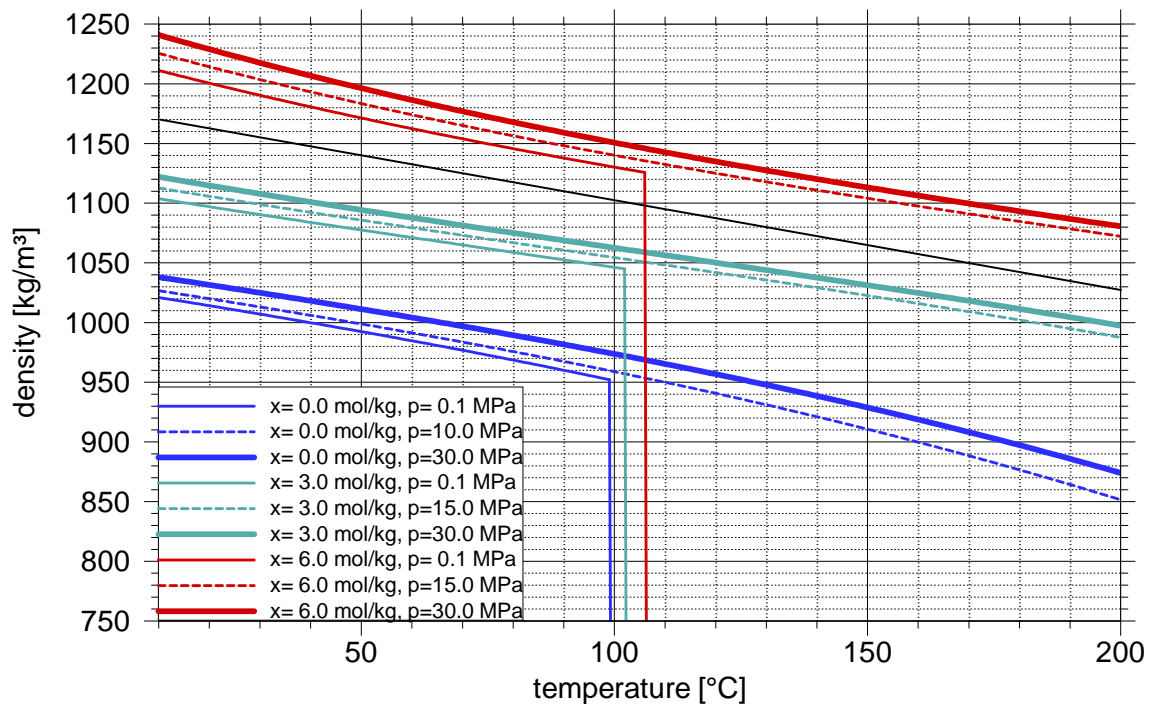
**Fig. 4.1** Vapour pressure of NaCl-solution

Conclusions:

- Influence of salinity on vapour pressure is moderate.
- Adding NaCl to pure water raises the temperature at which phase change of liquid water to water vapour occurs.

## 4.2 Density

The density of saline solutions as a function of temperature is shown in Fig. 4.2. The curves are almost linear. More or less independently from salinity or pressure the drop in density from 0 °C to 200 °C amounts approx. to 140 kg/m<sup>3</sup>. Note that the sharp bent of the curves at  $p = 0.1$  MPa represents the effect of phase change again. It is also evident from this figure that the boiling temperature rises with salinity.

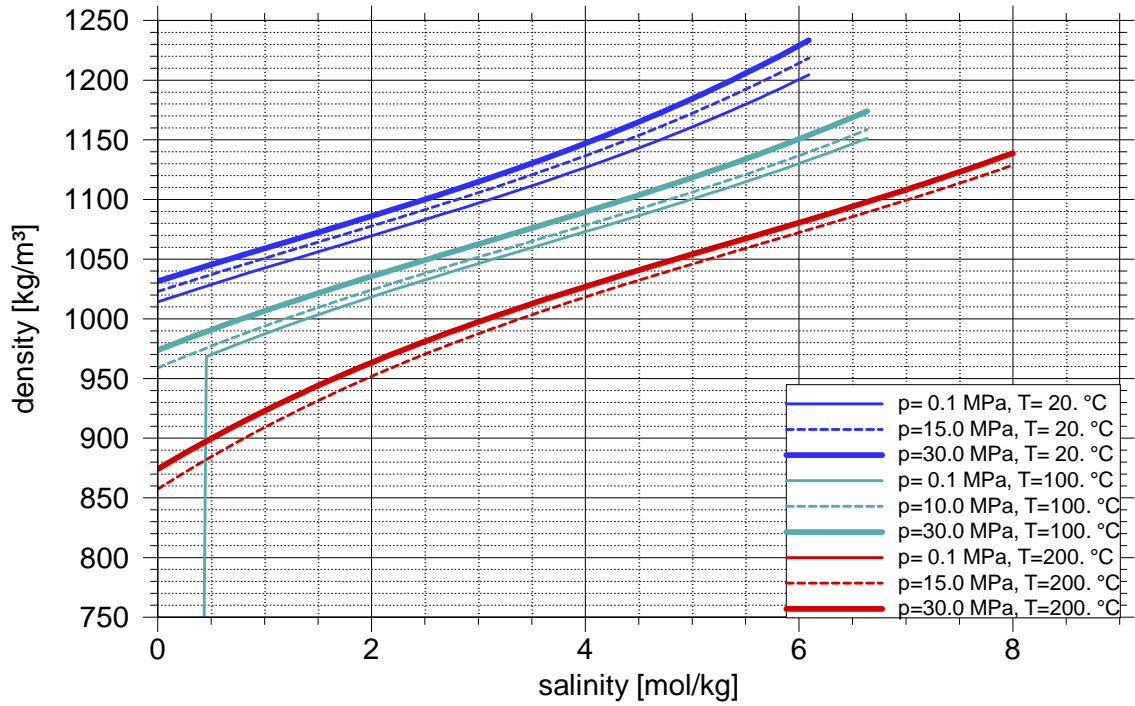


**Fig. 4.2** Density of NaCl-solution as a function of temperature (colour represents salinity and line style pressure)

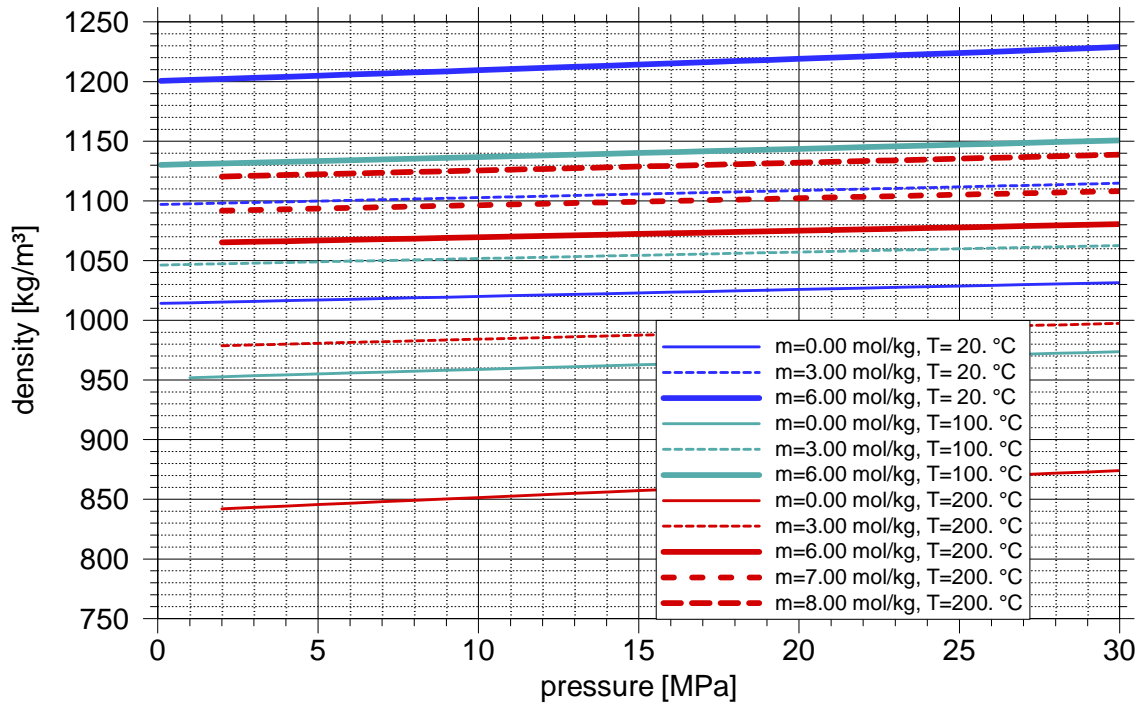
Plots of density vs. salinity as shown in Fig. 4.3 also follow more or less linear functions. At 0.1 MPa and 100 °C the solution requires a salt content of at least 0.2 mol/kg to avoid boiling of the solution. In Fig. 4.4 solution density is plotted vs. pressure. The increase with pressure is almost linear and amounts to 20 to 30 kg/m<sup>3</sup> for a pressure increase of 30 MPa depending on salinity and temperature. In order to keep the plot clear the curves are truncated where phase changes reduce density.

Conclusions:

- Influence of salinity on density is moderate.
- Influences of temperature/pressure on the solution are similar to pure water.



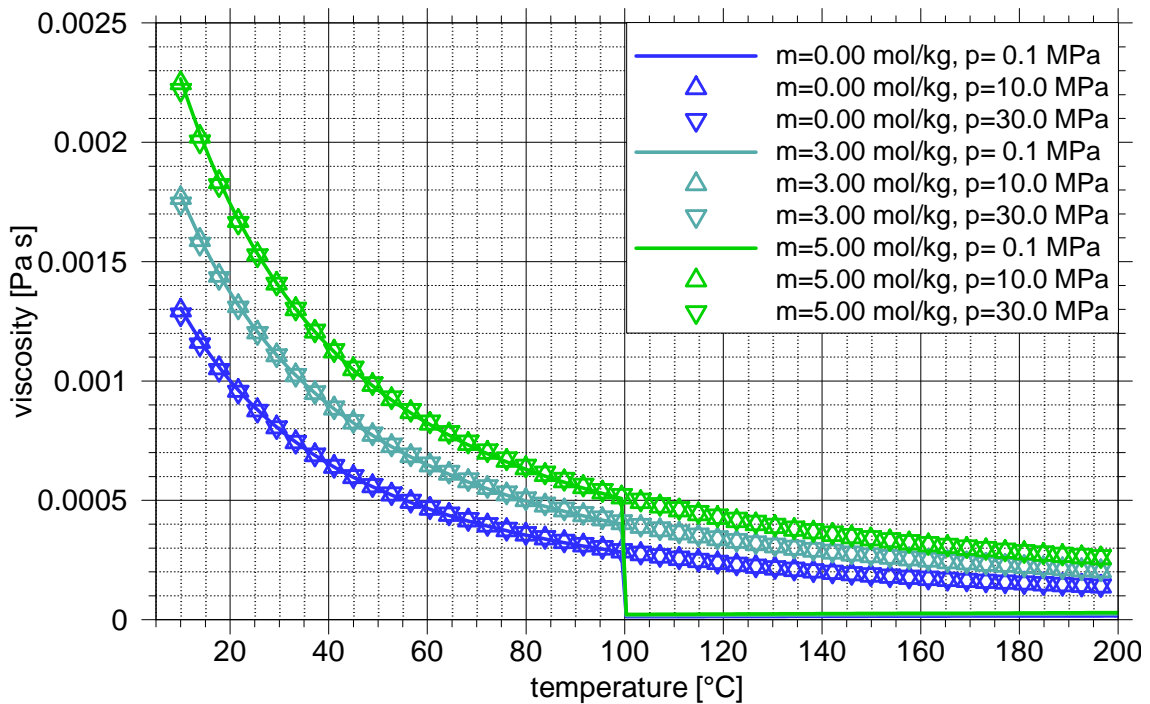
**Fig. 4.3** Density of NaCl-solution vs. salinity  
(colour represents temperature and line style pressure)



**Fig. 4.4** Density of NaCl-solution vs. pressure  
(colour represents temperature and line style salinity)

### 4.3 Viscosity

Viscosity drops by a factor between 4 and 5 at a temperature increase from 10 °C to 100 °C regardless of the salinity. From 100 °C to 200 °C viscosity is reduced by a factor of less than 2.



**Fig. 4.5** Viscosity of NaCl-solution

The effect of salinity on viscosity in the mathematical formulation is represented by a departure function that modifies the approach for pure water. The departure function is not dependent on pressure. Therefore there is virtually no effect of pressure on viscosity above 15 °C. Salinity increases viscosity by a factor of almost 2 from pure water to NaCl-saturated water.

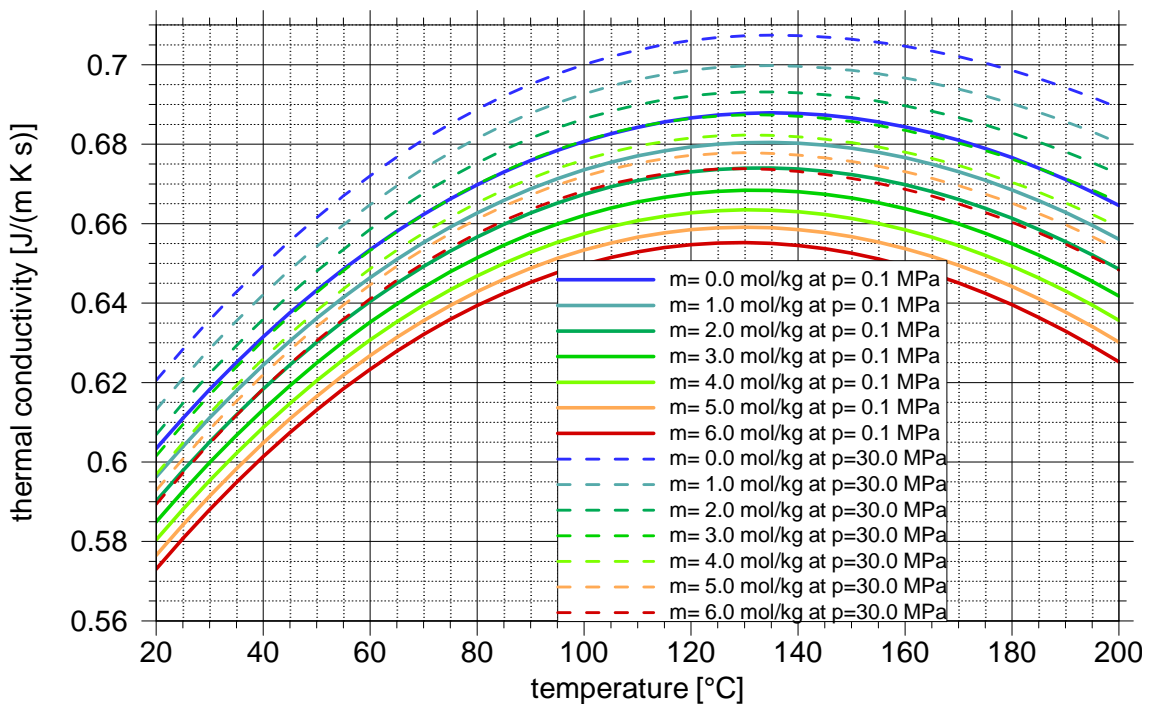
Conclusions:

- Influence of salinity on viscosity is strong.
- Influences of temperature/pressure on the solution are similar to pure water.

#### 4.4 Thermal conductivity

Increasing salinity reduces the thermal conductivity of NaCl-solutions. The decrease of thermal conductivity from pure water to a NaCl-concentration of 5 mol/kg amounts approx. to 5 % regardless of the temperature.

Contrary to the description in /KRÖ08/ a pressure dependency was found in the order of the dependency for pure water which increased thermal conductivity about 3.8 % after pressure increase of 30 MPa (q. v. section 2.4). These two effects appear to be comparable in magnitude. However, big local changes in salinity can occur due to transport of NaCl while local changes in pressure are not expected to be nearly as high as 30 MPa.



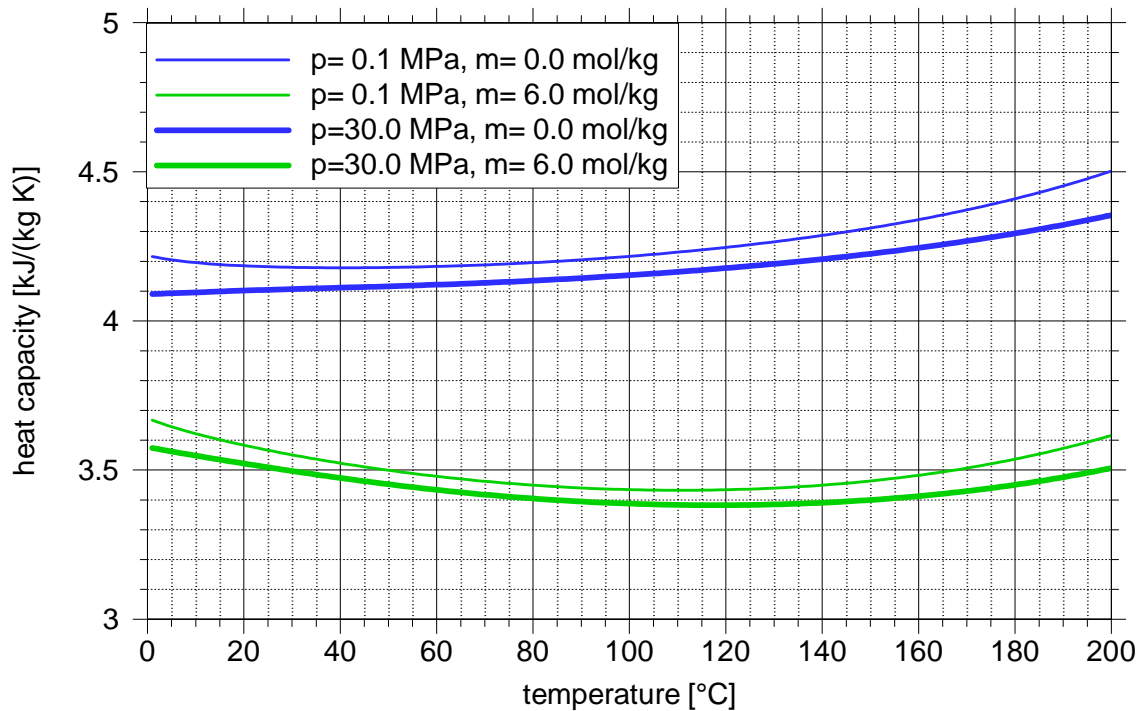
**Fig. 4.6** Thermal conductivity of NaCl-solution

Conclusions:

- The influence of salinity on thermal conductivity is moderate.
- Influences of temperature/pressure on the solution are similar to pure water.

## 4.5 Heat capacity

The heat capacity of a NaCl-solution with a salt concentration of 6 mol/kg at 20 °C is about 16 % lower than the value for pure water, at 100 °C about 22 % and at 200 °C about 24 %. The influence of pressure on heat capacity is at 6 mol/kg as low as for pure water.



