BTA/PE/10-01

The Influence of Solutes on the Properties of Aqueous Solutions and the Impact on Gas Production

April 2010

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TA Report number : BTA/PE/10-01

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Nomenclature and Conversion tables;

Symbols

a_x	Activity of a compound x
a,b,c,d	Constants in the Debye-Hückel equation
Cl^-	Chloride ion
G	Gibbs free energy
H	Enthalpy
I	Ionic strength
K	Solubility product
m	Molality
M	Molar mass of solvent
n_x	Number of moles of component x
Na^+	Natrium ion
p	Pressure
p_i	Initial pressure
$\overline{P}$	Average reservoir pressure
PI	Productivity Index
Q	Flow rate
r	Radius
r_c	Capillary radius
r_s	Sphere radius
R	Ideal gas constant
RH	Relative Humidity
SO_4^{2-}	Sulfate ion
T	Temperature
u	Intenal energy
v_0^L	Molar volume of the liquid
x	Mole fraction of solute (liquid)
y	Mole fraction (vapour)
z	Valence of the ion
Zn^{2+}	Zinc ion

Greek symbols

α, β	Phase notation (G, L or S)
μ_x	Chemical potential of component x
γ	Activity coefficient of an ion
$\gamma_\pm$	Mean activity coefficient of an ionic solution
ϕ	Fugacity coefficient
ϕ	Osmotic coefficient
υ	Stoichiometric coefficient

Superscripts

•	Initial condition
+	Positive electrolyte
-	Negative electrolyte
0	Standard conditions
H_i	Standard state: infinite dilute solution
G	Gaseous phase (vapour)
L	Liquid phase
ref	Reference
S	Solid phase
sat	Saturated

Subscripts

A	Pure solvent
act	Actual
b	Boiling; from liquid to gas
c	Critical
Cl^-	Chloride-electrolyte
cond	Condensation; from gas to liquid
DD	Draw down
evap	Evaporation; from liquid to gas
env	Environment
eq	Equilibrium
H_2O	Water
i	Component
j	Ionic species
melt	Melting; from solid to liquid
Na^+	Natrium-electrolyte
S	Aqueous solution / mixture
sat	Saturated
trans	Transition
vap	Vaporization; (see evaporation) from liquid to gas
wf	Flowing wellbore
x	Component

SI Metric Conversion Factors

Temperature related:

From → **To ↓**	**Celsius (°C)**	**Fahrenheit (°F)**	**Kelvin (K)**
°C	$\equiv 1$	$\frac{5}{9}\cdot([F]-32)$	$[K]-273.15$
°F	$\frac{9}{5}\cdot[C]+32$	$\equiv 1$	$1.8\cdot([K]-273.15)+32$
K	$[C]+273.15$	$\frac{5}{9}\cdot([F]-32)+273.15$	$\equiv 1$

Pressure related:

From → **To ↓**	**Pascal (Pa)**	**bar (bar)**	**atmosphere (atm)**	**pound-force per square inch (psi)**
1 Pa	$\equiv 1$ N/m^2	10^{-5}	9.8692×10^{-6}	145.04×10^{-6}
1 bar	100000	$\equiv 10^6$ dyn/cm^2	0.98692	14.5037744
1 atm	101325	1.01325	$\equiv 1$ atm	14.696
1 psi	6.894×10^3	68.948×10^{-3}	68.046×10^{-3}	$\equiv 1$ lbf/in^2

Production related:

From → **To ↓**	**Normal m^3 (Nm^3)^{1,a}**	**cubic foot (cf)**	**standard cubic feet (scf)^{2,b}**
Nm^3	1	[cf] / 38.04	[scf] / 37.326
cf	$38.04\cdot$[Nm^3]	1	-
scf	$37.326\cdot$[Nm^3]	-	1

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1 Introduction

Gas production is one of the key aspects in the oil and gas industry in the Netherlands and the North Sea. Unfortunately this gas production takes along a high water cut and a rapid performance decline as recovery progresses[a]. During production, the flow rate is constantly monitored, since it is important to see whether the gas production is still profitable.
A typical gas reservoir in the North Sea basin holds an initial pressure of about 500 bar and a temperature of 145°C. Due to production, the reservoir pressure will end up at a pressure of 200 to 250 bar.
For the production of hydrocarbons a flow needs to be created. This is obtained by creating a pressure drop. Hereby the bottom-hole pressure at the production well is maintained at a lower pressure than the average reservoir pressure (Figure 1-1). Meanwhile, the pressure of the surrounding rock will also radially decrease.

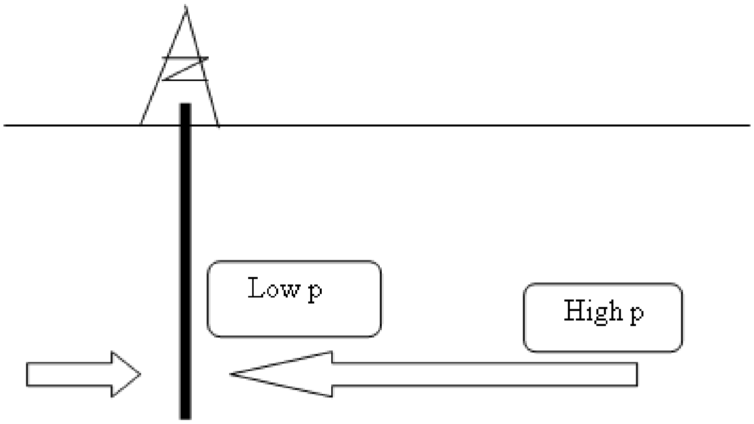

Figure 1-1 Flow direction due to pressure drop

Due to the pressure drop, gas and water will flow towards the producer. Thereby the production process (depth, velocity) is designed such that the amount of water (water cut) is as small as possible. During production, the quality of water is monitored down-hole and at surface.
Analysis of these data shows an increase in concentration of dissolved salts and minerals down hole, whereas the concentration of dissolved salts and minerals in the produced water at surface stayed more or less constant. In fact, the concentration of dissolved minerals and electrolytes in the water down hole was inclining with time combined with a decline in the gas production. In order to increase the production, fresh water treatments lasting half a day were applied. The water washes are not only time consuming, but also the complete production process must be paused. With water washes each 2-3 days (almost 170 times a year) this is an expensive solution.

As already told, many parameters are monitored at surface. Among them also the tubing head pressure and the flow rate, which can be seen in Figure 1-2.
By noting the time versus pressure, it can be concluded that from the end of March to the end of May there was a very rapid decline in the tubing head pressure and production rate. After a water wash at *the end of May*, the production rate was restored. Further water treatments at *the beginning of July and end of August* were required to maintain high flow rates. It is clear

that these treatments drove up the overall production rate. *From end of March to end of August* the production decline is limited to 100,000 Nm3/day [1], which is due to natural depletion.