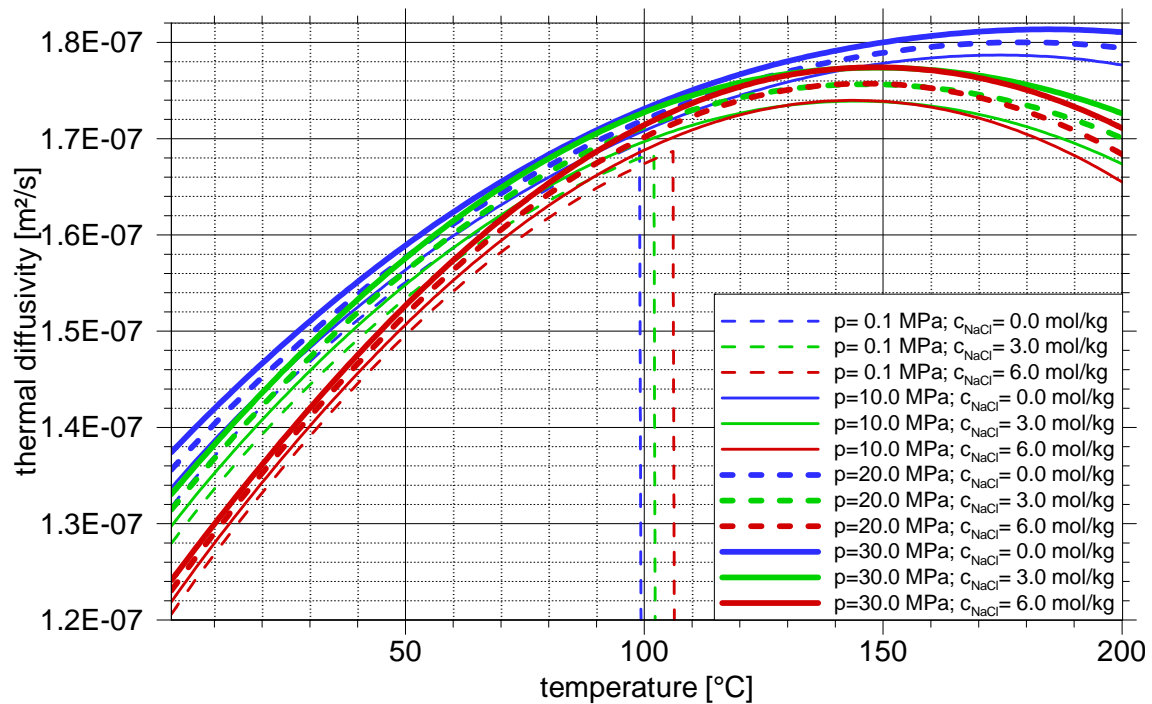
**Fig. 4.7** Heat capacity of NaCl-solution  
(colour represents salinity and line style pressure)

Conclusions:

- The influence of salinity on heat capacity is moderate.
- Influences of temperature/pressure on the solution are similar to pure water.

## 4.6 Thermal diffusivity

As shown in Fig. 4.8 dissolved NaCl in water reduces the thermal diffusivity of pure water up to 11 % at very low and very high temperatures. At temperatures around 100 °C the difference drops down to little more than 1 %. The influence of pressure on thermal diffusivity is under all conditions not higher than 1 %. Temperature changes thermal diffusivity up to 42 % in the considered temperature range.



**Fig. 4.8** Thermal diffusivity of NaCl-solution

Conclusions:

- The influence of salinity on thermal diffusivity is moderate.
- Influences of temperature/pressure on the solution are similar to pure water.

## 4.7 Enthalpy

As with pressure the enthalpy also decreases with salinity and the differences increase with temperature. The difference between enthalpy of pure water and of a solution with a concentration of 6 mol/kg amounts to 34 % at 20 °C, to 21 % at 100 °C, and to 20 % at 200 °C. These values vary by no more than 3 % over the whole pressure range.

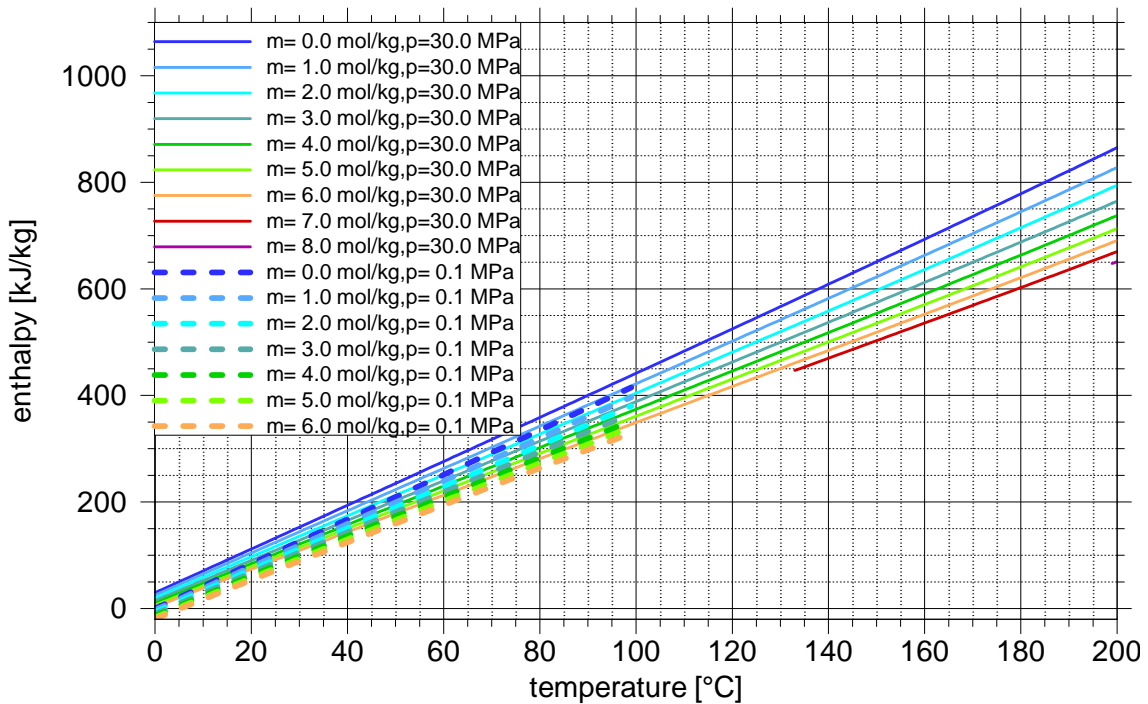


Fig. 4.9 Enthalpy of NaCl-solution

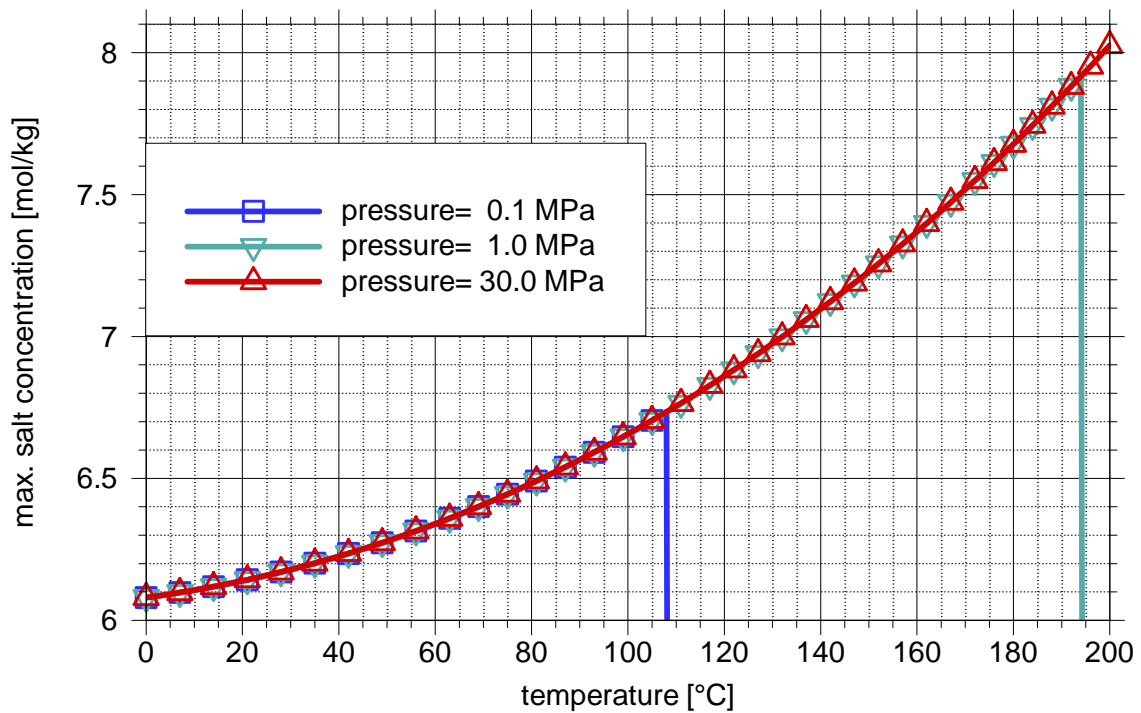
Conclusions:

- The enthalpy of NaCl-solution depends moderately on salinity.
- Influences of temperature/pressure on the solution are similar to pure water.



## 4.8 Solubility

The saturation concentration of NaCl in water amounts to 6.14 mol/kg at 20 °C, 6.66 mol/kg at 100 °C, and 8.03 mol/kg at 200 °C provided that the solution pressure exceeds the vapour pressure. Pressure does not enter the formulation for solubility in any other way. Note: the sharp bent in the curves for 0.1 MPa and 1 MPa reflects the point of phase change at NaCl-saturation concentration.



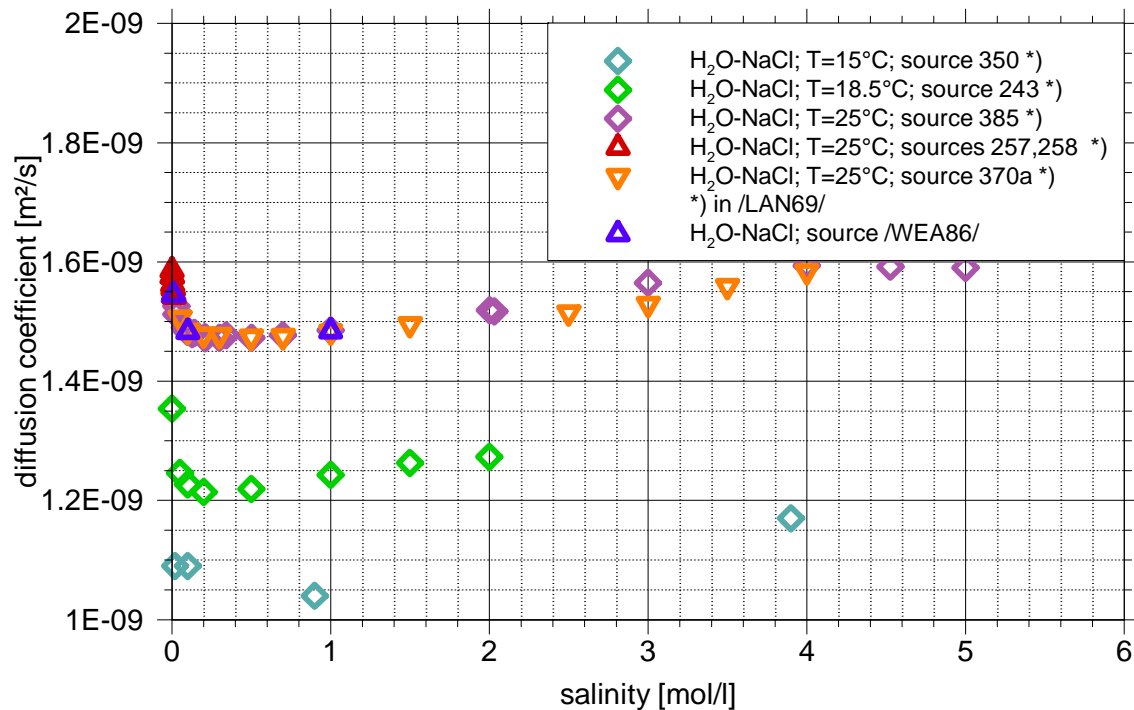
**Fig. 4.10** Solubility of salt in water

Conclusions:

- The influence of temperature on NaCl-solubility in water is moderate.
- There is no direct pressure dependency.
- Decrease of temperature can lower solubility below the actual salt concentration and lead subsequently to precipitation of salt.

## 4.9 Diffusion

Data for the dependency of the diffusion coefficient on salinity was found only for temperatures between 15 °C and 25 °C. A steep but little decrease with salinity appears to be characteristic in the range of a salinity of less than 0.2 mol/l. Above 0.2 mol/l the diffusion coefficient slowly rises again. The difference between the diffusivity of pure water and minimum diffusivity at 0.2 mol/l amounts to 8 % at 18.5 °C and 11 % at 25 °C.



## **5 Properties of dry rocks**

### **5.1 General remarks**

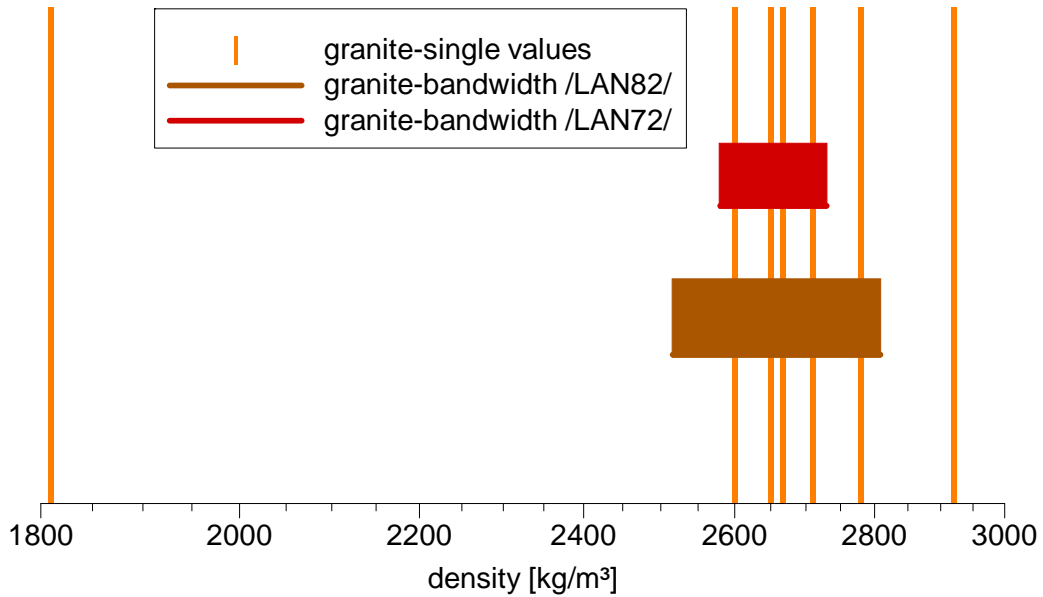
Water and sodium chloride are pure substances and as such their properties can be measured rather precisely. In contrast the expression „rock“ represents a large variety of materials that ultimately differ in their genesis in general as well as in their individual history. Rocks can be classified in three groups, namely igneous, sedimentary and metamorphic rocks, each of which is further divided into numerous subclasses. A certain rock type like granite – an igneous rock – can be found at different locations showing characteristic material parameters that nevertheless differ somewhat from site to site. Additionally, material parameters vary locally due to inhomogeneity. As a first approximation to properties of a specific rock, data from /VOS03/ for a large variety of rocks in the Alps is cited in the following. More generally valid is data from /LAN72/ and from /LAN82/.

### **5.2 Density**

The density of rocks in the Alps varies roughly between 2550 kg/m<sup>3</sup> and 2950 kg/m<sup>3</sup> with a mean value of approx. 2800 kg/m<sup>3</sup>. Unfortunately there is no way to reduce this uncertainty for a specific rock because structure and integrity depend on its individual history.

For the granite at the Grimsel test site the density of the undisturbed matrix is given as ~ 2710 kg/m<sup>3</sup> /KUL01/. Sources cited in /LAN82/ provide data between 2516 kg/m<sup>3</sup> and 2809 kg/m<sup>3</sup>. The related mean values are 2600, 2650, 2667, and 2780 kg/m<sup>3</sup>. In /LAN72/ comparable values lie between 2580 and 2730 kg/m<sup>3</sup> with two exceptions; there is one rather high value of 2920 kg/m<sup>3</sup> from Japan and one apparently questionable value of 1810 kg/m<sup>3</sup> from Scandinavia.

The variation in measured sandstone densities is even greater with values between 2000 and 2900 kg/m<sup>3</sup> /LAN82/, possibly because the density of sedimentary rock generally increases significantly with depth, especially within the first 1000 m. The mean, however, may nevertheless be close to the value for granite.



**Fig. 5.1** Density data for granite

The thermal expansion coefficient is very small for rocks /LAN82/. The density can therefore be considered to be constant up to a temperature of 300 °C.

Conclusions:

- Rock density is independent of all primary variables for all practical purposes.
- Rock density varies significantly depending on its history. A proper choice appears to be difficult without actual measurements.

### 5.3 Porosity

As with density also only rather unspecific porosity ranges can be given. They can be expected to lie between 0.9 % and 5.7 % for sedimentary rocks and between 1.0 % and 4.7 % for magmatic and metamorphic rocks. However, rock formations envisaged for CO<sub>2</sub>-storage in the deep underground may show a much higher porosity. Values usually in the range between 18 % and 27 % with local peaks up 36 % have been measured for sandstone /LAR 07/.

For the granite at the Grimsel test site the porosity of the undisturbed matrix is given as 0.85 – 1.00 % /KUL01/. The porosity of sandstone varies between 10 and 30 % in depths up to 1800 m /LAN82/.

Note that the porosity can be reduced by the effect of salt precipitation.

Conclusions:

- For non-swelling rocks porosity is independent of all primary variables which follows from the constant rock density.
- However, in the case of precipitating NaCl porosity can be reduced.
- Minimum porosity indicating a complete discontinuity of flow channels can be significantly above 0.

#### 5.4 Permeability

Permeability of rocks is as individual as density and porosity. Some typical value ranges are given in Tab. 1.1.

**Tab. 5.1** Typical permeabilities for some types of rock

rock	permeability [m <sup>2</sup> ]	source
undisturbed granite matrix	~ 2 10 <sup>-18</sup> 10 <sup>-20</sup> 10 <sup>-19</sup> to 10 <sup>-18</sup>	/KUL01/ (Grimsel site) /KUL02/ (Äspö HRL) /BEA72/
fractures in granite	10 <sup>-14</sup> to 10 <sup>-11</sup> 2 10 <sup>-14</sup> to 5 10 <sup>-12</sup>	/KUL02/ (Äspö HRL)
rock salt	< 10 <sup>-21</sup>	/MÖN09/
claystone	10 <sup>-21</sup> to 10 <sup>-20</sup>	/MÖN09/
dolomite	> 10 <sup>-17</sup> 10 <sup>-17</sup> to 10 <sup>-16</sup>	/KRÖ96/, /MÖN09/ /BEA72/
sandstone	10 <sup>-14</sup> to 10 <sup>-12</sup> 10 <sup>-15</sup> to 10 <sup>-14</sup>	/MÖN09/ /BEA72/

Conclusions:

- Rock permeability depends strongly on the rock type.
- Additionally, there are strong spatial variations.