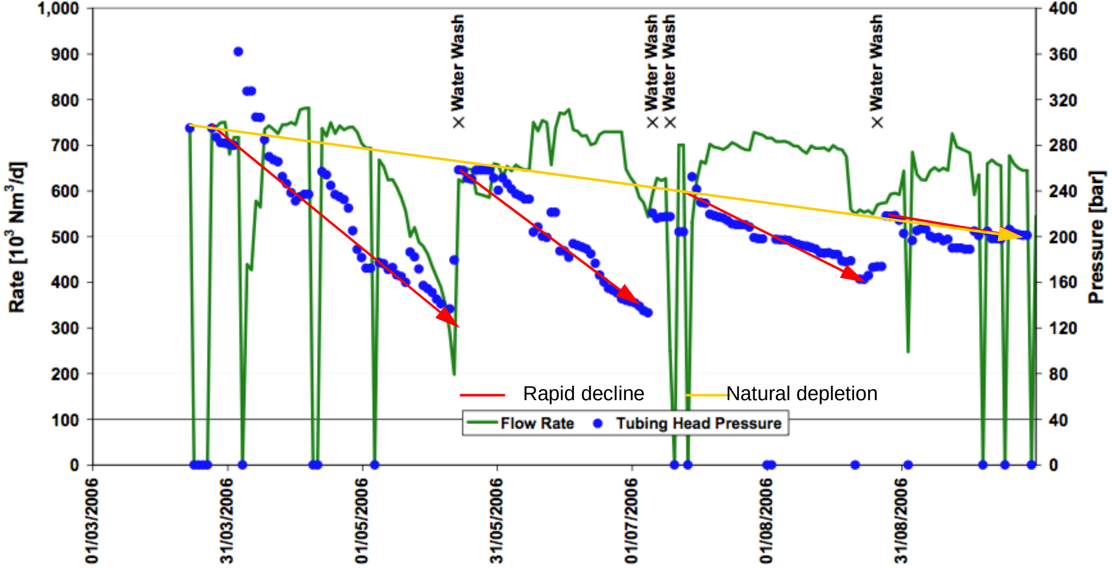

Figure 1-2 Flow rate and tubing head pressure plotted against time in a gas well which experiences salt precipitation problems. Water washes restore recovery [a]

Salt accumulation has been indicated by mechanical wire-line surveys, a video camera survey and by well performance data (Figure 1-2). Most salt was found in the upper perforations. Samples revealed that the scale consists of almost pure halite [a].

As mentioned earlier, the water washes had a great impact on the tubing head pressure and hence the production rate. Additionally the salt concentration in the produced water was also decreased. Video cameras allow us to compare the results before and after water washes (Figure 1-3 and Figure 1-4).
However, the water washes offer a solution to the problem without completely understanding the processes which are responsible for the production decline and incline of the salt concentration down hole. It is of great importance that these processes are identified and well understood for the sake of forecasting gas production and for the optimization of the recovery process design.

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[1] Nm^3/day; gas volume measured at standard pressure and temperature
1000Nm^3/day= 38040 cf/day

Figure 1-3 NaCl scale in the perforated zone of a gas well before fresh water treatment [a]

Figure 1-4 Perforated zone after fresh water treatment [a]

For the optimisation of the recovery process simulators are used which also account for the evaporation of formation/reservoir water. However, in existing simulators the influence of dissolved species and the precipitation of minerals are not yet taken into account properly. Before this behaviour can be incorporated into a simulator, a better understanding of the underlying processes is needed.

Van Dorp et al [a] performed simulations to describe the gas production, accounting for the evaporation of water to take along the increase of the salt concentration in the reservoir water. For the description of the evaporation an empirical equation as suggested by Tang and Etzion was used [b]. In this correlation the evaporation is described as a function of relative humidity and of wind (gas) velocity over a water surface. Accordingly, higher gas velocities result in higher evaporation rates [a]. However, in this correlation it is not accounted for the fact that evaporation of water is also influenced by the presence of solutes.

The aim of this bachelor thesis is to study the influence of dissolved electrolytes and pore sizes on the evaporation of water. For this reason, the first part of the theory in chapter two explains the basic behaviour of pure water, followed by the description of the influence of solutes, non-electrolytes and electrolytes, on the phase behaviour of water. The second part explains the influence of pore size on the physical-chemical properties with the help of the so-called Kelvin Equation. The proposed formulas include relative humidity, water activity and a term describing the pore structure. In chapter 3 the resulting graphs are discussed. In chapter 4 this will be summed up in which the conclusions will be given.

2 Theory

During the production of gas, not only hydrocarbon gases are produced, but also small amounts of formation water. In some cases even heavier hydrocarbons are produced, which condense as oil at surface conditions.

In order to obtain a flow, a pressure gradient is needed between the reservoir and the producer. Due to this pressure gradient, gas and formation water flow towards the production well. The biggest pressure drop is observed close to the production well. Due to this pressure drop, gas is able to expand and the desired gas drive is created. Also formation water reacts on the pressure decline e.g. by evaporating. At surface the temperature is so low that steam (water vapour) has condensed. The ratio of the volume of produced water and the volume of produced total liquids, is called water cut. During production the water cut has to be as low as possible. For the optimalization of the recovery process, there can be chosen from a number of simulators.

The productivity of a well is measured by the so-called Productivity Index [m3/d/bar] [c];

$$PI = \frac{Q}{\Delta p_{DD}} \tag{2-1}$$

in which Q is the flow rate and $\Delta p_{DD} = \overline{p} - p_{wf}$ [bar] describes the pressure drawdown.

For a good simulation of gas production, also the following processes need to be accounted for:

Firstly, due to the pressure release the gas expands in the porous medium. (Adiabatic) expansion of most gases results in cooling down of the gas. If the temperature decline is large enough, the gas might condense. For pure gases the temperature decrease due to pressure decline can be calculated using the so-called Joule-Thomson coefficient. For gas mixtures this is more complicated to calculate; the different components forming the gas mixture behave differently. Thus, the combination of composition, start temperature and pressure determines how much the temperature eventually declines due to the (adiabatic) expansion of the gas mixture and hence influences the amount of condensed gas mixture.

Secondly, reservoir water may evaporate. If it is assumed that reservoir water consists solely of water, the combination of temperature and pressure dictates how much water evaporates. However, reservoir water, also known as formation water, commonly contains dissolved species, electrolytes or non-electrolytes. Due to the presence of these solutes, the vapour pressure changes.

Another important issue is that, due to the pressure decline towards the production well, reservoir water starts evaporating while the non-volatile solutes stay in the remaining liquid phase. Hence, the concentration of these solutes increases as more water evaporates. As a consequence the (maximum) solubility of these solutes in the remaining water has been reached or even exceeded. If the concentration is higher than its solubility a solid phase forms. This is called precipitation. It is the major cause for clogging within the pores near the production well.

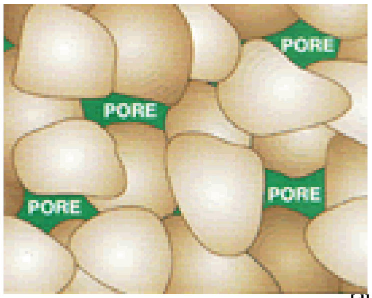

Figure 2-1 Pores between grains [d]

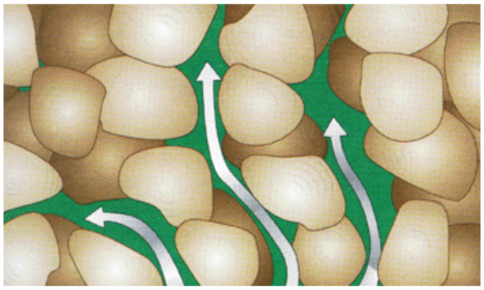

Figure 2-2 Flow occurres through connected pores (permeability) [d]

In a reservoir, grains are not always equal of size. Therefore also the pores differ in size. Due to the pores, the liquid/vapour interface is forced in a more curved shape. Due to this curved interface the pressure changes and hence the vapour pressure changes again. To understand all the processes, which can occur during gas production, the above described processes and their coupling need to be better understood.

This bachelor work focuses on the effect of solutes on evaporation of water, the impact of evaporation on the precipitation of the dissolved solutes (minerals, salts), and the effect of a porous medium on the evaporation of water and precipitation of solutes.
In order to understand these processes, we need to go back to the basics. Why do minerals precipitate? What is the effect of dissolved minerals on the evaporation of water? What is the effect of pores? Therefore we need to understand and be able to describe the influence of solutes on the properties of aqueous solutions and the impact on gas production.

2.1 Phase Behaviour

A phase diagrams shows the aggregation states of a matter at different temperatures and pressures (Figure 2-3). Within each phase, the material is uniform with respect to its chemical composition and physical state. For a pure component, the equilibrium lines mark the conditions under which two phases coexist at equilibrium. The shape of the diagram is different in details and depends on the substance (Figure 2-4). If a matter goes from liquid (L) to solid (S), it is called freezing. From solid to liquid is called melting or fusion. The line between the solid and liquid phase is called ‘Melting Curve’. The phase transition from liquid to gas (G) is called evaporation, and from gas to liquid is called condensation. The line which distinguishes these two phases is called the ‘Vapour Pressure Curve’. The ‘Sublimation Curve’ can also be crossed when sublimation or deposition is taking place. Then a solid turns into a gas or vice versa.

When the conditions are such that it is on one of the lines, two phases are in equilibrium. If the conditions are off the line entirely, there is only one stable phase of the substance.

The vapour-pressure curve ends at a temperature and pressure where gas and liquid become indistinguishable fluids due to the same density and properties. It is called the critical point (point B) and occurs at critical temperature (T_c) and critical pressure (p_c). If the temperature or pressure goes beyond T_c or p_c, it is called a supercritical fluid.

At point A, the three equilibrium lines cross and it is called the triple point. Only at this condition a solid, a liquid and a gas phase coexist.

The equations describing the equilibrium lines are derived from the fact that the chemical potentials of the two coexisting phases have to be the same.

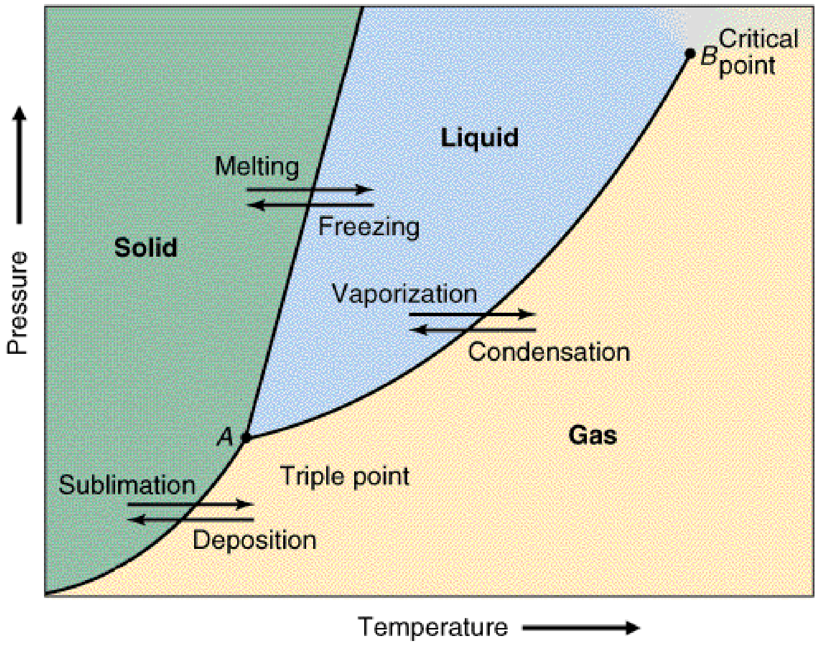

Figure 2-3 A typical phase diagram [e]

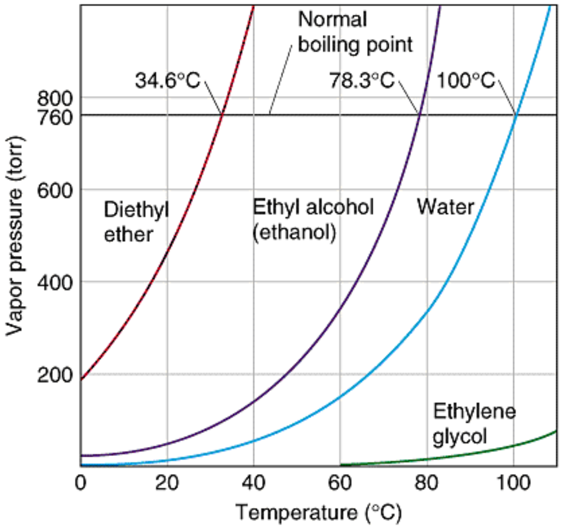

Figure 2-4 Vapour pressure (in torr [2]) of different components at different temperatures [e]

Energy

Phase transitions like melting, vaporization and sublimation consume energy which must be provided in some way. This in contrast to e.g. condensation which releases energy. The required energy is usually provided or released to the total system by heating, but can also be provided by pressure decrease. The higher the temperature, the larger the energy of the molecules. When the molecules are ordered in some kind of crystalline structure, it is called a solid (Figure 2-5). In a liquid, the molecules have more disorder and move more easily around each other. There is complete disorder or chaos, if the molecules can move freely. Then it is known as a gas. By transferring into another phase, bonds have to be broken. Therefore it will cost less energy to transfer a liquid into a gas, instead of transferring a solid into a gas (Figure 2-6).

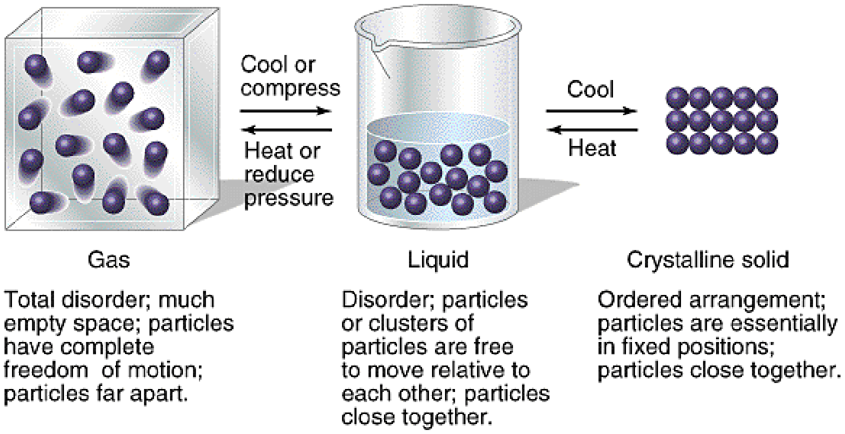

Figure 2-5 Structure of molecules within a gas, solid and liquid [e]

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[2] 1 torr = 1.32E-3 atm = 133.32 Pa = 1 mmHg, http://www.convertworld.com/en/pressure/Torr.html

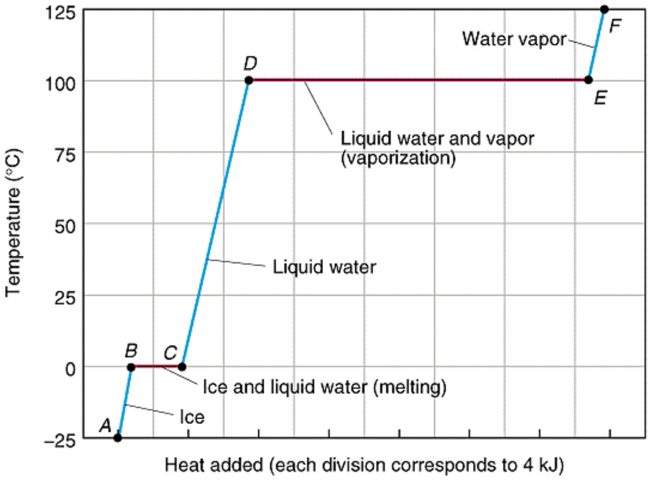

Figure 2-6 Added heat VS temperature at constant pressure. Heat required to take 1 gram of ice to vaporize to steam [e]

Thereby, it is interesting to note that liquid water can be overheated without forming vapour. This occurs when all gases (contaminants) are eliminated and water is uniformly heated, avoiding all vibrations. When the overheated water will be shaken or stirred, it will immediately violently evaporate [f].
The amount of energy needed to heat 1 gram of water for 1 Kelvin, is called the specific heat capacity. The heat released or consumed to change the aggregation state is called latent heat and is equal to the change of enthalpy or difference of enthalpy of the coexisting phases. The enthalpy of a phase increases linearly with temperature, and when dealing with a phase transition, a discontinuity occurs. All energy is then needed to break the bonds between molecules for the transition of the phase.