## 5.5 Thermal conductivity

At 25 °C the thermal conductivity lies in the range between 2 W/(m K) and 6 W/(m K). Thermal conductivity of rock was found by /VOS03/ to decrease with increasing temperature. This behaviour is more pronounced for rocks with high thermal conductivity at ambient temperature compared with those with lower thermal conductivity at ambient temperature. This trend is confirmed in /LAN72/ by a compilation of data for granite as well as for limestone.

A mathematical approach was therefore scaled to  $\lambda(0)$ , the thermal conductivity at 0 °C. A second formulation for scaling the conductivity at 25 °C down to the conductivity at 0 °C was also provided:

$$\lambda(T) = \frac{\lambda(0)}{0.99 + T \left( a - \frac{b}{\lambda(0)} \right)} \quad (5.1)$$

$$\lambda(0) = c\lambda(25) + \frac{1}{2} \sqrt{d(\lambda(25))^2 - e\lambda(25)} \quad (5.2)$$

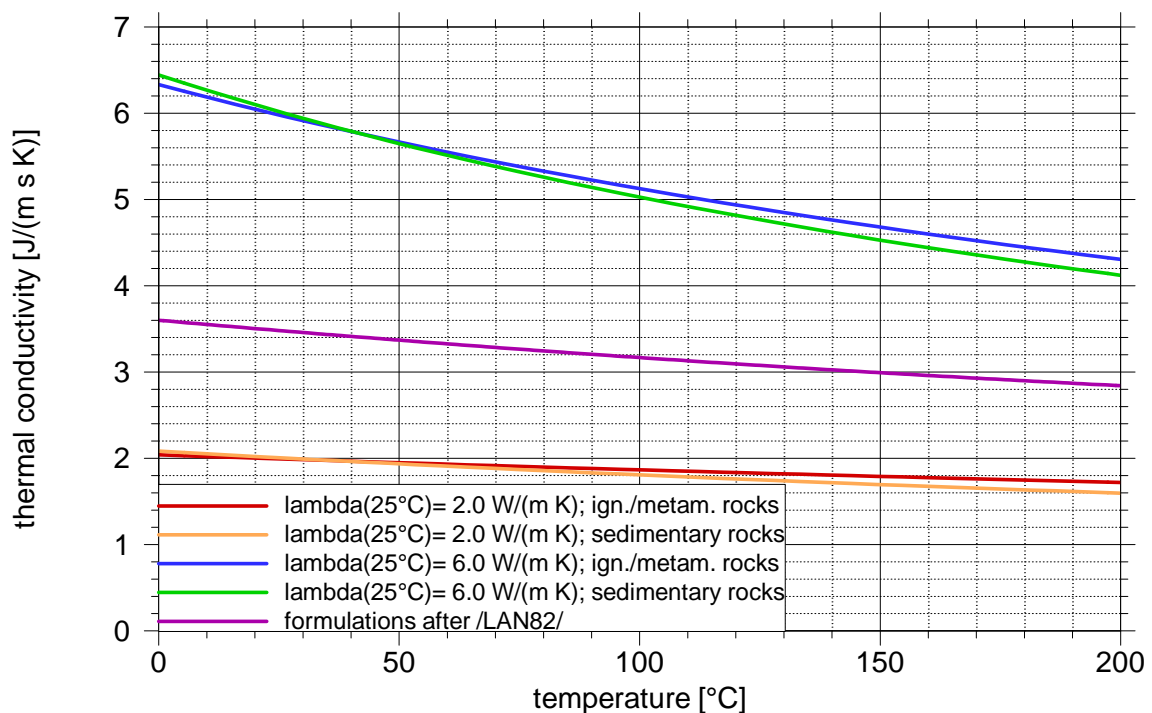
- $T$  - temperature [°C]  
 $a-e$  - constants (q. v. Tab. 5.2) [-]

Equations ( 5.1 ) and ( 5.2 ) are reported to be valid up to a temperature of 500 °C for igneous and metamorphic rock and up to a temperature of 300 °C for sedimentary rock.

Depending on the type of rock the constants  $a$  to  $e$  vary slightly according to Tab. 5.2. The constants  $a$  and  $b$  may be related. Taking the given uncertainties for  $a$  and  $b$  to the extreme leads to an increase in conductivity with temperature which is in direct contradiction to the statement cited above. However, /LAN72/ presents an example for a sandstone in Japan that shows a slight increase from 1.6 W/(m K) at 0 °C to 1.65 W/(m K) at 100 °C for water-saturated specimen). Unfortunately, the authors do not elaborate on that subject. The resulting curves based on the mean values for  $a$  and  $b$  are shown in Fig. 5.2.

**Tab. 5.2** Parameters for equations ( 5.1 ) and ( 5.2 )

parameter	rock type	
	igneous and metamorphic	sedimentary
a	$0.0030 \pm 0.0015$	$0.0034 \pm 0.0006$
b	$0.0042 \pm 0.0006$	$0.0039 \pm 0.0014$
c	0.53	0.54
d	1.13	1.16
e	0.42	0.39



**Fig. 5.2** Thermal conductivity of different rock types

/VOS03/ stresses that the temperature dependence of the thermal conductivity of different rock types is different. However, these differences appear to be of secondary importance in the considered temperature range compared with the influence of  $\lambda(0)$ . Temperature-dependency increases with  $\lambda(0)$ , too. While thermal conductivity decreases by a factor of approx. 0.80 for  $\lambda(0) = 2 \text{ W}/(\text{m K})$  in the considered temperature range. This factor decreases to approx. 0.66 for  $\lambda(0) = 6 \text{ W}/(\text{m K})$ .

Note that use of mean values for eq. ( 5.1 ) does not exactly reproduce the mean values of measured thermal conductivity data presented in /VOS03/.

Following /LAN82/ the mean values for  $\lambda(0)$  for igneous and metamorphic rocks lie between 2 and 4.5 W/(m K) (granite 3.05 W/(m K)) and for sedimentary rocks between 2 and 2.5 W/(m K) except for dolomite (3.62 W/(m K)), anhydrite (4.05 W/(m K)) and salt (4.00 W/(m K)).

The bandwidth of data for  $\lambda(0)$  for granite found in /LAN72/ encompasses a range from 2.25 to 3.8 W/(m K). Recommended values are 3.0 W/(m K) at 0° C, 2.6 W/(m K) at 100 °C and 2.4 W/(m K) at 200 °C. However, it is also stated that fine-grained granite shows lower values than coarse grained granite.

For comparison a general formulation from /LAN82/ for the thermal conductivity of rocks is added to Fig. 5.2, (violet line)

$$\lambda(T) = 3.6 - 0.4910^{-2}T + 0.6110^{-5}T^2 - 2.5810^{-9}T^3 \quad \text{with } T \text{ in [K]} \quad (5.3)$$

which lies between the formulations from /VOS03/ for low and for high values of  $\lambda(0)$  (c. f. Fig. 5.2).

Conclusions:

- The dependency of thermal conductivity on  $\lambda(0)$  and on temperature is moderate.
- The difference resulting from the two formulations for sedimentary and for igneous as well as metamorphic rocks can be neglected in the light of uncertainties concerning the parameter  $\lambda(0)$ .
- According to /VOS03/ the key value  $\lambda(0)$  varies within a bandwidth of 4 W/(m K). Data from /LAN82/ indicates a bandwidth of only 2 W/(m K) in the lower value spectrum.
- Comparison of data from /LAN82/ and from /VOS03/ show that the values given in these sources can only be used as a first approximation in cases for which no specific data exists.



## 5.6 Specific heat capacity

From the measurements (/VOS03/) shown in Fig. 5.3 it appears that the mean value for heat capacity is almost equal for metamorphic and igneous rocks but significantly higher for sedimentary rocks. However, deviations from these mean values are in the order of the difference between the resulting two curves.

While the data for heat capacity is presented in /VOS03/ there is no analytical formulation for the two curves. Therefore an ad hoc approach valid for the temperature range between 10 °C and 300 °C is given here:

$$c_{im}(T) = \frac{110}{300} * T - 110 * e^{-\frac{T}{70}} + 895 \quad \text{with } T \text{ in } [^{\circ}\text{C}] \quad (5.4)$$

$$c_s(T) = \frac{110}{300} * T - 130 * e^{-\frac{T}{70}} + 860 \quad (5.5)$$

$c_{im}$  - specific heat capacity for igneous and metamorphic rock [J/(kg K)]

$c_s$  - specific heat capacity for sedimentary rock [J/(kg K)]

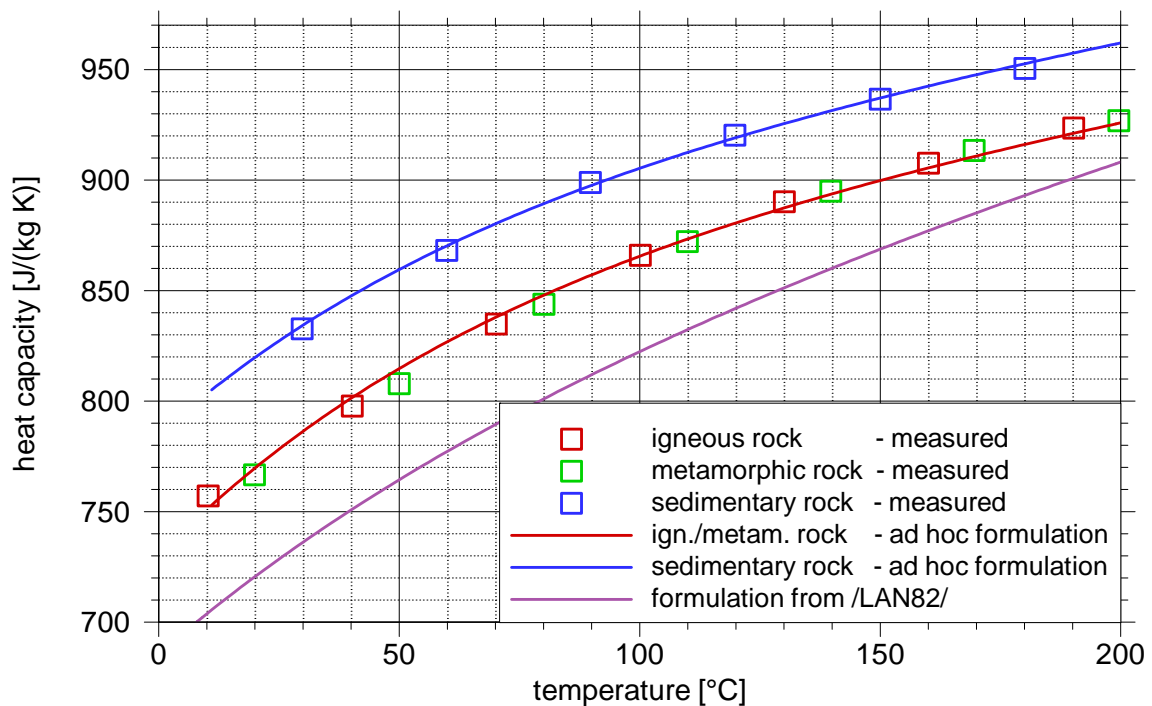


Fig. 5.3 Heat capacity of different rock types

According to these formulations the heat capacity for igneous and metamorphic rock increases from 753 [J/(kg K)] at 10 °C to 865 [J/(kg K)] at 100 °C and 926 [J/(kg K)] at 200 °C. Even slightly higher differences are found for sedimentary rock. Similar in trend but different in the absolute values is a formulation presented in /LAN82/ that is meant to be a general formulation for rocks:

$$c(T) = 754 * \left(1 + 6.14 \cdot 10^{-4} * T - 19280 / T^2\right) \text{ with } T \text{ in [K], } c \text{ in [J/(kg K)]} \quad (5.6)$$

In the light of these well founded formulations it appears to be curious that constant values for the specific heat capacity of granite can be found in /LAN67/ stated to be valid within very wide temperature ranges:

- 829 J/(kg K) for 16 °C to 100 °C,
- 912 J/(kg K) for 20 °C to 200 °C, and
- 1046 J/(kg K) for 20 °C to 400 °C.

However, they could represent some sort of a mean value in the referring temperature range. These values are still within the bandwidth of measured data provided by /VOS03/ and may – as the formulation from /LAN82/ – reflect the uncertainties introduced by including rocks from outside the Alps. Further single values from /LAN 82/ for granite at specific temperatures also lie within this bandwidth:

- 846/875 J/(kg K) at 100 °C and
- 938/950 J/(kg K) at 200 °C

Conclusions:

- Temperature-dependency of the heat capacity is moderate.
- For igneous and metamorphic rock the increase in heat capacity from 10 °C to 100 °C amounts to 11 % and the increase to 200 °C to 20 %.
- For sedimentary rock the increase is even slightly more pronounced.

## 5.7 Thermal diffusivity

Thermal diffusivity includes thermal conductivity, heat capacity and density of the rock. Due to uncertainties referring to the values of thermal conductivity at 25 °C  $\lambda(25)$ , constants  $a$  and  $b$  in eq. ( 5.1 ), and rock density  $\rho$  only some examples for the temperature-dependent curves can be given. For Fig. 5.4 the following input values were used:

- $\lambda(25) = 2$  and  $\lambda(25) = 6$
- mean values for  $a$  and  $b$
- $\rho_{\text{igneous rock}} = 2804 \text{ kg/m}^3$ ,  $\rho_{\text{metamorphic rock}} = 2852 \text{ kg/m}^3$ ,  $\rho_{\text{sedimentary rock}} = 2778 \text{ kg/m}^3$

The density data was back calculated from data in /VOS03/ as the mean of the ratio of thermal capacity and specific heat capacity which yields rock density. As with all the data concerning rock that was presented in the previous chapters, the figures for density should be used with extreme care.

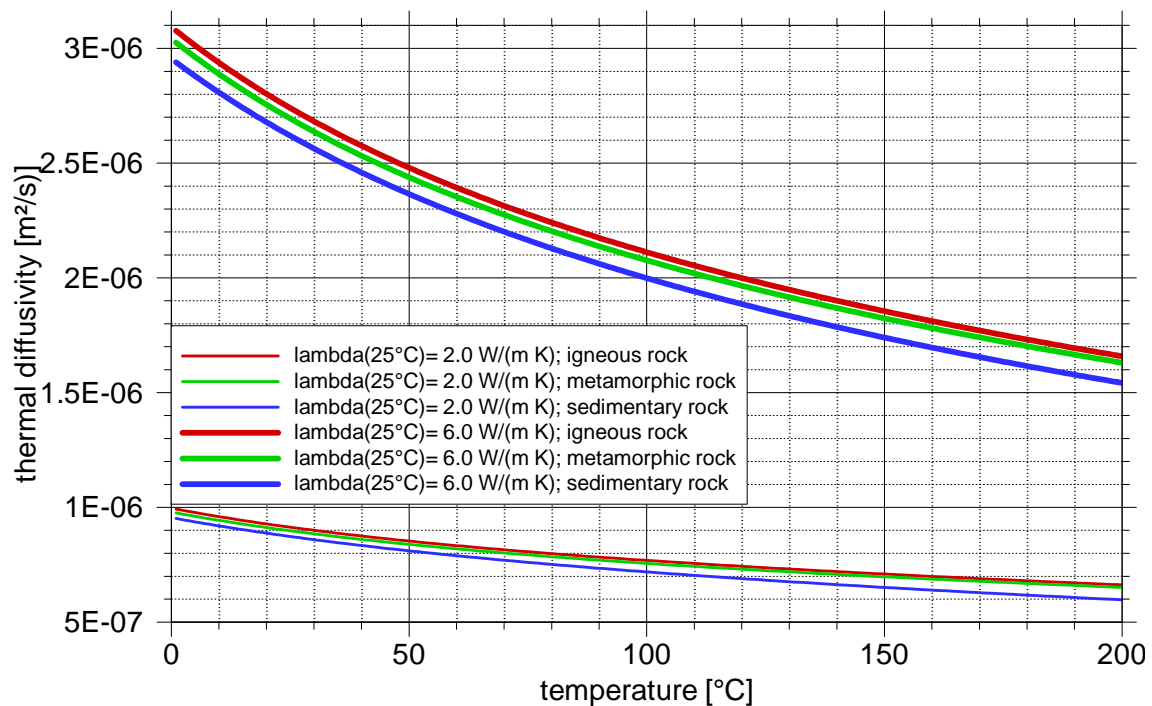


Fig. 5.4 Thermal diffusivity of different rock types

In the cases considered here thermal diffusivity covers a range from  $0.75 \cdot 10^{-6} \text{ m}^2/\text{s}$  to  $3.1 \cdot 10^{-6} \text{ m}^2/\text{s}$ . For a specific rock, though, only one curve applies. Changes up to 70 % are possible over the whole temperature range.

Conclusions:

- The influence of temperature on thermal diffusivity is moderate to strong depending on rock type and the value of  $\lambda(25)$ .

## 6 Properties of saturated rocks

### 6.1 Effects of precipitation

#### 6.1.1 Porosity

Porosity can be reduced by salt precipitation. The simplest approach to this phenomenon is to reduce porosity proportionally to the volume of precipitated salt. In this case porosity can theoretically decrease to 0. It is more probable, though, that the porous medium becomes already impermeable at a critical porosity greater than 0 as has been observed in the context of geothermal modelling /VER88/. In that case the process of precipitation comes to an end before the whole pore space is filled with solid salt. Values for critical porosities are highly uncertain.

Conclusions:

- In the case of NaCl precipitation porosity can be reduced.
- Minimum porosity indicating a complete discontinuity of flow channels can already be reached significantly above 0.

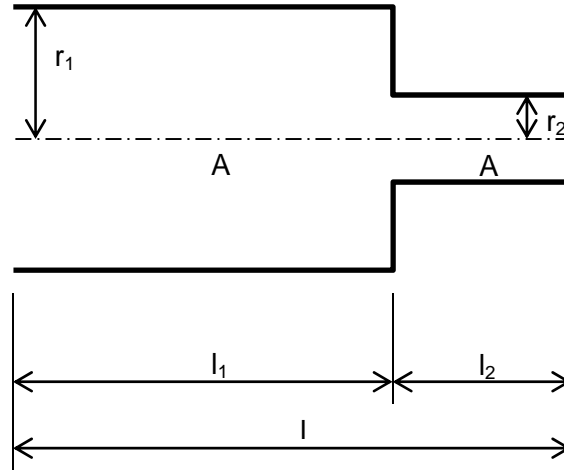
#### 6.1.2 Permeability

Like porosity permeability can be reduced by the effect of salt precipitation. For such a situation a simple approach taking this phenomenon into account has been developed in the framework of geothermal modelling /VER88/. For the sake of simplicity it is assumed there that the flow channels consist of cylindrical sections with only two different cross-section areas. The section with the large cross-section area  $A_1$  represents the pore, and the section with the small cross-section area  $A_2$  represents the bottleneck between two pores. In order to develop a model the sections are arranged in such a way that all sections of the same size are combined as indicated in Fig. 6.1. The total length of the flow path  $l$  is then subdivided into two segments  $l_1$  and  $l_2$ .

Using the standardised length  $\xi$

$$\xi = \frac{l_1}{l} \quad (6.1)$$

- $\xi$  - standardised length of the wider segment [-]
- $l_1$  - length of the wider segment [m]
- $l$  - total length of the flow path [m]



**Fig. 6.1** Idealised model of a flow channel with varying cross-section area

the ratio of the cross-sectional areas  $\omega$

$$\omega = \frac{A_1}{A_2} \quad (6.2)$$

- $\omega$  - ratio of the cross-sectional areas [-]
- $A_1$  - cross-section area of the wider segment [m<sup>2</sup>]
- $A_2$  - cross-section area of the smaller segment [m<sup>2</sup>]

and the standardised porosity  $\varphi$

$$\varphi = \frac{\Phi - \Phi_c}{\Phi_0 - \Phi_c} \quad (6.3)$$

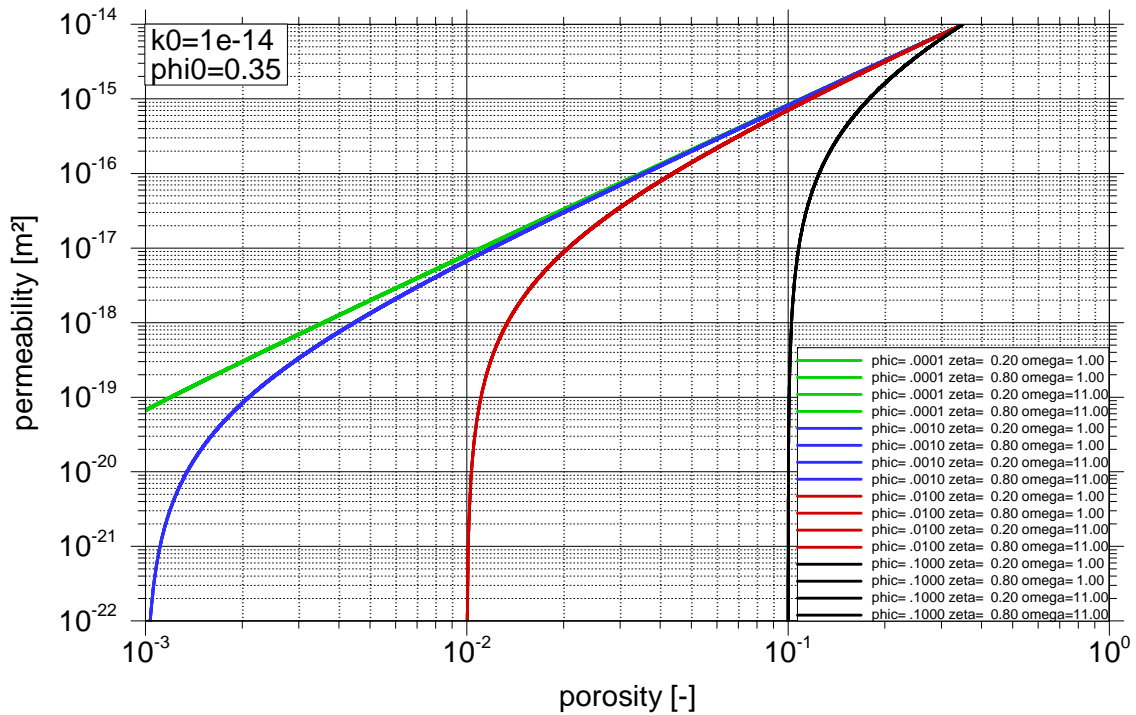
- $\varphi$  - standardised porosity [-]
- $\Phi_0$  - initial porosity [-]
- $\Phi_c$  - critical porosity [-]

the permeability can be expressed as a function of porosity /VER88/:

$$\frac{k}{k_0} = \varphi^2 \frac{\frac{\xi}{\omega^2} + 1 - \xi}{\xi \left( \frac{\varphi}{\omega + \varphi - 1} \right)^2 + 1 - \xi} \quad (6.4)$$

$k_0$  - initial permeability [m<sup>2</sup>]

Remark: Permeability appears to be rather insensitive to  $\xi$  and  $\omega$  in the relevant data range as shown in Fig. 6.2.



**Fig. 6.2** Exemplary porosity-permeability relation

Conclusions:

- The effect of precipitation on permeability can be approximated.
- Realistic values for the required parameters  $\xi$ ,  $\omega$ , and  $\Phi_c$  are hard difficult to come by.

## 6.2 Macroscopic parameters for heat transport

### 6.2.1 General considerations

On a microscopic level heat flow in a saturated porous medium occurs in the matrix as well as in the fluid-filled pore space according to the thermal properties of rock and fluid, respectively. Modelling of heat flow requires changing to a macroscopic level of observation to which thermal conductivity and the heat capacity have to be adapted.

A first step to derive such macroscopic parameters is to apply the assumption of a local<sup>3</sup> thermodynamic equilibrium, an assumption that is often found in the literature but rarely justified in detail. However, with respect to thermal processes in water-saturated rocks one can argue that the pore channels are very narrow in comparison to the enclosing volumes of rock so that the assumption of a fast lateral temperature equalisation within a cross-section of the channel is a well-founded assumption. Heat from the pore fluid is then quickly transported into the matrix because of the large thermal diffusivity in the rock in comparison to the relatively low thermal diffusivity in the solution (c. f. sections 2.6 and 5.7).

### 6.2.2 Thermal conductivity

If the thermal conductivity of a solution-saturated rock has not been directly measured the macroscopic parameter can be calculated making use of the physical analogue between electricity and heat flow. Like electrical conductivity in case of parallel connection the thermal conductivities of the different materials in a porous medium can simply be added if weighed by the respective volume fraction:

$$\lambda_{macroscopic} = (1 - \Phi)\lambda_{rock} + \Phi\lambda_{solution} \quad (6.5)$$

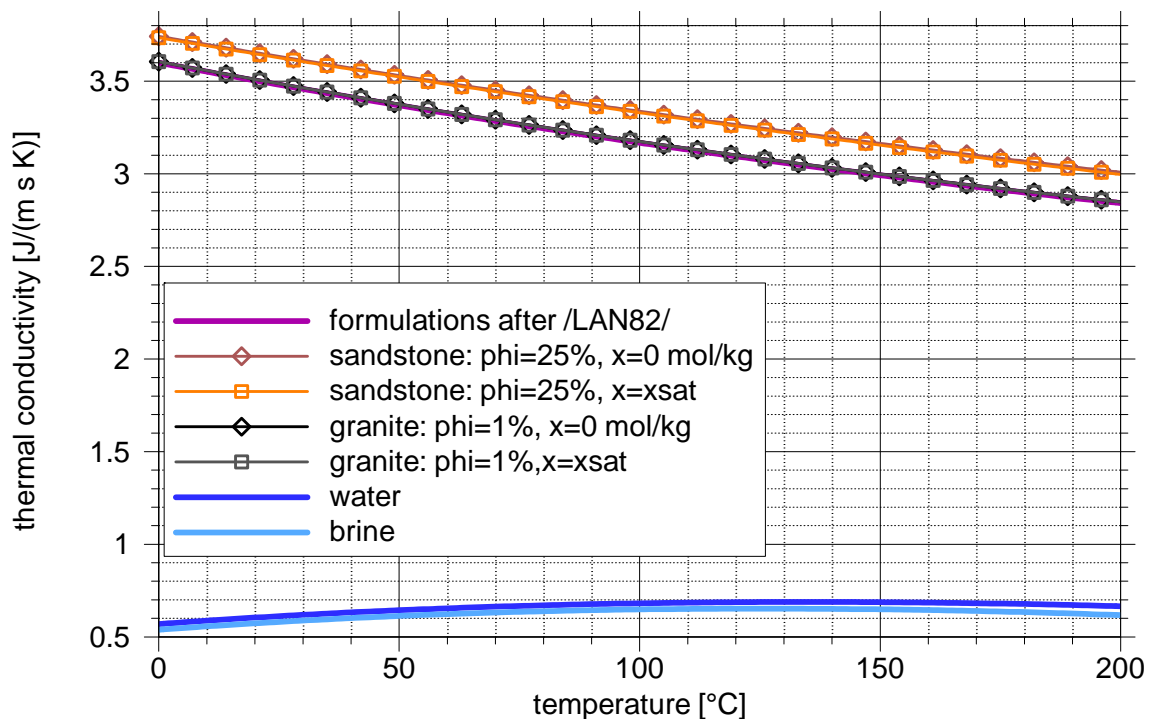
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<sup>3</sup> on the scale of an REV



- $\lambda_{macroscopic}$  - macroscopic thermal conductivity [J/(kg K)]
- $\lambda_{rock}$  - thermal conductivity of the rock matrix [J/(kg K)]
- $\lambda_{solution}$  - thermal conductivity of the solution [J/(kg K)]
- $\Phi$  - porosity [-]

Using the formulation from /LAN 82/ as a basis for the thermal conductivity of rocks the influence of water and brine on thermal conductivity for a typical granite ( $\Phi = 1\%$ ) and the typical sandstone ( $\Phi = 25\%$ ) are shown in Fig. 6.3.



**Fig. 6.3** Thermal conductivities for rock, solution and saturated rock

The influence of salinity on the overall thermal conductivity amounts to 0.30 % for sandstone and less than 0.01 % for granite.

Conclusions:

- The influence of solution salinity on thermal conductivity is negligible for granite as well as for sandstone.
- Thermal conductivity of saturated rock is dominated by the rock properties.

### 6.2.3 Heat capacity

Heat capacity is related to the mass so that the macroscopic heat capacity can easily be calculated as the sum of substance specific value times the respective mass fraction:

$$c_{macroscopic} = x_{bulk}^{rock} c_{rock} + x_{bulk}^{solution} c_{solution} \quad (6.6)$$

$$\text{with } x_{bulk}^i = \frac{m_i}{m_{bulk}}; \quad i = rock, solution \quad (6.7)$$

$$\text{and } x_{bulk}^{rock} + x_{bulk}^{solution} = 1$$

$c_{macroscopic}$	-	macroscopic heat capacity [J/(kg K)]
$c_{rock}$	-	heat capacity of the rock matrix [J/(kg K)]
$c_{solution}$	-	heat capacity of the solution [J/(kg K)]
$x_{bulk}^{rock}$	-	mass fraction of the rock matrix [-]
$x_{bulk}^{solution}$	-	mass fraction of the solution [-]
$m_{bulk}$	-	bulk mass [kg]
$m_{rock}$	-	rock mass [kg]
$m_{solution}$	-	mass of the solution [kg]

To illustrate the effect on the overall heat capacity of water saturated rock examples for two different types of rock with typical hydraulic properties are given here:

- sandstone
  - porosity of 25 %
  - density of 2600 kg/m<sup>3</sup> and
- granite
  - porosity of 1 %
  - density of 2700 kg/m<sup>3</sup>.

Heat capacities for the two types of rock, water and brine as well as the combined rock-solution system are plotted in Fig. 6.4. The same plot with a different scale for  $c$  is shown

in Fig. 6.5. The Maximum difference between dry and wet granite lies in the order of 1 %. The differences resulting from the effect of salinity are even much less. The heat capacity of sandstone is increased by approx. 45 % due to the presence of water. The maximum difference accounting for a varying salinity amounts to 4 %.

Conclusions:

- The influence of salinity on the heat capacity is
  - negligible in case of granite (due to the low porosity)
  - low in case of sandstone.
- The influence of the fluid heat capacity on the overall heat capacity is
  - negligible in case of granite (due to the low porosity)
  - moderate in case of sandstone.
- Heat capacity of saturated rock is dominated by the rock properties.

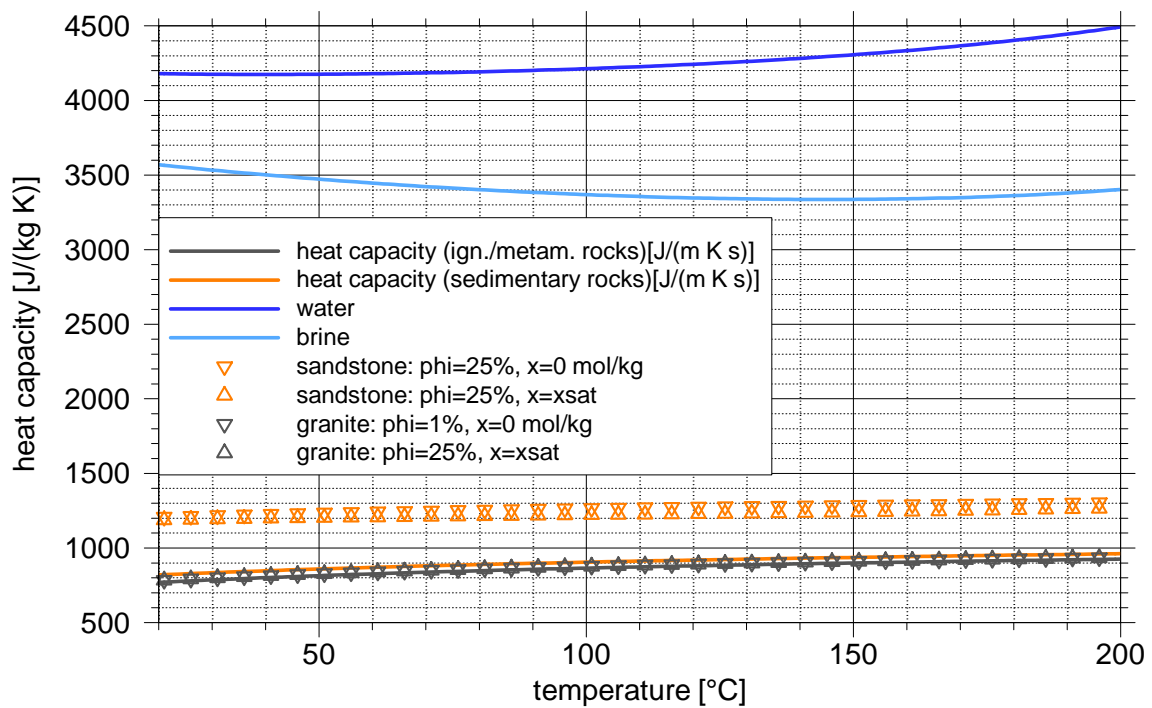
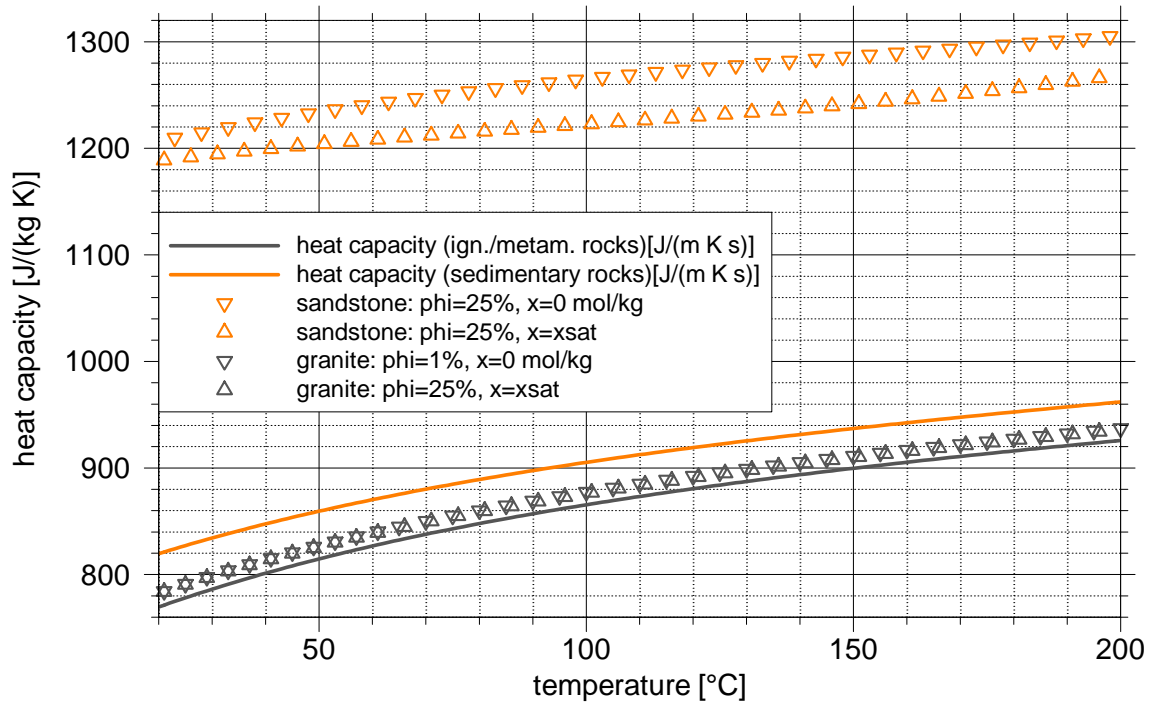


Fig. 6.4 Heat capacities for rock, solution and saturated rock



**Fig. 6.5** Heat capacities for rock and saturated rock

## 7 Summary and conclusions

### 7.1 Fluid properties

The influence of the primary variables on fluid and rock parameters according to the influence classes as defined in Tab. 1.1 are compiled in Tab. 7.1. All fluid parameters depend either moderately or strongly on temperature. The same applies to salinity with the exception of diffusivity where only little influence was found. In contrast, fluid pressure has only little or no influence on the fluid parameters. One exception, though, is the enthalpy at low temperatures where moderate influence was found.

**Tab. 7.1** Evaluation of dependencies for saline water

	none/negligible	little	moderate	strong
density		●	●●	
vapour pressure	●		●	●
viscosity		●		●●
thermal conductivity		●	●●	
heat capacity		●	●●	
thermal diffusivity		●	●●	
enthalpy			●●	●
solubility	●		●	
diffusivity	●	●		●

- temperature
- salinity
- pressure

Depending on the problem at hand temperature and/or salinity can change strongly. In combination with the considerable influence on the state variables this requires an iterative solution scheme for the numerical model. This is usually already realised in fully-coupled variable-density codes.

As a rule, pressure does not vary very much neither locally nor temporally, but changes significantly over large depths due to the depth-dependent hydrostatic pressure. In a numerical model the pressure-dependency may therefore be adequately approximated either by a local constant value or by using the local value from the previous time level for the pressure-dependent property on the actual time level, thus avoiding the necessity of an iteration of pressure.

## 7.2 Rock properties

Salinity and pressure are associated with the solution and thus cannot influence the material parameters of dry rock. Evaluation of the remaining temperature-dependencies for dry rock are summarised in Tab. 7.2. While density, porosity and gas permeability are not affected by temperature the parameters relevant for heat flow in most cases are moderately to strongly influenced by temperature depending on the rock in question. Here, it is not possible to relate a certain type of rock to a specific category of dependency. The degree of dependency depends rather on the individual rock characteristics than on a certain rock type.

**Tab. 7.2** Evaluation of dependencies for dry rock

	none/negligible	little	moderate	strong
density	●			
porosity	●			
permeability	●			
thermal conductivity			●	●
heat capacity			●	
thermal diffusivity		●	●	●

● temperature

In Tab. 7.3. the evaluations for saturated rock are summarized. As mentioned before the thermal behavior is dominated by the rock parameters as becomes evident by comparison with Tab. 7.2. Additionally, the influence of certain conditions leading to precipitation which is accompanied by reduction of porosity and permeability are accounted for.