Chemical Potential

The chemical potential (μ_i) of a species, i, is the molar Gibbs energy (G):

$$\overline{G_i} = \frac{\partial G}{\partial n_i} = \mu_i \qquad \textbf{(2-2)}$$

A general description for the transition from an initial condition to another condition is given by;

$$\underbrace{\mu_i^{\alpha}(T,p)}_{chem.potential} = \underbrace{\mu_i^{\bullet,\alpha}(T,p^0)}_{std.potential} + \underbrace{RT\ln\left(a_i\right)}_{deviation\_from\_std.cond} \qquad \textbf{(2-3)}$$

Here a_i is the activity of the component i and is dimensionless. If the standard state is described (e.g. pure solid, liquid, or ideal gas), $\mu_i^{\bullet}$ is used and a_i is by definition one if as standard state the pure component is chosen. Else μ_i^{ref} is used and a_i is defined as $a_i = \frac{f_i}{f^0}$.

As already explained in the previous sub-chapter, the condensation-evaporation reaction can be expressed as a chemical reaction;

$$H_2O(gas) \underset{evaporation}{\overset{condensation}{\rightleftharpoons}} H_2O(liquid)$$

Liquids

For a solid or liquid phase, $f_i = x_i\gamma_i p(T)$ and $f^0 = p^0(T)$. Since $p(T) = p^0(T)$ it cancels in the denominator and thus a_i in equation 2-3 can be replaced by $x_i\gamma_i$ if the pure component standard state is used. The following equation is then obtained;

$$\mu_i^{L/S}(T,p) = \mu_i^{\bullet,L/S}(T,p^0) + RT\ln\left(x_i\gamma_i\right)^{L/S} \qquad \textbf{(2-4)}$$

where x_i is the mole fraction (x_i =1 for pure solvent i) and γ_i is a dimensionless activity coefficient of component i. Later on, in chapter 2.2.3, the activity coefficient of electrolyte solutions will be explained in more detail. Therefore a model of the Debye-Hückel theory will be used to calculate this activity coefficient (Appendix 0).

The activity part of equation 2-4, $RT\ln\left(x_i\gamma_i\right)$ can be split up by;

$$\underbrace{RT\ln x_i}_{free\_energy\_of\_mixing} + \underbrace{RT\ln\gamma_i}_{potential\_free\_energy}$$

Here the free energy of mixing is given by the $\ln x_i$ term and the activity coefficient term which accounts for non-ideality, the inter-molecular interactions [g].

Gases

For a gaseous mixture, $f_i = y_i\phi_i p(T)$ and $f^0 = p^0(T)$. The chemical potential for an ideal gaseous mixture differs from a real gas. The gaseous mixture is given at temperature T and pressure p thus:

$$\mu_i^{G}(T,p) = \mu_i^{ideal\_gas}(T,p^0) + RT\ln\left(\frac{y_i\phi_i p}{p^0}\right)^{G} \qquad \textbf{(2-5)}$$

Here, the activity a_i is replaced for an ideal gas by $\frac{y_i\phi_i p}{p^0}$. Since $p^{sat} = \frac{p}{p^0}$, the activity can also be replaced by $y_i\phi_i p^{sat}$. The mole fraction of gas is denoted by y_i and ϕ_i is the fugacity coefficient. This coefficient describes the interactions between gas molecules with respect to 'no interactions'. This is necessary because the standard state is the pure ideal gas for which it is assumed that there are no interactions.

In real life, interactions will take place and thus this correction factor is needed. All real gasses become ideal in the limit as the pressure approaches zero [h], hence the limit $\lim_{p\to 0}\phi_i(p) = 1$ can be used.

Thus;

- Standard state <u>ideal gas</u> at temperature T and pressure p^0

  $$\mu_i^{G}(T,p) = \mu_i^{ideal\_gas}(T,p^0) + RT\ln\left(\frac{y_i\phi_i p}{p^0}\right) \quad (3)$$

  ϕ_i is the fugacity coefficient which describes the interactions between gas molecules with respect to no interactions. So with a standard state of an ideal gas it is first assumed that there are no interactions, but the interactions will be assumed within the deviation. p^0 is commonly chosen to be 1 bar and can thus be ousted

- Standard state <u>pure component</u> at temperature T and pressure p

  $$\mu_i^{G}(T,p) = \mu_i^{\bullet,G}(T,p^0) + RT\ln\left(x_i\gamma_i\right)^{G} \qquad (4).$$

γ_i is the activity coefficient which describes the interactions between gas molecules with respect to uniform interactions between molecules. It is equal to one if the chosen standard state, namely the description of pure gas. x_i is now the mole fractions of component i in the gas phase.
The factor between the standard state of an ideal gas and a pure component is described by; $\frac{\phi_i p = 1}{p^0 \gamma_i}$.

In this work, it is assumed that the gas phase behaves ideally, so that the fugacity coefficient is equal to one; $\phi_i = 1$.

2.1.1 Pure Water

As is said on page 11, the shape of phase diagrams differs for different substances. The phase diagram of water looks different than the one of other components. As can be seen in Figure 2-7, the melting curve has a negative slope, whereas the curve in the phase diagram of Figure 2-3 has a positive slope. This is related to the fact of ice having a lower density than liquid water. Now, by increasing pressure a matter derives into a higher density. Ice will therefore melt instead of becoming denser in solid state.
The critical point of water exists at a temperature of 374°C and a pressure of 218 atm (647 K and 22.1 MPa) [i]. At this point, the properties of the two phases become indistinguishable because the densities of both vapour and liquid phase are then identical.
The triple point of water can be found at a temperature of 0.01°C and 0.006 atm. This means that at these conditions ice, liquid water and water vapour coexist in a stable equilibrium [i].

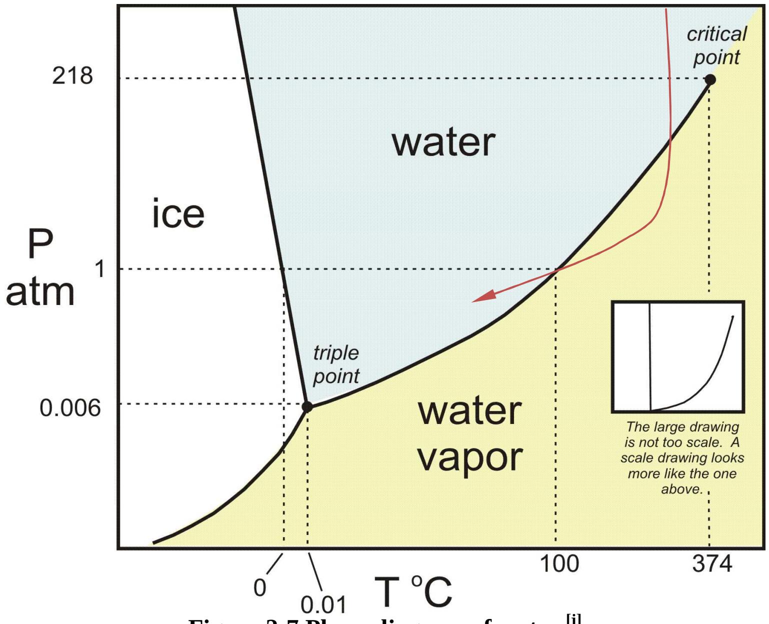

Figure 2-7 Phase diagram of water [j]

The commonly known boiling point of water is 100° Celsius (at atmospheric pressure). In general, when water starts boiling, it means that evaporation takes place usually due to heating. As can be seen in Figure 2-7, the temperature at which the liquid phase starts boiling is related to pressure. Therefore, the whole line between liquid water and water vapour can be seen as boiling points. The circumstances on earth are (usually) 1 atmosphere. Therefore 100°C is used as the reference boiling point. But when pressure decreases, e.g. in the mountains, also the vapour pressure decreases and water will then boil at a lower temperature. The same can be said for the freezing temperature. At the standard pressure of 1 atm. the freezing temperature is 0° C. But again, at other pressures the component freezes at other temperatures. The vapour pressure curve can be described by the semi-empirical Antoine Equation, and will be explained in section 2.2.1.