**Tab. 7.3** Evaluation of dependencies for saturated rock

	none/negligible	little	moderate	strong
porosity <sup>*)</sup>				● ●
permeability <sup>*)</sup>				● ●
thermal conductivity			●	●
heat capacity			●	

● temperature

● salinity of the solution

<sup>\*)</sup> in case of precipitation

### **7.3 Possible problems arising with non-isothermal modelling**

#### **Phase change of the fluid**

High temperature in combination with low pressure can lead to a change from the liquid to the gaseous state of water. Theoretically, such a combination of conditions can occur only up to a depth of about 150 m within the parameter range considered here. If such conditions are encountered during a single-phase flow simulation the results are unrealistic from that point on.

If phase changes cannot be excluded by the definition of the model the phase state of the fluid is therefore to be monitored in the whole space-time domain of the model. The criterion for phase changes is given by the ratio of fluid pressure to vapour pressure which always has to be greater than or equal to 1. This is why vapour pressure has to be regarded in the modelling even if it does not appear in the mathematical model.

#### **Precipitation/dissolution of salt**

Another problem arises in situations where a fluid of high salinity cools down. If the calculated salt concentration exceeds the local saturation value the corresponding excess mass of NaCl precipitates which changes porosity and thereby also permeability. If such conditions are to be anticipated the local solubility must be monitored.

If precipitation is not considered in the model a simulation encountering these conditions should consequently be stopped. The alternative would be to calculate the precipitating salt mass and the subsequent reduction of porosity and permeability. However, there are only very simple general approaches to modelling changes in the pore space due to precipitation.

Note that precipitated salt dissolves again if temperature increases. The amount of precipitated salt must therefore be noted during the simulation for a correct mass balance.





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## A Appendix A: Formulations

### A.1 Pure water

#### A.1.1 Vapour pressure

Source: /IAP97/

$$\frac{p_s}{p^*} = \left[ \frac{2C}{-B + (B^2 - 4AC)^{1/2}} \right]^4 \quad (\text{A.1})$$

- $p_s$  - vapour saturation pressure [MPa]  
 $p^*$  - reference pressure (c. f. Appendix B)  
 $A, B, C$  - ansatz functions (q. v. eq. ( A.2 ))

$$\begin{aligned} A &= \mathcal{G}^2 + n_1 \mathcal{G} + n_2 \\ B &= n_3 \mathcal{G}^2 + n_4 \mathcal{G} + n_5 \\ C &= n_6 \mathcal{G}^2 + n_7 \mathcal{G} + n_8 \end{aligned} \quad (\text{A.2})$$

- $\mathcal{G}$  - ansatz function (q. v. eq. ( A.3 ))  
 $n_1$  to  $n_6$ , - constants (c. f. Appendix B)

$$\mathcal{G} = \frac{T}{T^*} + \frac{n_9}{\left( \frac{T}{T^*} \right)^{-n_{10}}} \quad (\text{A.3})$$

- $T$  - temperature [K]  
 $T^*$  - reference temperature (c. f. Appendix B)  
 $n_9, n_{10}$ , - constants (c. f. Appendix B)

#### Range of validity

- temperature:  $273.15 \text{ K} < T < 647.096 \text{ K}$

### A.1.2 Density

Source: /IAP97/

$$\rho = \frac{1}{v} \quad (\text{A.4})$$

- $\rho$  - water density [kg/m<sup>3</sup>]  
 $v$  - specific volume [m<sup>3</sup>/kg]

$$v \frac{p}{R_{H_2O} T} = \pi \gamma_\pi \quad (\text{A.5})$$

- $p$  - pressure [MPa]  
 $T$  - temperature [K]  
 $R_{H_2O}$  - specific gas constant for water vapour (c. f. Appendix B)  
 $\pi$  - standardised pressure (q. v. eq. ( A.6 )) [-]  
 $\gamma_\pi$  - ansatz function (q. v. eq. ( A.7 ))

$$\pi = \frac{p}{p^*} \quad (\text{A.6})$$

- $p^*$  - reference pressure (c. f. Appendix B)

$$\gamma_\pi = \sum_{i=1}^{34} -n_i I_i (7.1 - \pi)^{J_i - 1} (\tau - 1.222)^{J_i} \quad (\text{A.7})$$

- $\tau$  - standardised temperature (q. v. eq. ( A.8 )) [-]  
 $n_i, I_i, J_i$  - constants (c. f. Appendix B)

$$\tau = \frac{T^*}{T} \quad (\text{A.8})$$

- $T^*$  - reference temperature (c. f. Appendix B)

#### Range of validity

- temperature: 273.15 K <  $T$  < 623.15 K
- pressure:  $p_s(T) < p < 100$  MPa  
 $p_s(T)$  - vapour saturation pressure [MPa] (q. v. eq. ( A.1 ))

### A.1.3 Viscosity

Source: /IAP03/

$$\bar{\eta} = \bar{\eta}_0(\bar{T}) \cdot \bar{\eta}_1(\bar{T}, \bar{\rho}) \cdot \bar{\eta}_2(\bar{T}, \bar{\rho}) \quad (\text{A.9})$$

- $\bar{\eta}$  - standardised viscosity (q. v. eq.s ( A.10 ) [-]  
 $\bar{T}$  - standardised temperature (q. v. eq.s ( A.10 ) [-]  
 $\bar{\rho}$  - standardised density (q. v. eq.s ( A.10 ) [-]  
 $\bar{\eta}_0, \bar{\eta}_1, \bar{\eta}_2$  - ansatz functions [-] (q. v. eq.s ( A.11 ) to ( A.13 ))

$$\bar{T} = \frac{T}{T^*}, \quad \bar{\rho} = \frac{\rho}{\rho^*}, \quad \bar{\eta} = \frac{\eta}{\eta^*} \quad (\text{A.10})$$

- $T$  - temperature [K]  
 $\rho$  - density [kg/m<sup>3</sup>]  
 $\eta$  - viscosity [Pa s]  
 $T^*, \rho^*, \eta^*$  - reference values (c. f. Appendix B)

$$\bar{\eta}_0 = \frac{\sqrt{\bar{T}}}{\sum_{i=0}^3 \frac{H_i}{\bar{T}^i}} \quad (\text{A.11})$$

- $H_i$  - constants (c. f. Appendix B)

$$\bar{\eta}_1 = e^{\left[ \bar{\rho} \sum_{i=0}^5 \sum_{j=0}^6 H_{ij} \left( \frac{1}{\bar{T}} - 1 \right)^i (\bar{\rho} - 1)^j \right]} \quad (\text{A.12})$$

- $H_{ij}$  - constants (c. f. Appendix B)

$$\bar{\eta}_2 = 1 \quad (\text{A.13})$$

#### Range of validity

- pressure:  $p < 500 \text{ MPa}$  for  $0 \text{ }^\circ\text{C} < T < 150 \text{ }^\circ\text{C}$   
 $p < 350 \text{ MPa}$  for  $150 \text{ }^\circ\text{C} < T < 600 \text{ }^\circ\text{C}$   
 $p < 300 \text{ MPa}$  for  $600 \text{ }^\circ\text{C} < T < 900 \text{ }^\circ\text{C}$

#### A.1.4 Thermal conductivity

**Source:** /YUS75/ (cited in /PHI81/)

$$\lambda = -0.92247 + 2.8395 T' - 1.8007 T'^2 + 0.52577 T'^3 - 0.07344 T'^4 \quad (\text{A.14})$$

$\lambda$  - thermal conductivity of pure water [J/(m K s)]

$T'$  - normalised temperature [-]

$$T' = \frac{T + 273.15}{273.15} \quad (\text{A.15})$$

$T$  - temperature [°C]

#### Range of validity

- temperature:  $20 \text{ °C} < T < 330 \text{ °C}$

**Source:** data: /LAN72/; formulation: this report

$$\lambda(p, T) = \lambda(T) * \frac{p - p_0}{10^7} 0.0095 \quad \text{for } T < 408.15 \text{ K} \quad (\text{A.16})$$

$$\lambda(p, T) = \lambda(T) * \frac{p - p_0}{10^7} 0.0095 * \left[ 1 + 7.1 \cdot 10^{-5} (T - 408.15)^2 \right] \quad \text{for } T > 408.15 \text{ K}$$

$\lambda$  - thermal conductivity [J/(s m K)]

$p$  - pressure [Ps]

$p_0$  - atmospheric pressure [Ps]

$T$  - temperature [K]

#### Range of validity

- temperature (see eq. ( A.16 ) )

### A.1.5 Enthalpy

Source: /IAP97/

$$\frac{h}{R_{H_2O}T} = \tau\gamma_\tau \quad (\text{A.17})$$

$h$  - enthalpy [kJ/kg]

$R_{H_2O}$  - specific gas constant for water vapour (c. f. Appendix B)

$T$  - temperature [K]

$\gamma_\tau$  - ansatz function (q. v. eq. ( A.19 ))

$\tau$  - standardised temperature (q. v. eq. ( A.18 )) [-]

$$\tau = \frac{T^*}{T} \quad (\text{A.18})$$

$T^*$  - reference temperature (c. f. Appendix B)

$$\gamma_\tau = \sum_{i=1}^{34} n_i (7.1 - \pi)^{I_i} J_i (\tau - 1.222)^{J_i - 1} \quad (\text{A.19})$$

$n_i, I_i, J_i$  - constants (c. f. Appendix B)

$\pi$  - standardised pressure [-]

$$\pi = \frac{p}{p^*} \quad (\text{A.20})$$

$p^*$  - reference pressure (c. f. Appendix B)

$p$  - pressure [MPa]

#### Range of validity

- temperature:  $273.15 \text{ K} < T < 623.15 \text{ K}$

- pressure:  $p_s(T) < p < 100 \text{ MPa}$

$p_s(T)$  - vapour saturation pressure [MPa] (q. v. eq. ( A.1 ))

### A.1.6 Heat capacity

Source: /IAP97/

$$\frac{c_p}{R} = -\tau^2 \gamma_{\tau\tau} \quad (\text{A.21})$$

- $c_p$  - isobaric heat capacity [kJ/(kg K)]  
 $R$  - specific gas constant for water vapour [kJ/( kg K )] (c. f. Appendix B)  
 $\gamma_{\tau\tau}$  - ansatz function  
 $\tau$  - standardised temperature [-] (q. v. eq. ( A.18 ))

$$\gamma_{\tau\tau} = \sum_{i=1}^{34} n_i (7.1 - \pi)^{I_i} J_i (J_i - 1) (\tau - 1.222)^{(J_i - 2)} \quad (\text{A.22})$$

- $\pi$  - standardised pressure [-] (q. v. eq. ( A.20 ))  
 $n_i, I_i, J_i$  - constants for eq. ( A.19 ) (c. f. Appendix B)

#### Range of validity

- temperature:  $273.15 \text{ K} < T < 623.15 \text{ K}$
- pressure:  $p_s(T) < p < 100 \text{ MPa}$   
 $p_s(T)$  - vapour saturation pressure [MPa] (q. v. eq. ( A.1 ))

### A.1.7 Diffusion

Sources: data: /LAN69/, /DAN92/; formulation: /KRÖ08/

$$D_{H_2O}^{CO_2} = 10^{-9} + 7.8 \cdot 10^{-11} T - 4 \cdot 10^{-13} [T(100 - T)] \quad (\text{A.23})$$

- $D_{H_2O}^{CO_2}$  - Diffusion coefficient of CO<sub>2</sub> in water [m<sup>2</sup>/s]  
 $T$  - Temperature [°C]  
 $m_{H_2O}^{CO_2}$  - molality of CO<sub>2</sub> in the water-phase [mol/kg]

#### Range of validity

- temperature:  $0 \text{ °C} < T < 100 \text{ °C}$



## A.2 NaCl

### A.2.1 Enthalpy

**Source:** /DAU89/

$$h = \frac{36710 \cdot T + 62.77 \cdot T^2 / 2 - 0.06667 \cdot T^3 / 3 + 0.000028 \cdot T^4 / 4}{58440} - 204.5698 \quad (\text{A.24})$$

$h$  - enthalpy of pure NaCl [kJ/kg]

$T$  - temperature [°C]

**Range of validity** is not specified, but secondary literature gives hints:

- temperature:  $0 \text{ °C} < T < 350 \text{ °C}$
- salinity: 0 to full NaCl saturation

### A.2.2 Heat capacity

**Source:** using /DAU89/ from section "A.2.1 enthalpy"

$$c = \frac{\partial h_{NaCl}}{\partial T} = \frac{36710 + 62.77 \cdot T - 0.06667 \cdot T^2 + 0.000028 \cdot T^3}{58440} \quad (\text{A.25})$$

$c$  - heat capacity of NaCl [kJ/(kg K)]

$h_{NaCl}$  - enthalpy of pure salt [kJ/kg] (q. v. eq. ( A.24 ))

$T$  - temperature [°C]

**Range of validity** is not specified, but secondary literature gives hints:

- temperature:  $0 \text{ °C} < T < 350 \text{ °C}$
- salinity: 0 to full NaCl saturation (as in the tabulated data from /HAA76/)

### A.3 NaCl-solutions

#### A.3.1 Vapour pressure

Sources: /HAA76/, /BAT97/

$$\ln T_0 = f \ln T \quad (\text{A.26})$$

- $T$  - brine temperature [K]  
 $T_0$  - temperature of pure water (referring to brine temperature via ( A.26 )) [K]  
 $f$  - ansatz function (q. v. eq. ( A.27 ))

$$f = \frac{1}{(a + bT)} \quad (\text{A.27})$$

- $a$  - ansatz function (q. v. eq. ( A.28 ))  
 $b$  - ansatz function (q. v. eq. ( A.29 ))

$$a = 1 + a_1m + a_2m^2 + a_3m^3 \quad (\text{A.28})$$

- $m$  - molality of NaCl in the water-phase [mol/kg]  
 $a_i$  - constants (c. f. Appendix B)

$$b = 0 + b_1m + b_2m^2 + b_3m^3 + b_4m^4 + b_5m^5 \quad (\text{A.29})$$

- $b_i$  - constants (c. f. Appendix B)

The equivalent temperature for pure water at the same vapour pressure is calculated by a formulation from /HAA76/. Instead of the approach from /HAA76/ for vapour pressure of pure water /BAT97/ suggests to use the formulation from /IFC67/ which is an older version as that of /IAP97/ given above.

#### Range of validity

- temperature:  $262.15 \text{ K} < T < 623.15 \text{ K}$

### A.3.2 Density

Sources: /HAA76/, /PHI81/

$$\rho = A + Bf + Cf^2 + Df^3 \quad (\text{A.30})$$

$\rho$  - density of water with dissolved NaCl [g/cm<sup>3</sup>]

$A, B, C, D$  - constants (c. f. Appendix B)

$f$  - ansatz function (q. v. eq. ( A.31 ))

$$f = c_1 e^{a_1 m} + c_2 e^{a_2 T} + c_3 e^{a_3 p} \quad (\text{A.31})$$

$m$  - molality of NaCl in the water-phase [mol/kg]

$T$  - Temperature [°C]

$p$  - pressure [bar]

$a_i, c_i$  - constants (c. f. Appendix B)

#### Range of validity

– salinity:  $0.25 \text{ mol/kg} < m < 5 \text{ mol/kg}$

– temperature:  $10 \text{ °C} \leq T \leq 350 \text{ °C}$

– pressure:  $p_s(T) < p < 50 \text{ MPa}$

$p_s(T)$  - vapour saturation pressure [MPa] (q. v. eq. ( A.1 ))

### A.3.3 Viscosity

Source: /PHI81/

$$\frac{\eta}{\eta_w} = 1 + am + bm^2 + cm^3 + dT(1 - e^{km}) \quad (\text{A.32})$$

$\eta$  - viscosity [Pa s]

$\eta_w$  - viscosity of pure water [Pa s] (c. f. eq. ( A.9 ))

$T$  - temperature [°C]

$m$  - molality of NaCl in the water-phase [mol/kg]

$a, b, c, d, k$  - constants (c. f. Appendix B)

### Range of validity

- temperature:  $10\text{ °C} < T < 350\text{ °C}$
- pressure:  $0.1\text{ MPa} < p < 50\text{ MPa}$  (for eq. ( A.9 ))
- salinity:  $0\text{ mol/kg} < m < 5\text{ mol/kg}^4$

### A.3.4 Thermal conductivity

**Source:** /YUS75/ (cited in /PHI81/)

$$\frac{\lambda}{\lambda_w} = 1.0 - \left[ 2.3434 \cdot 10^{-3} - 7.924 \cdot 10^{-6} T + 3.924 \cdot 10^{-8} T^2 \right] S + \left[ 1.06 \cdot 10^{-5} - 2 \cdot 10^{-8} T - 1.2 \cdot 10^{-10} T^2 \right] S^2 \quad (\text{A.33})$$

- $\lambda$  - thermal conductivity of water with dissolved NaCl [J/(m K s)]
- $\lambda_w$  - thermal conductivity of pure water [J/(m K s)] (q. v. eq. ( A.14 ))
- $T$  - temperature [°C]
- $S$  - ansatz function [-] (q. v. eq. ( A.34 ))

$$S = \frac{5844.3m}{1000 + 58.443m} \quad (\text{A.34})$$

- $m$  - molality of NaCl in the water-phase [mol/kg]

### Range of validity

- temperature:  $20\text{ °C} < T < 330\text{ °C}$
- pressure:  $0\text{ mol/kg} < m < 5\text{ mol/kg}$

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<sup>4</sup> NaCl-saturated solution contains 359 g<sub>NaCl</sub>/l<sub>H<sub>2</sub>O</sub> solution at 25 °C which equals 6.1 mol<sub>NaCl</sub>/kg<sub>H<sub>2</sub>O</sub>.

### A.3.5 Enthalpy

Source: /MIC81/

$$h = X_{H_2O}^{H_2O} h_{H_2O} + X_{H_2O}^{NaCl} h_{NaCl} + m \Delta h_{H_2O}^{NaCl} \quad (A.35)$$

- $h$  - enthalpy of water with dissolved NaCl [kJ/kg]  
 $X_{H_2O}^{H_2O}$  - mass fraction of water [-] (q. v. eq. ( A.36 ))  
 $X_{H_2O}^{NaCl}$  - mass fraction of salt [-] (q. v. eq. ( A.37 ))  
 $h_{H_2O}$  - enthalpy of pure water [kJ/kg] (q. v. eq. ( A.17 ))  
 $h_{NaCl}$  - enthalpy of pure salt [kJ/kg] (q. v. eq. ( A.24 ))  
 $\Delta h_{H_2O}^{NaCl}$  - enthalpy of mixing [kJ/kg] (q. v. eq. ( A.38 ))  
 $T$  - temperature [°C]  
 $m$  - molality of NaCl in the water-phase [mol/kg]

$$X_{H_2O}^{H_2O} = \frac{1000}{1000 + 58.44m} \quad (A.36)$$

$$X_{H_2O}^{NaCl} = \frac{58.44m}{1000 + 58.44m} \quad (A.37)$$

$$\Delta h_{H_2O}^{NaCl} = \frac{4.184}{1000 + 58.44m} \sum_{i=0}^3 \sum_{j=0}^2 a_{ij} T^i m^j \quad (A.38)$$

- $a_{ij}$  - constants (c. f. Appendix B)

**Range of validity** is not specified, but secondary literature gives hints:

- temperature:  $0 \text{ °C} < T < 350 \text{ °C}$
- salinity: 0 to full NaCl saturation (as in the tabulated data from /HAA76/)

Note that the formulations for  $h_{H_2O}$  and for  $h_{NaCl}$  given /MIC81/ are replaced by the more accurate formulations from /IAP97/ and /DAU89/, respectively. Note further that for reasons discussed in /KRÖ08/ the enthalpy of mixing should not be multiplied by the molality as suggested by /MIC81/ but by the related mass fraction.