It can be seen that at reservoir conditions (140°C and 296 atm.), water exists as a liquid. Since there is a pressure drop required to induce a flow towards the production well, the conditions cross the vapour pressure curve (red arrow in Figure 2-7). Therefore the formation water vaporizes. At surface conditions even more pressure decrease is obtained.
Due to the sudden gas expansion, the gas temperature is cooling rapidly [3] and the conditions move along the red arrow towards the left. By crossing the vapour pressure curve, the obtained vapour condensates back to liquid.

2.1.2 Aqueous Solutions

By adding a specific amount of solute to a solvent, there is one more degree of freedom so that there is not a line displaying the vapour-liquid equilibrium but an area. The transition from the liquid phase to the liquid-vapour two phase region is called a bubble point. The transition from a vapour phase to the liquid-vapour region is the dew point. The projection of the bubble and dew point curves in a pressure-temperature diagram is shown in Figure 2-8. It can be seen that the VL equilibrium curve and the SL equilibrium curve shifted to higher and lower temperatures respectively compared to the equilibrium curves of the pure solvent. The shifting of these curves is proportional to the amount of added solute [k].

In an isobaric condition the freezing curve shifts to lower temperatures, whereas the boiling points shift to higher temperatures. The changes in these properties due to the amount of dissolved solute are the so-called colligative properties. Commonly in these situations, the quantity of the dissolved substance is small compared to the quantity of solvent.

A crucial fact is that the solute is non-volatile, and is therefore only present in the liquid phase, neither in the gaseous phase nor in the solid phase, since the solute will then precipitate in a pure form. Therefore the liquid phase gets ‘extended’ due to this addition and, at the same pressure, there will be obtained a decrease of the freezing point and an increase of the boiling point (Figure 2-8). At isothermal conditions, the addition of a solute results in decrease of the vapour pressure. The behaviour of pure water can be described by the pink lines in the p,T-diagram of Figure 2-8. When a solute is added, the melting and vapour pressure curves shift towards the blue lines.

For the study on the influence of solutes and the impact of gas production, only the elevation of the boiling point and the lowering of the vapour pressure are of interest.

Due to solute, the aqueous solution is less volatile and therefore the vapour pressure decreases. This brings along that it will take longer for formation water to evaporate.

The vapour pressure decrease can be described with help of Raoult’s law [j] for an ideal situation and otherwise by the modified Raoult’s law.

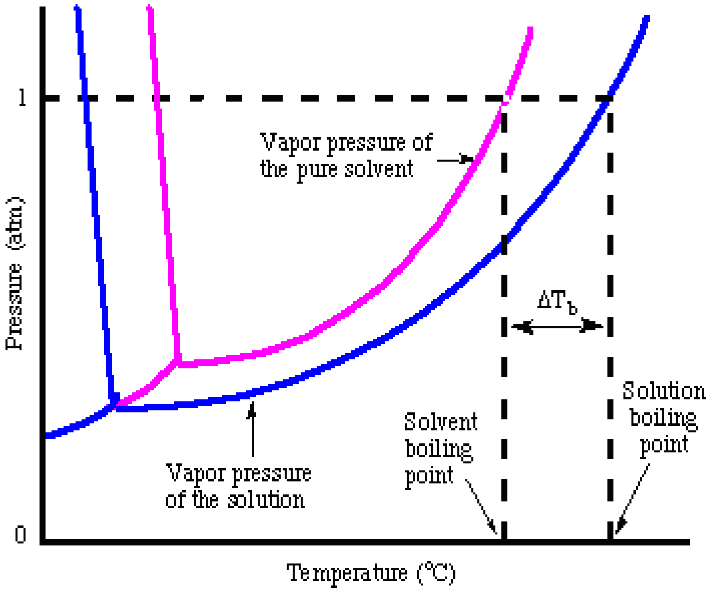

Figure 2-8 Phase diagram for a solvent and its solution with a non-volatile solute [j]

Solubility

Besides that the maximum solubility of a solute in a solvent depends on the kind of solute, it also is a function of temperature and pressure (Figure 2-9). Once the maximum saturation rate has reached, a solvent can no longer absorb solute and the solute forms a solid phase. When the solute transfers from being into solution towards the solid phase it is called precipitation. As can be seen in Figure 2-9, solubility (usually) increases with temperature. Sometimes, when the dissolving is an exothermic reaction, increase of temperature decreases the solubility. However, this is not the case within this report, and will thus not be discussed further. When the amount of dissolved solute is less than its maximum solubility, the solvent is assumed to be under-saturated (Figure 2-10). This means that the solvent can still absorb more solute. When the amount of solute in the system is above the maximum solubility, the solvent is called to be over-saturated. This can be observed, e.g., when a solute is dissolved at a higher temperature and the solution cools down. The solute will not immediately precipitate, since the threshold to become solid takes a lot of energy. But when a small amount of energy which exceeds this threshold is provided, the solute will start to precipitate until the maximum solubility and hence the equilibrium is reached.

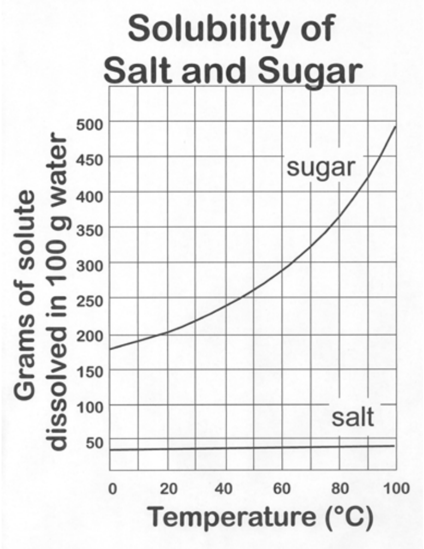

Figure 2-9 Temperature dependence of the solubility of salt and sugar in water [l]

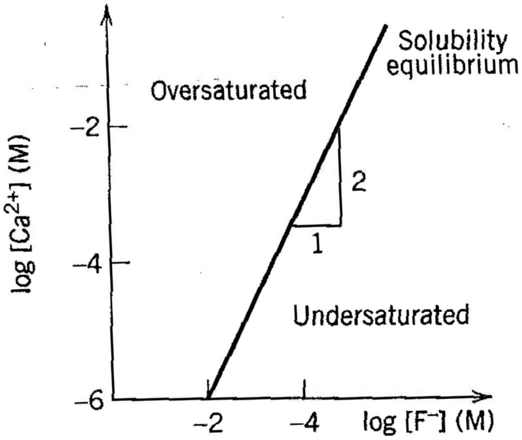

Figure 2-10 Solubility equilibrium line [m]

Now, if the hydrocarbon gas cools down (due to the adiabatic expansion [3]), also the liquid phase cools down. Consequently, the solubility decreases and the formation water becomes oversaturated. This means that from this moment on there is no equilibrium anymore and the solution is in a meta-stable state. However, the solute will not directly start to precipitate because there is not enough energy. A second cause for the oversaturation is that, once reservoir water starts evaporating due to the pressure decrease at the production well, it will leave the solute in the remaining formation water. The cause of the increase in concentration in time (as explained in the Introduction), is therefore to find within the pressure decrease, which takes along two major consequences. Once the energy-threshold is reached, the minerals will start precipitating immediately and will clog the pores along their way to the production well. This might be a possible explanation for the fact that the tubing head pressure declines at the same time.

---

[3] Joule-Thompson effect

2.1.3 Aqueous Electrolyte Solutions

In general, aqueous electrolyte solutions do not differ very much from aqueous solutions. An electrolyte is any substance containing free ions that make the substance electrically conductive [n]. The most typical electrolyte is an ionic solution. Electrolytes commonly exist as solutions of acids, bases or salts. Also substances which react with water, can produce ions, e.g. carbon dioxide gas dissolves in water to produce a solution which contains hydronium, carbonate, and hydrogen carbonate ions. Molten salts can be electrolytes as well.
An electrolyte solution is called concentrated if contains a high concentration of ions. When the solution contains a low concentration, it is called diluted.
Furthermore electrolytes can also be distinct in their rate of solubility. When a high proportion of the solute dissociates, the electrolyte is strong, but if most of the solute does not dissociate, the electrolyte is weak.

The changes in the colligative properties (as explained in chapter 2.1.2), also hold for electrolyte solutions. However, there are some differences involved, since dissolving of an electrolyte takes along the fact that it dissociates into charged ions. This has an effect on the interactions between species of different molecules since the interactions are now long-range interactions and not short-range as for uncharged species. Besides also the temperature has an effect on the solubility (Figure 2-11 and Figure 2-12).

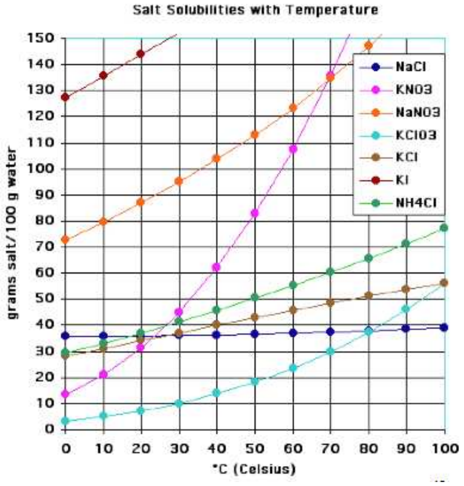

Figure 2-11 The solubilities of salts with temperature [o]

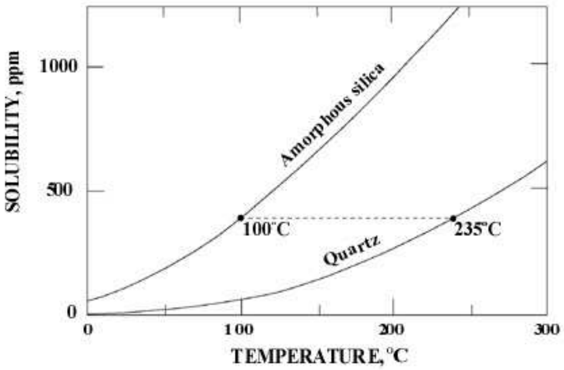

Figure 2-12 Solubility of Quartz VS Temperature [p]

Chemically pure water does not occur in nature. Natural water -and thus especially formation water, involving high pressures and temperatures- is mostly an aqueous electrolyte solutions. It contains dissolved minerals/salts, certain amounts of dissolved gases and also suspensions of the rock.

As already stated, colligative properties describe the property changes, due to the presence of solutes, based on the concentration of the dissolved component.
If minerals or salts dissolve in water, e.g. NaCl, the solution is a non-ideal solution (Figure 2-13). A solution is called non-ideal if the interactions between the molecules are not uniform.

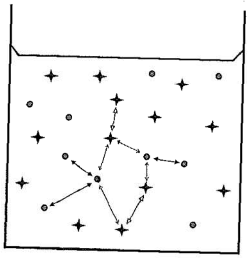

Figure 2-13 Physical model of a non-ideal solution [q]

Since ions are charged points, the behaviour of the ions depends mainly on the charge of other ions in the solution. The arrangement of the ions is therefore not randomly distributed anymore [q]; the ions can attract or repel each other.

Even in a dilute system, the Coulomb forces originating from the charges are present. This can be seen in Figure 0-1. E.g. the mean activity coefficient for the same concentration of NaCl is different than the one of $ZnCl_2$. This can be explained by the fact that 1 mole NaCl dissociates in 1 mole Na^+ and 1 mole Cl^-(1:1), whereas $ZnCl_2$ dissociates into 1 mole Zn^{2+} and 2 moles Cl^-(2:1). In total there will be 2 moles of dissolved ions when 1 mole of NaCl is dissolved versus 3 moles of ions when 1 mole of $ZnCl_2$ is dissolved. The activity coefficient for dilutions up to around 0.01m can be described by the Debye-Hückel theory, which is explained in appendix 0. A negative activity coefficient increases the solubility.

As can be seen in Figure 2-14, smaller concentrations take along a negative activity coefficient, but at one point it turns from decreasing into increasing, and the activity coefficient becomes positive. The Debye-Hückel theory does not describe this change and thus will continue decreasing with increasing ion strength.

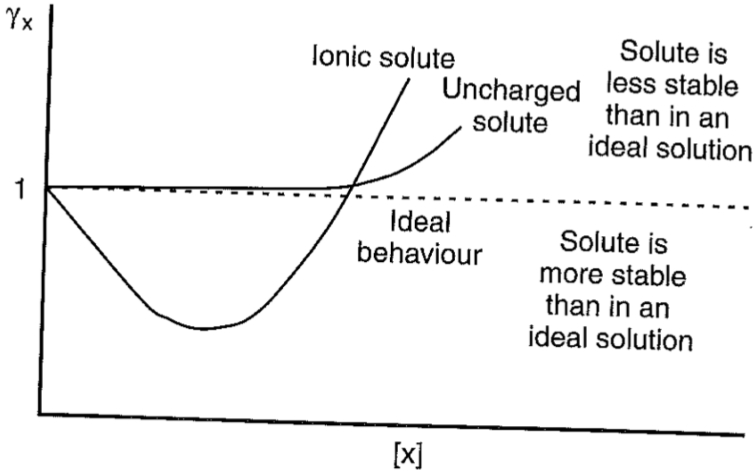

Figure 2-14 Mean activity coefficient versus solute concentration [q]

2.2 Phase Equilibrium Description

A closed system is defined as that there is no exchange of matter with the surrounding. In other words; the system ends up with the same amount of molecules as it has started. This is in contrast to an 'open system' where some material gets lost to the ambient. *Within this work, it is chosen to deal with a closed system for simplicity.*

To describe a phase equilibrium between the phases α and β, the chemical potential of a component i (μ_i) of the coexisting phases is equal:

$$\boxed{\mu_i^{\alpha}(T,p)=\mu_i^{\beta}(T,p)} \qquad \textbf{(2-6)}$$

The chemical potential of a liquid phase was already given by

$$\mu_i^{L/S}(T,p)=\mu_i^{\bullet,L/S}(T,p^0)+RT\ln\left(x_i\gamma_i\right)^{L/S} \qquad \textbf{(2-4)}$$

The chemical potential of a gaseous or vapour phase was given by

$$\mu_i^{G}(T,p)=\mu_i^{ideal\_gas}(T,p^0)+RT\ln\left(\frac{y_i\phi_i p}{p^0}\right)^{G} \qquad \textbf{(2-5)}$$

The evaporation-condensation process in solutions depends mainly on relative humidity (RH_{env}). As a matter of fact, evaporation can be distinguished into two stages (Figure 2-15). The first stage of evaporation corresponds to surface evaporation of the water and is linear versus time. This stage depends mainly on the capillary forces and the nature of the solution. The second stage of the drying process corresponds to the diffusion of water vapour inside the porous media towards the surface. It has a much slower rate of evaporation than the first stage. Water loss in the rock is not complete as critical moisture content in equilibrium with environmental conditions remains along the second part of the evaporation curve [r].
Thus, from a thermodynamic point of view the combination of the above equations predicts that when both the water activity of the solution and the vapour, are equal to RH_{env}, the gaseous water and the liquid water of the brine are in equilibrium [r].