### A.3.6 Heat capacity

Source: /IAP97/, /MIC81/

$$\begin{aligned}
 c &= X_{H_2O} \frac{\partial h_1}{\partial T} + X_{NaCl} \frac{\partial h_2}{\partial T} + X_{H_2O} \frac{\partial(\Delta h_m)}{\partial T} \\
 &= X_{H_2O} c_w + X_{NaCl} c_{NaCl} + X_{H_2O} \frac{\partial(\Delta h_m)}{\partial T}
 \end{aligned}
 \tag{A.39}$$

- $c$  - heat capacity of water with dissolved NaCl [kJ/(kg K)]  
 $c_w$  - heat capacity of pure water [kJ/(kg K)] (q. v. eq. ( A.21 ))  
 $c_{NaCl}$  - heat capacity of NaCl [kJ/(kg K)] (q. v. eq. ( A.25 ))  
 $X_{H_2O}$  - mass fraction of water [-] (q. v. eq. ( A.36 ))  
 $X_{NaCl}$  - mass fraction of salt [-] (q. v. eq. ( A.37 ))  
 $h_1$  - enthalpy of pure water [kJ/kg] (q. v. eq. ( A.17 ))  
 $h_2$  - enthalpy of pure salt [kJ/kg] (q. v. eq. ( A.24 ))  
 $\Delta h$  - enthalpy of mixing [kJ/kg] (q. v. eq. ( A.38 ))  
 $T$  - temperature [°C]

$$\frac{\partial(\Delta h)}{\partial T} = \frac{4.184}{1000 + 58.44m} \sum_{i=0}^3 \sum_{j=0}^2 a_{ij} i T^{(i-1)} m^j
 \tag{A.40}$$

- $m$  - molality of NaCl in the water-phase [kg/mol]

**Range of validity** is not specified, but secondary literature gives hints:

- temperature:  $0\text{ °C} < T < 350\text{ °C}$
- salinity: 0 to full NaCl saturation (as in the tabulated data from /HAA76/)

### A.3.7 Solubility

Source: /POT77/ (cited in /CHO87/)

$$\bar{L}_{water}^{NaCl} = (26.218 + 0.0072 T + 0.000106 T^2) / 100 \quad (\text{A.41})$$

$\bar{L}_{water}^{NaCl}$  - solubility of NaCl in liquid water [kg/kg] (q. v. eq. ( A.42 ))

$T$  - temperature [°C]

Conversion to molality:

$$L_{water}^{NaCl} = \frac{\bar{L}_{water}^{NaCl}}{(1 - \bar{L}_{water}^{NaCl}) M^{NaCl}} \quad (\text{A.42})$$

$L_{water}^{NaCl}$  - solubility of NaCl in liquid water [mol/kg]

$M^{NaCl}$  - molecular weight of NaCl [kg/mol] (c. f. Appendix B)

#### Range of validity

- temperature:  $0 < T < 800$  °C claimed by /POT77/  
 $0 < T < 400$  °C recommended by /CHO87/





## B Appendix B: Constants

### B.1 Vapour pressure of pure water

eq.s ( A.1 ) to ( A.3 ):

$$p^* = 1 \text{ MPa}$$

$$T^* = 1 \text{ K}$$

$$n_1 = 0.116\ 705\ 214\ 527\ 67\ 10^4$$

$$n_2 = -0.724\ 213\ 167\ 032\ 06\ 10^6$$

$$n_3 = -0.170\ 738\ 469\ 400\ 92\ 10^2$$

$$n_4 = 0.120\ 208\ 247\ 024\ 70\ 10^5$$

$$n_5 = -0.323\ 255\ 503\ 223\ 33\ 10^7$$

$$n_6 = 0.149\ 151\ 086\ 135\ 30\ 10^2$$

$$n_7 = -0.482\ 326\ 573\ 615\ 91\ 10^4$$

$$n_8 = 0.405\ 113\ 405\ 420\ 57\ 10^6$$

$$n_9 = -0.238\ 555\ 575\ 678\ 49$$

$$n_{10} = 0.650\ 175\ 348\ 447\ 98\ 10^3$$

### B.2 Density of liquid water

eq.s ( A.4 ) to ( A.8 ):

$$p^* = 16.53 \text{ MPa}$$

$$T^* = 1386 \text{ K}$$

$$R^{H_2O} = 0.461526 \text{ kJ/( kg K )}$$

$i$	$I_i$	$J_i$	$n_i$
1	0	-2	0.146 329 712 131 67 $10^0$
2	0	-1	-0.845 481 871 691 14 $10^0$
3	0	0	-0.375 636 036 720 40 $10^1$
4	0	1	0.338 551 691 683 85 $10^1$
5	0	2	-0.957 919 633 878 72 $10^0$
6	0	3	0.157 720 385 132 28 $10^0$
7	0	4	-0.166 164 171 995 01 $10^{-1}$
8	0	5	0.812 146 299 835 68 $10^{-3}$
9	1	-9	0.283 190 801 238 04 $10^{-3}$
10	1	-7	-0.607 063 015 658 74 $10^{-3}$
11	1	-1	-0.189 900 682 184 19 $10^{-1}$
12	1	0	-0.325 297 487 705 05 $10^{-1}$
13	1	1	-0.218 417 171 754 14 $10^{-1}$
14	1	3	-0.528 383 579 699 30 $10^{-4}$
15	2	-3	-0.471 843 210 732 67 $10^{-3}$
16	2	0	-0.300 017 807 930 26 $10^{-3}$
17	2	1	0.476 613 939 069 87 $10^{-4}$
18	2	3	-0.441 418 453 308 46 $10^{-5}$
19	2	17	-0.726 949 962 975 94 $10^{-15}$

20	3	-4	-0.316 796 448 450 54 10 <sup>-4</sup>
21	3	0	-0.282 707 979 853 12 10 <sup>-5</sup>
22	3	6	-0.852 051 281 201 03 10 <sup>-9</sup>
23	4	-5	-0.224 252 819 080 00 10 <sup>-5</sup>
24	4	-2	-0.651 712228956 01 10 <sup>-6</sup>
25	4	10	-0.143 417299379 24 10 <sup>-12</sup>
26	5	-8	-0.405 169968601 17 10 <sup>-6</sup>
27	8	-11	-0.127 343017416 41 10 <sup>-8</sup>
28	8	-6	-0.174 248712306 34 10 <sup>-9</sup>
29	21	-29	-0.687 621312955 31 10 <sup>-18</sup>
30	23	-31	0.144 783078285 21 10 <sup>-19</sup>
31	29	-38	0.263 357816627 95 10 <sup>-22</sup>
32	30	-39	-0.119 476226400 71 10 <sup>-22</sup>
33	31	-40	0.182 280945814 04 10 <sup>-23</sup>
34	32	-41	-0.935 370872924 58 10 <sup>-25</sup>

### B.3 Viscosity of pure water

eq.s ( A.9 ) to ( A.13 ):

$$T^* = 647.226 \text{ K}$$

$$\rho^* = 317.763 \text{ kg/m}^3$$

$$\eta^* = 55.071 \cdot 10^{-6} \text{ Pa s}$$

$$H_0 = 1.000 \ 000$$

$$H_1 = 0.978 \ 197$$

$$H_2 = 0.579 \ 829$$

$$H_3 = -0.202 \ 354$$

<i>i</i>	<i>j</i>	$H_{ij}$
0	0	0.513 204 7
1	0	0.320 565 6
4	0	-0.778 256 7
5	0	0.188 544 7
0	1	0.215 177 8
1	1	0.731 788 3
2	1	1.241 044
3	1	1.476 783
0	2	-0.281 810 7
1	2	-1.070 786
2	2	-1.263 184
0	3	0.177 806 4
1	3	0.460 504 0
2	3	0.234 037 9
3	3	-0.492 417 9
0	4	-0.041 766 10
3	4	0.160 043 5
1	5	-0.015 783 86
3	6	-0.003 629 481

(coefficients omitted from this list are equal to zero)

#### B.4 Enthalpy of pure water

eq.s ( A.17 ) to ( A.20 ):

$R^{H_2O}$ ,  $T^*$ ,  $I_i$ ,  $J_i$ ,  $n_i$  (see density of pure water)

#### B.5 Enthalpy of water with dissolved NaCl

eq. ( A.38 ):

$i$	$j$	$a_{ij}$	
0	0	+9633.6	Correction from /GUD89/: $a_{00} = -9633.6$
0	1	-4080.0	
0	2	286.49	
1	0	166.58	
1	1	68.577	
1	2	-4.6856	
2	0	-0.90963	
2	1	-0.36524	
2	2	$0.249667 \cdot 10^{-1}$	
3	0	$0.17965 \cdot 10^{-2}$	
3	1	$0.71924 \cdot 10^{-3}$	
3	2	$-0.4900 \cdot 10^{-4}$	

#### B.6 Heat capacity of pure water

eq.s ( A.21 ), ( A.22 )

$R^{H_2O}$ ,  $T^*$ ,  $I_i$ ,  $J_i$ ,  $n_i$  (see density of pure water)

#### B.7 Vapour pressure of water with dissolved NaCl

eq.s ( A.26 ) to ( A.29 ):

$a_1 = 5.935\ 82 \cdot 10^{-6}$	$b_1 = 1.154\ 20 \cdot 10^{-6}$	$e_0 = 12.508\ 49\ 100$
$a_2 = -5.19386 \cdot 10^{-5}$	$b_2 = 1.412\ 54 \cdot 10^{-7}$	$e_1 = -4.616\ 913 \cdot 10^3$
$a_3 = 1.231\ 56 \cdot 10^{-5}$	$b_3 = -1.924\ 76 \cdot 10^{-8}$	$e_2 = 3.193\ 455 \cdot 10^{-4}$
	$b_4 = -1.707\ 17 \cdot 10^{-9}$	$e_3 = 1.196\ 500 \cdot 10^{-11}$
	$b_5 = 1.053\ 90 \cdot 10^{-10}$	$e_4 = -1.013\ 137 \cdot 10^{-2}$
		$e_5 = -5.714\ 8 \cdot 10^{-3}$
		$e_6 = 2.937\ 0 \cdot 10^5$

#### B.8 Brine density

eq.s ( A.30 ), ( A.31 ):

$A = -3.033\ 405$	$a_1 = -0.004\ 539$	$c_1 = -9.9595$
$B = 10.128\ 163$	$a_2 = -0.000\ 163\ 8$	$c_2 = 7.0845$
$C = -8.750\ 567$	$a_3 = 0.000\ 025\ 51$	$c_3 = 3.9093$
$D = 2.663107$		

( $a_1 = -0.005$  vapour saturated value)

**B.9            Viscosity of water with dissolved NaCl**

eq. ( A.32 )

$$a = 0.0816$$

$$b = 0.0122$$

$$c = 0.000\ 128$$

$$d = 0.000\ 629$$

$$k = -0.7$$

**B.10           Solubility of NaCl in liquid water**

eq.s ( A.41 ) and ( A.42 )

$$M^{NaCl} = 0.05844\ \text{kg/mol}$$

## C Appendix C: Comparison with other formulations

### C.1 Introductory remark

The state variables required for modelling thermohaline flow can depend on pressure  $p$ , temperature  $T$  and salinity which are called primary variables here. There are different ways to express the salinity in terms of salt concentrations. Required in the context of this section are

- the salt mass fraction  $c$ , defined as the mass of salt divided by the mass of solution
- the relative salt mass fraction  $c_{rel}$ , defined as the ratio of salt mass fraction to salt mass fraction of the saturated solution (brine), and
- the mass fraction of the saturated solution  $c_m$ ; here, the solution is assumed to be a mixture of brine and pure water and  $c_m$  is defined as the mass of brine divided by the mass of solution.

By separating a salt solution into three parts – the mass of salt, the mass of water required to form a saturated salt solution and the mass of the remaining pure water – it can easily be shown that  $c_{rel}$  equals  $c_m$ .

A mathematical formulation for a state variable will be called equation-of-state (EOS) further on. Such an equation of state reflects whether the influence of one primary variable – say temperature – is independent of the other primary variables – here: pressure and salinity. In case of independence separate functions for each primary variable can be formulated and combined by addition or multiplication (separation approach e. g. /FEI99/). Otherwise the primary variables cannot be separated in the formulation.

With a view to numerical simulations a separation approach is advantageous because it can save considerable computation time. In isothermal models, for example, a temperature dependent term can simply be skipped. Therefore the possibility of applying such a separation approach to fluid density and viscosity will be discussed in this section. Also a comparison with some formulations used in numerical simulators as well as special new relations will be given.

## C.2 Density

### C.2.1 Mathematical approach after /BEA87/

Setting up the total derivative of the density  $\rho(p, T, c)$

$$d\rho = \frac{\partial\rho}{\partial p} dp + \frac{\partial\rho}{\partial T} dT + \frac{\partial\rho}{\partial c} dc \quad (\text{C.1})$$

leads to expressions that are usually interpreted as the compressibility, the coefficient of thermal expansion, and the coefficient of density change due to salinity change, respectively:

$$\kappa = \frac{1}{\rho} \frac{\partial\rho}{\partial p}, \quad \alpha = -\frac{1}{\rho} \frac{\partial\rho}{\partial T}, \quad \text{and} \quad \beta = \frac{1}{\rho} \frac{\partial\rho}{\partial c} \quad (\text{C.2})$$

$\kappa$  - compressibility [1/Pa]

$\alpha$  - coefficient of thermal expansivity [1/K]

$\beta$  - coefficient of density change due to salinity change [-]

Assuming that the expressions  $\kappa$ ,  $\alpha$  and  $\beta$  are constants allows integration of the total derivative which yields the exponential relation

$$\rho = \rho_0 e^{-\alpha(T-T_0)} e^{\kappa(p-p_0)} e^{\beta(c-c_0)} \quad (\text{C.3})$$

$\rho_0$  - reference density at  $p_0$ ,  $T_0$  and  $c_0$  [kg/m<sup>3</sup>]

$p_0$  - reference pressure [Pa]

$T_0$  - reference temperature [K]

$c_0$  - reference salt mass fraction [-]

For most practical purposes even the linearised form of ( C.3 ) suffices according to /BEA87/<sup>5</sup>:

$$\rho = \rho_0 [1 + \kappa(p - p_0) + \alpha(T - T_0) + \beta(c - c_0)] \quad (\text{C.4})$$

Deriving ( C.3 ) shows clearly that constant values for  $\kappa$ ,  $\alpha$  and  $\beta$  can only be applied where they represent a good approximation of the expressions ( C.2 ). In other words it has to be made sure that constant values for  $\kappa$ ,  $\alpha$  and  $\beta$  are appropriate in the value range considered for the primary variables. A compilation of data for  $\kappa$  and  $\alpha$  for temperatures between -30 °C and 150 °C in /WEA86/ shows, however, that this is only the case within a very narrow temperature range. Formulation ( C.3 ) is exemplarily evaluated graphically in Fig. C.1 for pure water at atmospheric pressure and for two temperatures, 20 °C and 110 °C. For reference the formulation from /IAP97/ is also plotted. The data required for evaluating relation ( C.3 ) is taken from /WEA86/ and compiled in Tab. C.1. Formulation ( C.3 ) describes the temperature-dependency of water only within a range of approx.  $\pm 20$  °C around the reference temperature appropriately as shown in Fig. C.1.

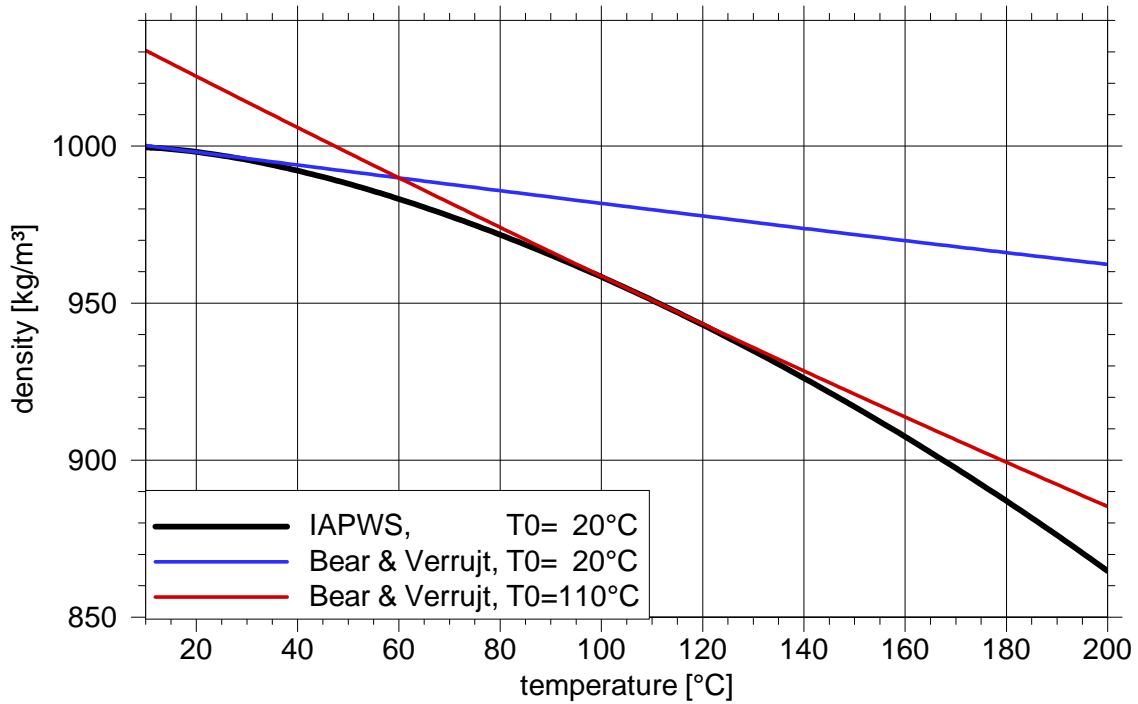
**Tab. C.1** Data used for Fig. C.1

$T_0$ [°C]	$\rho_0$ [kg/m <sup>3</sup> ]	$\alpha$ [1/K]
20	998.161	0.0002068
110	950.947	0.0008036

Note, that /OLD98/ use two measured data points for temperature and density to replace the partial derivative of density with respect to temperature  $\partial\rho/\partial T$  in ( C.2 ) with the difference quotient. This ultimately allows approximation of the thermal expansivity even in unusual temperature ranges if at least two data points are available.

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<sup>5</sup> However, the exact exponential form maybe favorable for numerical simulations of physically unstable flow conditions as for instance in the so-called Elder-problem (e. g. /KRÖ94/).