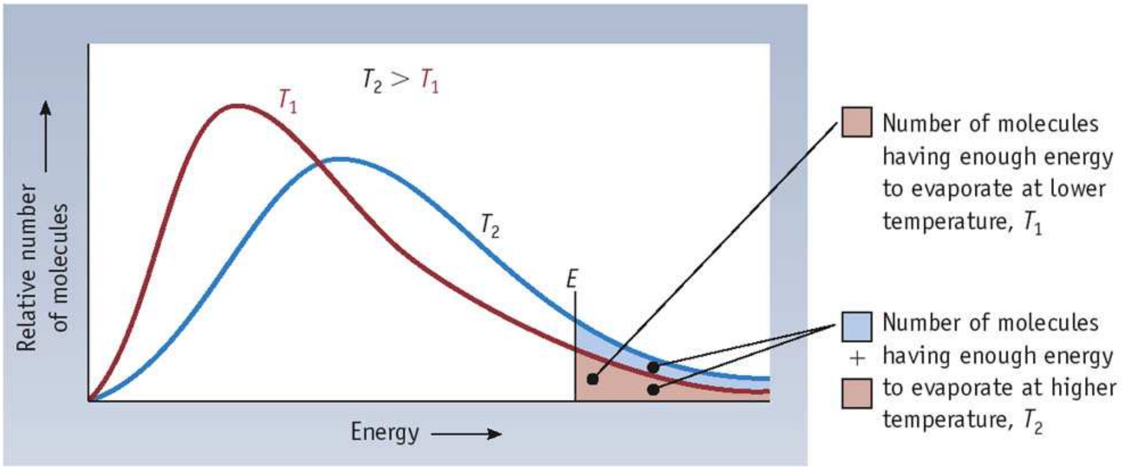

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Figure 2-15 Evaporation has two stages [e]

2.2.1 Pure Components

The starting point, or initial condition, is a pure solvent A which is at conditions of a pressure p and boiling temperature $T_{b,A}^{\bullet}$. The final state is a mixture of the solvent with a dissolved substance, S, at pressure p and a new boiling temperature of $T_{b,S}$.

The subscript b stands for boiling point, A for pure solvent and S for mixture/solution. The superscript $^{\bullet}$ stands for standard condition of the pure component, and L and G stand for the liquid and the gas phase respectively.

As stated in chapter 2.1, the vapour pressure curve represents the points of the gas liquid equilibrium (GLE). There is equilibrium when the chemical conditions of liquid and vapour phase are equal. Thus;

$$\mu_A^{\bullet,L}\left(T_{b,A}^{\bullet},p\right)=\mu_A^{\bullet,G}\left(T_{b,A}^{\bullet},p\right) \qquad \textbf{(2-7)}$$

This shows a combination of the equations 2-4 and 2-5. Since the starting points, $\mu_A^{\bullet,L}\left(T_{b,A}^{\bullet},p^0\right)$ and $\mu_A^{\bullet,G}\left(T_{b,A}^{\bullet},p^0\right)$ are the same (due to the same temperature and pressure), both sides can be divided by RT and the exponent can be taken from both sides, only the activity is left to make the difference and hence this must be equal at equilibrium. Thus;

$$x_i\gamma_i=\frac{y_i\phi_i p}{p^0} \qquad \textbf{(2-8)}$$

As can be read in the appendix ‘Vapour Pressure Decrease’, the relation between the vapour pressure curve and the temperature can be described by the so-called Antoine Equation [4]. It is a semi-empirical equation which can be derived based on the equality stated above. Using the Antoine Equation requires three component-specific constants and the temperature T at which the pressure needs to be calculated. The Antoine Equation has been used and adopted by many reasearchers. It is therefore important to use the right parameters together with the formula which is given and to respect the boundary conditions. In addition, plus or minus signs might differ by the constants and also whether to use the natural logaritm or the $\log_{10}$. It is also important to be careful with the units which the formula uses. In literature the Antoine Eqution has the following general format;

$$\log_{10}(p)=A\pm\left(\frac{B}{T\pm C}\right) \qquad \textbf{(2-9)}$$

Usually the pressure is given in mmHg, where other Antoine Equation formulas give the pressure in bar or Pascal. Temperature might be given in Kelvin, but also in degree Celsius is not uncommon.

To overcome the limits of the general Antoine Equation, a simple extension by additional terms is used. The Extended Antoine Equation has the general format of;

$$P=\exp\left(A+\left(\frac{B}{T+C}\right)+DT+ET^2+F\ln(T)\right) \qquad \textbf{(2-10)}$$

The additional parameters increase the flexibility of the equation and allow the description of the entire vapour pressure curve.

---

[4] Only valid for pure components

For the Antoine Equation which was used within this thesis, the following formula's have been used;

$$\log_{10}(p) = A - \left(\frac{B}{T + C - 273.15} \right) \tag{2-11}$$

Also the extended version by Wagner was used. It was mentioned in the book 'Properties of Gases and Liquids';

$$\ln(p) = \ln p_c + \left(\frac{T_c}{T} \right)(a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6) \tag{2-12}$$

with

$$\tau = \left(1 - \frac{T}{T_c} \right) \tag{2-13}$$

The parameters for water are given in section 3.1. Calculating the temperature from the extended formula was more complex, since temperature is also settled in the parameter 'τ'. Hence an iterative process had to be used.

2.2.2 Multi Component Systems

To understand the underlying principles of the colligative properties as explained in chapter 2.1.2, this paragraph will underpin these processes by formulas. With a mixture, two equilibria can be accounted for; the gas-liquid equilibrium and the solid-liquid equilibrium. The gas-liquid equilibrium (VLE) is described by the modified law of Raoult, which is here a combination of equations 2-4 and 2-5.

Enthalpy

In order to calculate the evaporation enthalpy, an equilibrium between the liquid and vapour (real gas) phase has to be settled. This means that equation 2-7 has to be used together with equations 2-4 and 2-5;

$$\mu_i^{\bullet,G}(T,p) + RT\ln(x_i\gamma_i)^G = \mu_i^{\bullet,L}(T,p) + RT\ln(x_i\gamma_i)^L \qquad \textbf{(2-14)}$$

The next step is to bring the standard potentials to the left and the deviations of standard potential to the right;

$$\mu_i^{\bullet,G}(T,p) - \mu_i^{\bullet,L}(T,p) = RT\ln(x_i\gamma_i)^L - RT\ln(x_i\gamma_i)^G \qquad \textbf{(2-15)}$$

Since equation 2-2 states that the chemical potential is equal to the Gibbs Free energy and the term on the right can be put together, it can be stated that;

$$\overline{G}_i^{\bullet,G}(T,p) - \overline{G}_i^{\bullet,L}(T,p) = RT\ln\frac{(x_i\gamma_i)^L}{(x_i\gamma_i)^G} \qquad \textbf{(2-16)}$$

The left hand side of the equation describes the process in which the pure component A in the liquid phase completely transforms into a gaseous phase at constant temperature and pressure; it is called vaporization (from liquid to gas). Furthermore $(x_i\gamma_i)^G \rightarrow 1$ for pure gases thus for simplicity equation 2-16 turns into:

$$\Delta\overline{G}_{i,vap}^{\bullet}(T,p) = RT\ln(x_i\gamma_i)^L \qquad \textbf{(2-17)}$$

Now, it can also be said that the enthalpy of evaporation is the same as the enthalpy of the gaseous phase (endpoint) subtracted by the enthalpy of the liquid phase (starting point). Thus:

$$\Delta\overline{H_{vap}^{\bullet}}(T,p) = \overline{H^{\bullet,G}}(T,p) - \overline{H^{\bullet,L}}(T,p) \qquad \textbf{(2-18)}$$

The Gibbs energy can also be written as a function of the enthalpy, namely:

$$\Delta\overline{G}_{i,transition}^{\bullet}(T,p) = \Delta\overline{H_{i,transition}^{\bullet}}(T,p)\cdot\left(1-\frac{T}{T_{b,i}}\right) \qquad \textbf{(2-19)}$$

Combining equations 2-17 and 2-19 gives therefore:

$$\Delta\overline{H_{i,vap}^{\bullet}}(T,p) = \frac{RT\ln(x_i\gamma_i)^L}{\left(1-\frac{T}{T_{b,i}}\right)} \qquad \textbf{(2-20)}$$

For a more detailed explanation of the effect due to solutes on the colligative properties see appendices 'Elevation of Boiling Point' and 'Vapour Pressure Decrease'.