**Fig. C.1** Temperature-dependency for pure water after /BEA87/ and after /IAP97/

Formulation ( C.3 ) represents a separation approach in the sense of /FEI99/. Each of the exponential functions can therefore be replaced by other formulations some of which are given in /FEI99/. Dependence on temperature also used in /MOL02/ is described there as

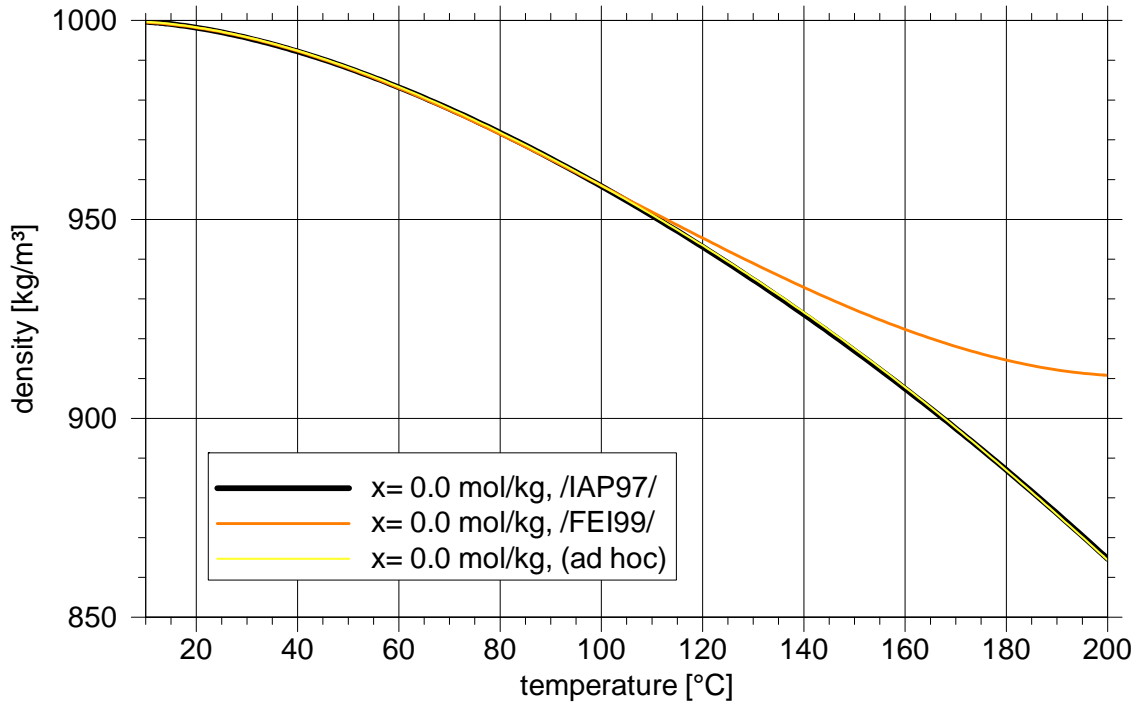
$$\rho^*(T_{\circ C}) = \frac{999.79}{998.2} \left\{ 1 + (T_{\circ C} - 4)^2 \cdot \left[ -6.562 \cdot 10^{-6} + 2.166 \cdot 10^{-8} \cdot (T_{\circ C} - 4) \right] \right\} \quad (C.5)$$

$T_{\circ C}$  - temperature [°C]

A comparison with the formulation of /IAP97/ shows that eq. ( C.5 ) is apparently fitted to data in the temperature range between 10 °C and 100 °C where the match is excellent. Beyond 100 °C, however, density according to eq. ( C.5 ) begins to deviate strongly from the formulation of /IAP97/ as shown in Fig. C.2. An ad-hoc formulation valid in the whole temperature range between 0 °C and 200 °C is also depicted in Fig. C.2:

$$\rho(T_{\circ C}) = 999.974 - \left( \frac{T_{\circ C}}{12.1} - 0.28 \right)^2 + \left( \frac{T_{\circ C}}{34} \right)^3 - \left( \frac{T_{\circ C}}{78} \right)^5 + \left( \frac{T_{\circ C}}{120} \right)^7 \quad (C.6)$$





**Fig. C.2** Temperature-dependency for pure water after /FEI99/ and after /IAP97/

The formulations for the dependence on concentration used in /FEI99/ are discussed in the next section.

### C.2.2 Alternative theoretical approach after /HER88/ and /OLD98/

An alternative theoretical approach is based on a proposal from /HER88/ that was initially derived for the salinity-dependent density only. It was based on the idea that a NaCl-solution of arbitrary salt concentration can be obtained by mixing pure water with saturated brine.

Assuming that the volumes of pure water and brine are additive the resulting solution density can easily be derived to be

$$\frac{1}{\rho} = \frac{1-c_m}{\rho_w} + \frac{c_m}{\rho_{sat}} \quad (\text{C.7})$$

$\rho$  - density of the solution [kg/m<sup>3</sup>]

$\rho_w$  - density of pure water [kg/m<sup>3</sup>]

$\rho_{sat}$  - density of salt solution at saturation concentration [kg/m<sup>3</sup>]

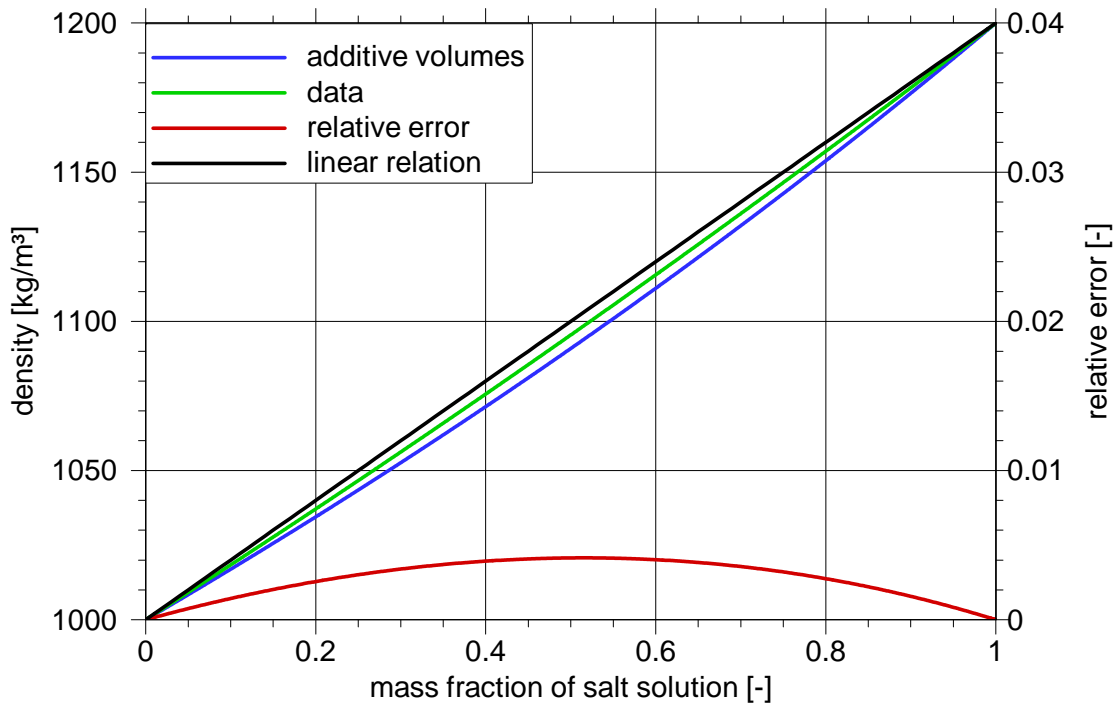
In reality pure water and brine are only approximately additive. In order to show the resulting error formulation ( C.7 ) was compared with a very good fit to experimental data for NaCl-solutions that was also given in /HER88/:

$$\rho = \rho_w \left( \frac{\rho_{sat}}{\rho_w} \right)^{c_m} \quad (C.8)$$

Formulation ( C.8 ) is valid for the whole salinity range from pure water up to saturation concentration at 20 °C and at atmospheric pressure. Note that a Taylor series expansion reveals identity of ( C.8 ) and the concentration-dependent term in ( C.3 ):

$$\rho_w \left( \frac{\rho_{sat}}{\rho_w} \right)^{c_m} = \rho_0 e^{\beta(c-c_0)} \quad \text{for } c = c_{rel}, c_0 = 0 \text{ and } \beta = \ln \left( \frac{\rho_{sat}}{\rho_0} \right) \quad (C.9)$$

Fig. C.3 proves formulation ( C.7 ) to be a reasonable approximation of ( C.8 ) with an error of less than 0.5 %. For reference also a linear relationship between the mass fraction of the salt solution and density is plotted.



**Fig. C.3** Error due to the assumption of additive volumes; after /HER88/

According to /OLD98/ the effects of pressure  $p$  and temperature  $T$  enter the formulation easily by using

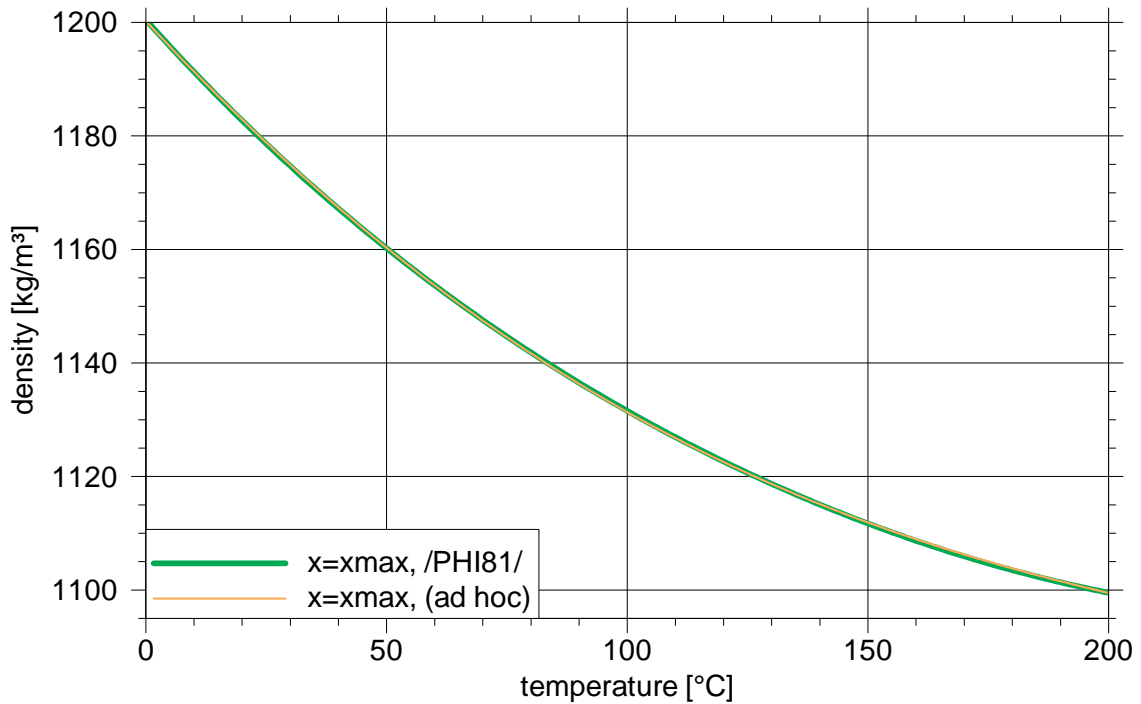
$$\frac{1}{\rho(p, T, c_m)} = \frac{1 - c_m}{\rho_w(p, T)} + \frac{c_m}{\rho_{sat}(p, T)} \quad (C.10)$$

instead of eq. ( C.7 ). The only difference between eq.s ( C.7 ) and ( C.10 ) concerns the density of pure water and the density of brine which are now functions of temperature and pressure. The effects of compressibility and thermal expansion can be incorporated by temperature- and pressure-dependent formulations for the density of pure water and of brine.

The authors apply eq. ( C.3 ) for this purpose where the coefficients for compressibility and thermal expansion may be different for brine and pure water. Only if these coefficients are chosen to be identical formulation ( C.10 ) would still fall into the category of a separation approach. Otherwise the influences of pressure, temperature and salinity cannot formally be separated.

For pure water the temperature-dependency is the same as in the approach of /BEA87/. It thus follows that the approach of /HER88/ must be used with the same care as the approach of /BEA87/ with respect to the temperature range in which the formulation is valid. To circumvent this problem, empirical relations for the density of pure water and of saturated NaCl-solution can be considered. For saturated salt solution an ad-hoc relation is provided here (see also Fig. C.4):

$$\rho_{sat 0}(T_{\circ C}) = -\left(\frac{T_{\circ C}}{111}\right)^4 + \left(\frac{T_{\circ C}}{20.8} - 9.5\right)^2 + 1110 \quad (C.11)$$



**Fig. C.4** Ad-hoc relation for the temperature dependency of saturated salt solution

For pure water refer to eq. ( C.6 ).

### C.2.3 Approaches compared

The approaches from /IAP97/ for pure water and from /PHI81/ for NaCl-solutions are considered here to represent a large variety of data from actual density measurements. They are used as a reference for evaluating the performance of the formulations discussed above. To depict the uncertainty of  $\pm 2\%$  in the formulation of /PHI81/ all plots also contain the referring error boundaries. Generally, the formulation for pure water from /IAP97/ lies within the error boundaries of the formulation from /PHI81/ that is also valid in the whole range of salt concentration (see Fig. C.5).

Compared will be

- A the mathematical approach from /BEA87/,
- B the approach from /HER88/ based on mixing pure water with saturated salt solution and extended by /OLD98/,
- C the approach from /HER88/ but extended with the ad-hoc formulations ( C.6 ) and ( C.11 ),

- D an approach suggested in /FEI99/, and
- E a modification of /FEI99/ where the formulation for temperature dependency from /MOL02/ is replaced by the ad-hoc formulation ( C.6 ).

$$A: \rho = \rho_0 e^{-\alpha(T-T_0)} e^{\beta(c-c_0)}$$

$$B: \rho = \frac{1}{\frac{1-c_m}{\rho_{w0} e^{-\alpha_w(T-T_0)}} + \frac{c_m}{\rho_{sat0} e^{-\alpha_{sat}(T-T_0)}}$$

$$C: \rho = \frac{1}{\frac{1-c_m}{\rho(T)} + \frac{c_m}{\rho_{sat0}(T)}}$$

( C.12 )

for  $\rho(T)$  see ( C.6 ) and for  $\rho_{sat0}(T)$  ( C.11 )

$$D: \rho = \rho_0 \rho^*(T) \frac{1}{(1-c) + \frac{c}{\rho_{max}/\rho_0}} \quad (\text{for } \rho^*(T) \text{ see ( C.5 )})$$

$$E: \rho = \rho(T) \frac{1}{(1-c) + \frac{c}{\rho_{max}/\rho_0}} \quad (\text{for } \rho(T) \text{ see ( C.6 )})$$

Approaches A, B and D require a reference density  $\rho_0$  at pressure  $p_0$ , temperature  $T_0$  and concentration  $c_0$ . Since temperature-dependence is comparatively poorly reproduced by A and B as shown in Fig. C.1 two different reference conditions are investigated, one at 20 °C and one at 110 °C. Reference temperature for approach D, however, is fixed at  $T_0 = 20$  °C since an empirical approach is used. The empirical relation  $\rho(T)$  in approach E contains already a reference density.

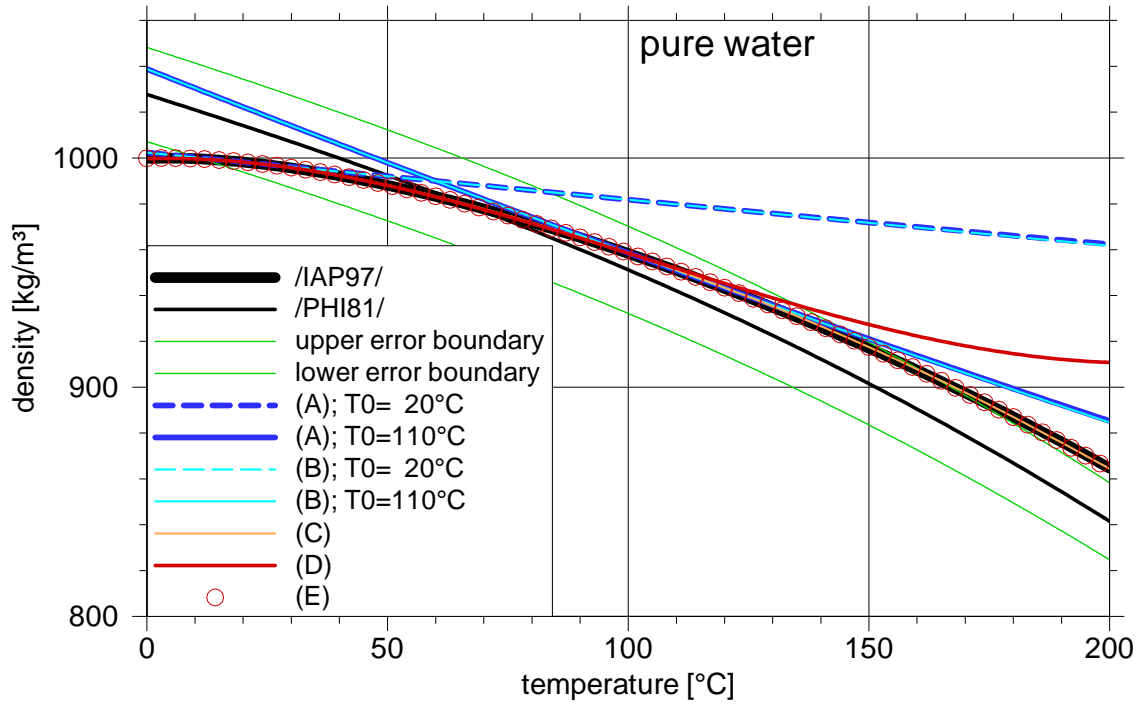
Formulations A and B include the same mathematical approach for temperature-dependence while this term is replaced in C, D and E by empirical formulations. For the lack of data concerning the coefficient of thermal expansion for brines  $\alpha$ , the same values for pure water as for saturated NaCl-solution are used in B. Also the same reference conditions are used for pure water and for saturated NaCl-solution. Since thermal expansion coefficients as well as reference conditions are generally allowed to be different

in formulation B the results presented here can just be an indication for the performance of the density model by /HER88/.

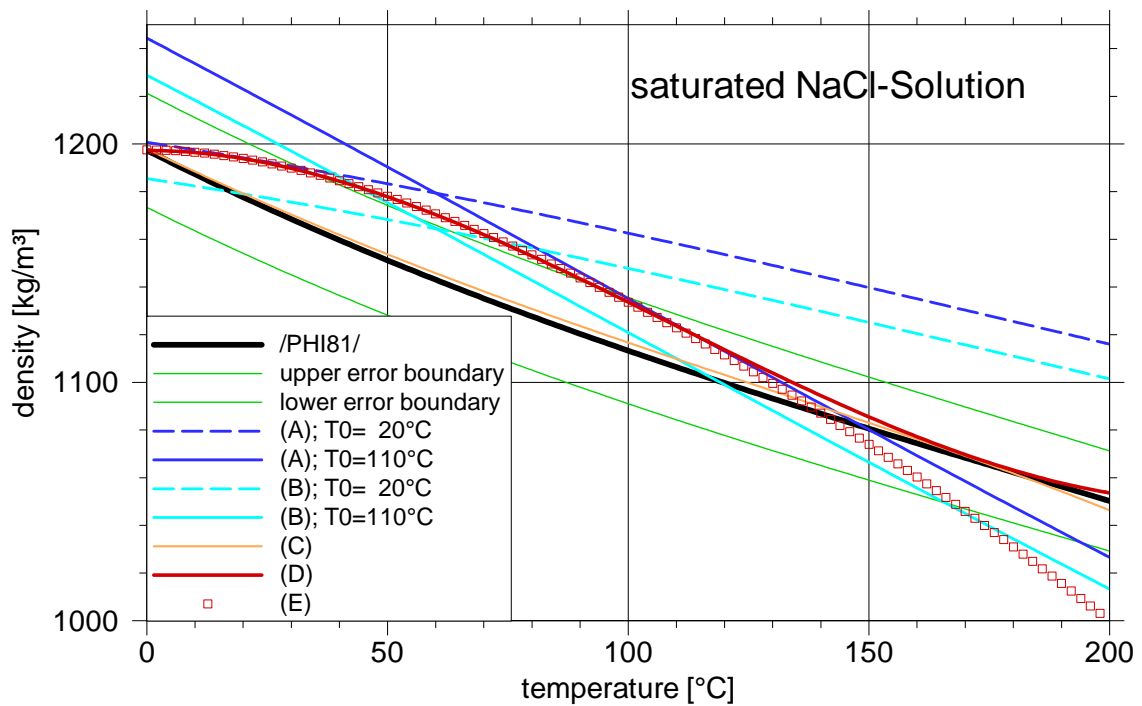
#### **C.2.4 Comparison on the basis of temperature**

Fig. C.5 and Fig. C.6 show the results of the different density models for pure water as well as for a highly saline solution. For pure water (Fig. C.5) i. e. without an additional influence from dissolved NaCl the approaches A and B produce identical results because they use the same approach for the temperature term. In case of the highly saline solution the different approaches for the concentration term lead to a vertical shift from A to B in Fig. C.6. Due to the ill-fitting slope at  $T_0 = 20\text{ °C}$  the resulting curves of approaches A and B state a good approximation only in a quite narrow temperature range in the vicinity of the reference temperature. While A actually produces a tangent to the curve from /PHI81/ B is always a little bit off. Better matching are the results for  $T_0 = 110\text{ °C}$  than for  $T_0 = 20\text{ °C}$ .

The curve from D for pure water deviates only above  $110\text{ °C}$  noticeably from the curve from /IAP97/. Including the ad-hoc formulation ( C.6 ) as in E the match must obviously be fitting well. For nearly saturated NaCl-solution the results from D look generally quite different to the model from /PHI81/. However, it violates the error margin of 2 % in the whole temperature range only to a very small extent. It appears that the error in the temperature approach above  $100\text{ °C}$  relates by chance to the different shape of the density curve at high NaCl-concentration. Approach E – the modified version of D – shows even worse results than D. Best matching is C – the approach from /HER88/ with the ad-hoc formulations ( C.6 ) and ( C.11 ) for the density of pure water and of saturated salt water.



**Fig. C.5** Performance of different density models for pure water;  $\rho = f(T)$



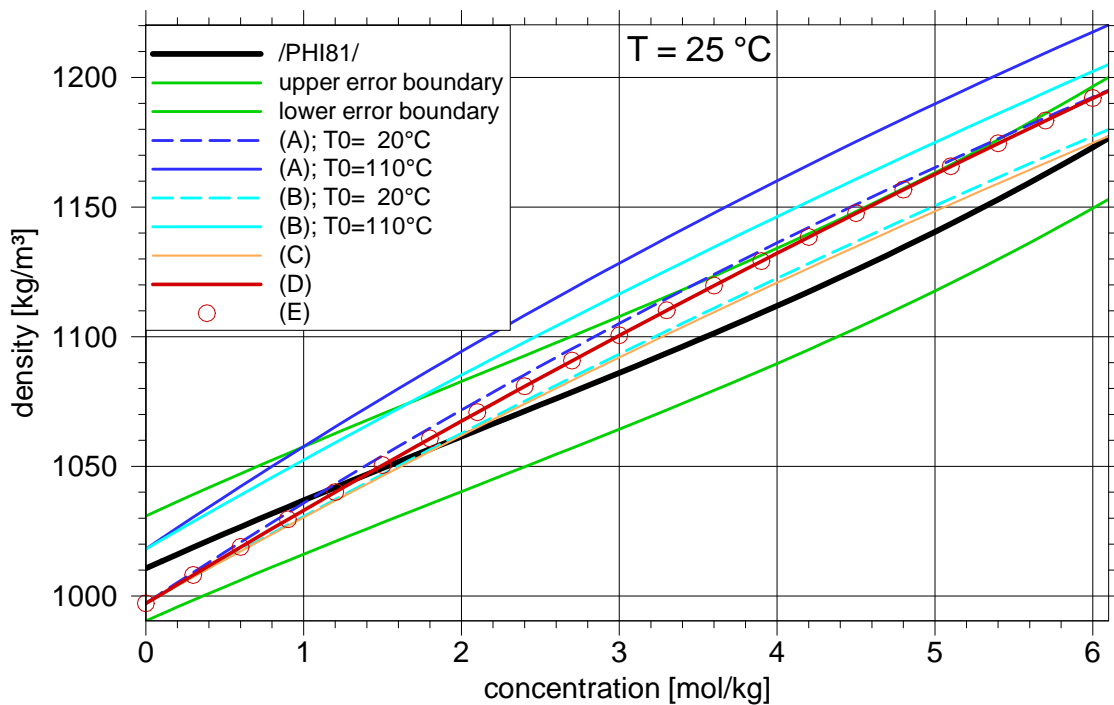
**Fig. C.6** Performance of different density models for highly saline water;  $\rho = f(T)$

### C.2.5 Comparison on the basis of salt concentration

Fig. C.7 and Fig. C.8 show the same comparison as Fig. C.5 and Fig. C.6 but density is plotted here versus relative concentration at  $T = 25\text{ °C}$  and at  $T = 200\text{ °C}$ , respectively, instead of versus temperature.

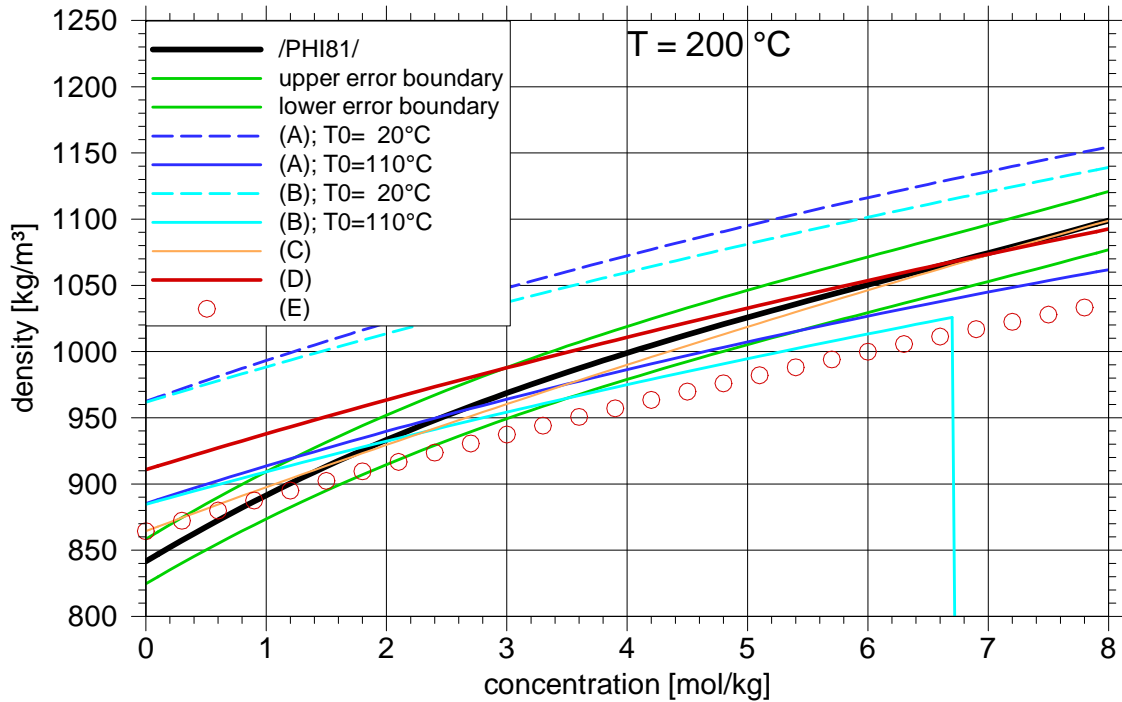
At ambient temperature and  $T_0 = 20\text{ °C}$  all models produce curves within the error boundaries from /PHI81/ even if they in general appear to be less curvilinear. But at  $200\text{ °C}$  only approach C produces rather satisfying results that are, however, a little bit too high for very low concentrations.

A better match of A and B was found at  $T_0 = 110\text{ °C}$  but it was still not a really satisfying one. Other reference conditions were also investigated in order to improve the match. But optimising the match in the density plot versus concentration means deteriorating the match in the density plot over temperature and vice versa. Thus there appears to be no optimal parameter combination for approaches A and B.



**Fig. C.7** Performance of different density models;  $\rho = f(c)$ ,  $T_0 = 20\text{ °C}$





**Fig. C.8** Performance of different density models;  $\rho = f(c)$ ,  $T_0 = 110\text{ °C}$

### C.2.6 Summary

Approaches A and B represent the reference curves reasonably well within a rather limited range of temperature and salt concentration around the reference conditions. These reference conditions should thus be chosen in such a way that the reference values for a specific model lie in the middle of the expected variable ranges. The temperature range is then restricted to approx.  $T_0 \pm 20\text{ °C}$ . Density as a function of salt concentration can be well represented for temperatures below  $50\text{ °C}$ . In case of temperatures above  $50\text{ °C}$  only a limited range covering approx.  $3\text{ mol/kg}$  appears to be matching satisfyingly.

Up to  $100\text{ °C}$  and lower salt concentrations approaches D und E match the reference curves reasonably well. Above  $100\text{ °C}$  this applies only for E.

Formulation C works fine for almost the whole temperature and salinity range. Deviations from the reference curves remain always in an acceptable order of magnitude.

### C.3 Viscosity

Laboratory data for the viscosity of pure water are excellently represented by the formulation from /IAP03/. The approach from /PHI81/ is taken here as a reference for brine viscosity.

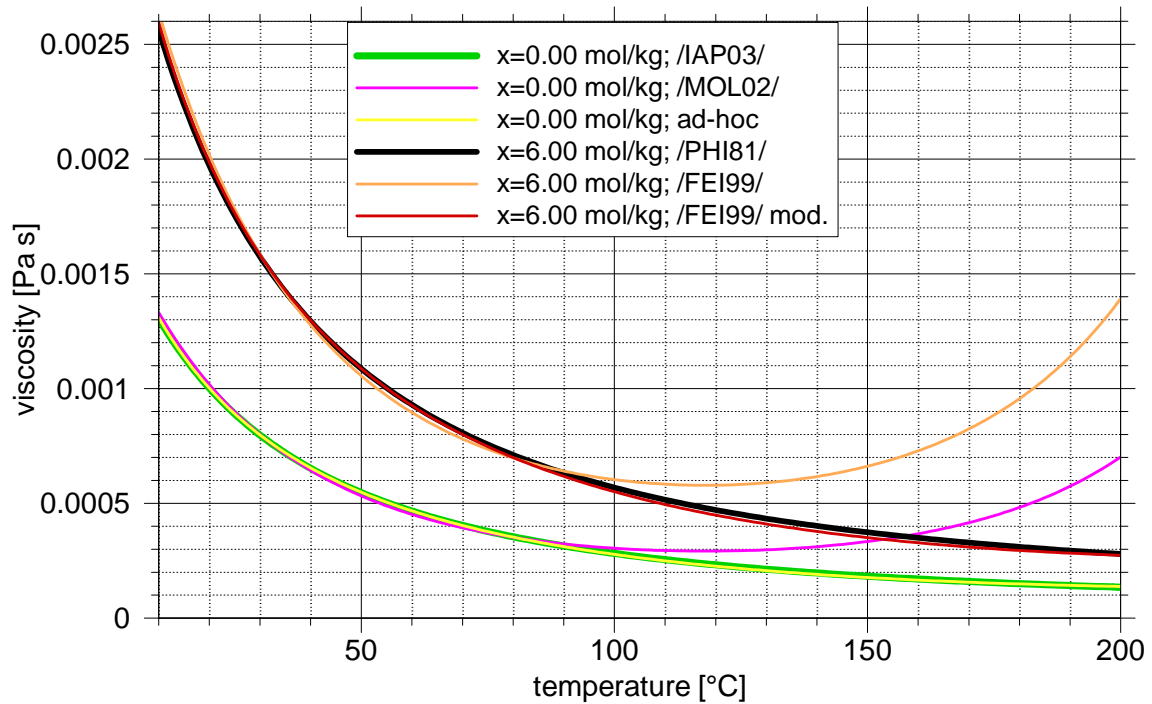
While there are several formulations for the dependence of water viscosity on either temperature or salt concentration there are few formulations considering both. Besides /PHI81/ only the separation approach of /FEI99/ was found to account for both effects. Other formulations considered only either salt concentration (/LEV85/ and /HER88/) or temperature (/MOL02/). Introduced is also an ad-hoc formulation simplifying the approach from /IAP03/ by restricting its validity to atmospheric pressure and the temperature range considered here.

$$\begin{aligned}
 \text{/MOL02/:} \quad \eta_M(T_{\circ C}) &= 1.787 \cdot 10^{-3} e^{T_{\circ C}(-3.073 \cdot 10^{-2} + 1.303 \cdot 10^{-4} T_{\circ C})} \\
 \text{(ad hoc):} \quad \eta_{ad\,hoc}(T_{\circ C}) &= \frac{3.5}{(17 T_{\circ C} + 575)^{1.18}} + 6 \cdot 10^{-5} \left( \frac{T_{\circ C}}{200} \right)^2 - 1.2 \cdot 10^{-4} \\
 \text{/LEV85/:} \quad \eta_L(c_m) &= 1.002 \cdot (1 + 1.85 c_m - 4.1 c_m^2 + 44.5 c_m^3) \quad (\text{C.13}) \\
 \text{/HER88/:} \quad \eta_H(c_m) &= 1.002 (1 + 0.4819 c_m - 0.2774 c_m^2 + 0.7814 c_m^3) \\
 \text{/FEI99/:} \quad \eta_F(c, T_{\circ C}) &= \eta_L(c_m) \cdot \eta_M(T_{\circ C}) \\
 \text{/FEI99/ mod.:} \quad \eta_F(c, T_{\circ C}) &= \eta_L(c_m) \cdot \eta_{ad\,hoc}(T_{\circ C})
 \end{aligned}$$

The performance of different viscosity models for pure water as well as for nearly saturated NaCl-solution as a function of temperature is shown in Fig. C.9. For pure water the approaches from /MOL02/ and from /FEI99/ are identical. Up to a temperature of 100 °C they match the reference curve for pure water from /IAP03/ very well. In the whole temperature range the ad-hoc approach matches the reference curve nicely.

The combined effect of temperature and salinity is also well represented up to a temperature of 100 °C by the approach from /FEI99/. The deviation above 100 °C is apparently

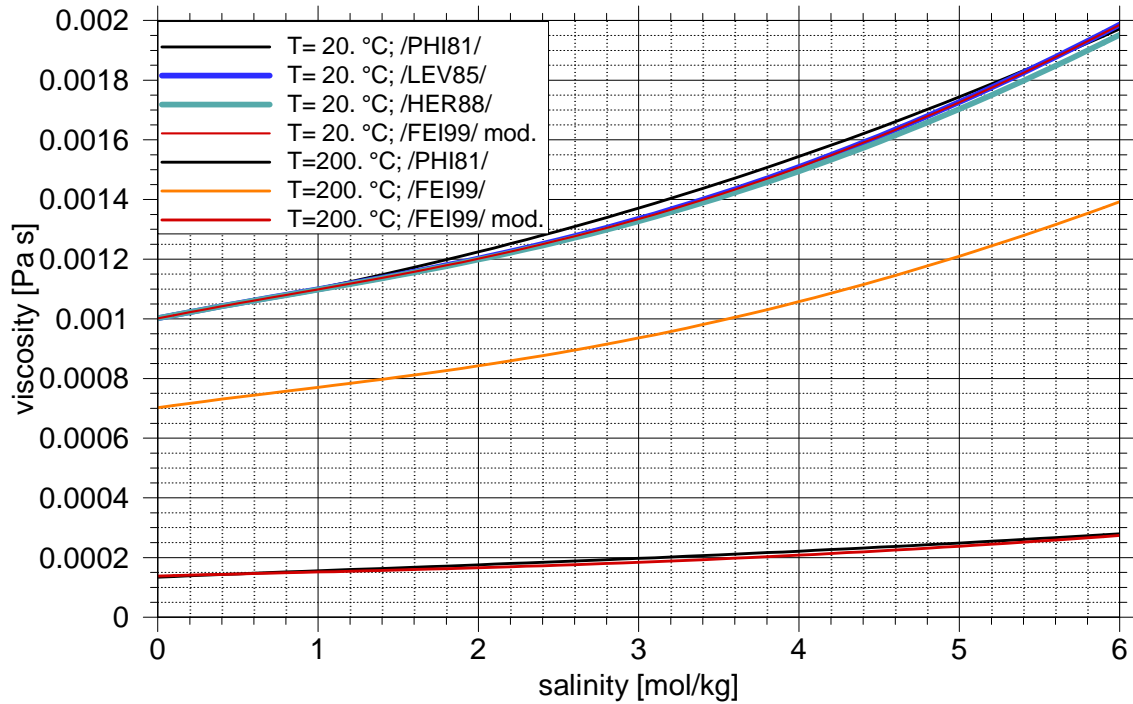
caused by the formulation from /MOL02/. If the approach from /MOL02/ is replaced by the ad-hoc formulation the separation approach from /FEI99/ produces a good match with this reference curve also.



**Fig. C.9** Performance of different viscosity models;  $\eta = f(T)$

Viscosity as a function of NaCl-concentration is shown in Fig. C.10. The formulations from /LEV85/ and /HER88/ for room temperature are matching the reference curve from /PHI81/ very well. The same applies for the approach from /FEI99/ since it is at 20 °C identical with the formulation from /LEV85/.

Because of the problems with the temperature-dependent part above 100 °C the results according to /FEI99/ are quite off the reference curve from /PHI81/ at 200 °C in terms of absolute values as well as in terms of slope. This can obviously be corrected by replacing the formulation from /MOL02/ by the ad-hoc formulation.



**Fig. C.10** Performance of different viscosity models;  $\eta = f(c)$

Viscosity for temperatures up to 100 °C is well represented by the separation approach suggested in /FEI99/ including the formulations from /MOL02/ and /LEV85/. For higher temperatures either the formulation from /PHI81/ or a modified approach according to /FEI99/ with the ad-hoc formulation instead of the formulation from /MOL02/ should be used.

Remark: /LEV85/ and /HER88/ have already pointed out that salinity variations influence the density-dependent groundwater flow not only via density but also significantly via viscosity. It should be kept in mind that salinity can change the density by a factor of 1.2 but the viscosity by a factor of 2.



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