Solubility product

The solubility product of a solute is very important within aqueous (electrolyte) solutions for the Solid-Liquid equilibrium. A solvent can only absorb a certain quantity of solute at a certain temperature (Figure 2-11). Once this amount is reached, the solute will not longer be dissolved, and stays solid. Sometimes, the solubility product decreases e.g. due to temperature decrease. Then the solute will precipitate until the maximum solubility. This will be explained in chapter 2.2.4.

2.2.3 Aqueous Electrolyte Solutions

Also electrolytes have a maximum solubility. Hereby the charge of the ions has a certain impact.

The difference between the dissolution of a salt and for example sugar is that electrolytes dissociate. When a salt dissolves, it separates into its naturally-occurring elements; NaCl for example separates into Na^+ and Cl^-.

Positively-charged ions are called cations whereas negatively-charged ions are called anions. Ions attract the opposite charged ions and reject the ions of the same charge.

By dissolving 1 mol of a salt, there are acquired at least 2 or more moles of ions in solution; e.g.1 mole of the table salt Natrium-Chloride (NaCl) transforms into 1 mole of Na^+ and 1 mole of Cl^-.

Salts are electroneutral, meaning in their solid state, they do not carry a charge, thus it is equal in electro-negativity by

$$\upsilon_+ z_+ + \upsilon_- z_- = 0 \qquad \textbf{(2-21)}$$

Here, υ is the stoichiometric coefficient which determines how often a certain ion occurs in a specific electrolyte. z is the charge / valence of the ion. Thus, the valence of the different ions determines the chemical formula of a salt.

The dissolution of an electrolyte in water can be described by a chemical reaction, the dissociation. For a salt AB one gets;

$$AB(s) \rightarrow AB(aq) \rightarrow \upsilon_+ A^{z+}(aq) + \upsilon_- B^{z-}(aq) \qquad \textbf{(2-22)}$$

The chemical potential of an electrolyte can be split up in the contributions of the cation and the anion by;

$$\mu = \upsilon_+ \mu_+ + \upsilon_- \mu_- \qquad \textbf{(2-23)}$$

The chemical potentials of each charge can be written generally as (see also equation 2-3);

$$\mu_+ = \mu_+^\bullet + RT\ln\left(a_+\right) \quad \textbf{and} \quad \mu_- = \mu_-^\bullet + RT\ln\left(a_-\right) \qquad \textbf{(2-24)}$$

The activity of each species depends on the activity coefficient γ and the molality, m, of the species [mol/L] [5]. The charge of an ion determines the activity an ion with respect to the undissociated electrolyte:

$$a_{A^+} = \frac{m_{A^+}\gamma_{A^+}}{m^\bullet} \quad \textbf{and} \quad a_{B^-} = \frac{m_{B^-}\gamma_{B^-}}{m^\bullet} \qquad \textbf{(2-25)}$$

m is the molality of the species and can be calculated by;

$$m_{A^+} = \upsilon_+ m_{AB} \quad \textbf{and} \quad m_{B^-} = \upsilon_- m_{AB} \qquad \textbf{(2-26)}$$

---

[5] The superscript • here represents the chosen standard state, which can be left unspecified at this point but is usually taken to be the solute or Henry's law standard state [s]

The solubility product K (equal to the dissociation constant) of salt AB is defined as;

$$K = \frac{\left(a_{A^+}\right)^{\upsilon_+}\left(a_{B^-}\right)^{\upsilon_-}}{a_{AB}} \qquad \textbf{(2-27)}$$

The activity of the solid electrolyte AB is equal to one because the pure component standard state is used. Therefore the solid phase solely consists of electrolyte AB, thus

$$a_{AB} = 1 \qquad \textbf{(2-28)}$$

Combining this with equation 2-27 gives the solubility product

$$K = \left(a_{A^+}\right)^{\upsilon_+}\left(a_{B^-}\right)^{\upsilon_-} \qquad \textbf{(2-29)}$$

As already stated, the solubility product, K, is not zero, but has a certain value. This is a property of the solute and is related to the temperature.

To compute the mole fraction of the solute, again the cations and anions must be split up;

$$x_+ = \frac{n_+}{n_+ + n_- + n_{H_2O}} \quad \textbf{and} \quad x_- = \frac{n_-}{n_+ + n_- + n_{H_2O}} \qquad \textbf{(2-30)}$$

The fraction of the pure solvent can be calculated by;

$$x_{H_2O} = 1 - x_+ - x_- \qquad \textbf{(2-31)}$$

For a strong electrolyte that dissociates into υ_+ cations and υ_- anions, the molality can be calculated like equation 16, but now multiplied by the stochiometric coefficient by [s]:

$$x_+ = \frac{\upsilon_+ m_S}{\frac{1000}{M_A} + \upsilon m_S} \approx \frac{\upsilon_+ m_S M_A}{1000 g \cdot kg^{-1}} \quad \textbf{and} \quad x_- \approx \frac{\upsilon_- m_S M_A}{1000 g \cdot kg^{-1}} \qquad \textbf{(2-32)}$$

During experiments only $a_\pm$ can be determined. Therefore the mean activity for a 1-1 electrolyte is defined by $a_\pm = \sqrt{\left(a_- a_+\right)}$ and so a_+ and a_- can acquired.

If γ=1, it is assumed that the solution behaves ideal and the activity is solely described by the composition of the mixtures. Another important aspect is that the activity coefficient is concentration dependent, as can be seen in Figure 2-14.

When a solute is present at a very low concentration, the ions have a negligible effect on the properties of the average water molecule and the solution can be considered as ideal.
But, even with low salt concentrations, the interactions between the ions are strong. Due to the strong interactions, the enthalpy and entropy still change when a small amount of salt is dissolved [q]. This is because at low concentrations a negative activity coefficient is obtained. A negative activity contributes to a higher solubility, so more solute can be dissolved.

The mean activity of the electrolytes can be calculated using different models such as Debye-Hückel, B-dot and Pitzer [r]. The Debye-Hückel theory provides a quantitative model for calculating the solute-solute electrostatic interactions in an aqueous electrolyte solution.

Via the mean activity, the water activity, a_w, can be calculated. This is an important factor, to compare with the relative humidity, RH_{env}, which is a factor of the water vapour of the air and the liquid water of the brine; $RH_{env} = \frac{p_w^{sat,air}}{p_w^{L,brine}}$.
Evaporation takes place when the water activity is greater then the environmental relative humidity ($a_w > RH_{env}$) but when $a_w < RH_{env}$, condensation occurs. Fore a more detailed explanation about the Debye-Hückel theory, see appendix 0.

The effect of the activity coefficient is documented by a Matlab code which is attached in the annex 'Activity_Coefficient_Iteration.m'. It started with a $\gamma_\pm = 1$*, after which it calculated S. Than it iterates untill the minimum error has reached.*

2.2.4 Precipitation Equilibrium of Aqueous Solutions

The solubility product is related to the temperature of the solvent. The higher the temperature, the more solvent can be dissolved due to a higher solubility product (see Figure 2-9 and Figure 2-11). The solubility product is dependent on the activity. An ‘active’ form of the compound is a very fine crystalline precipitate with a disordered lattice. It is generally formed incipiently from strongly over-saturated solutions. Such an active precipitate may persist in metastable equilibrium with the solution and may convert only slowly into a more stable ‘inactive’ form. Measurements of the solubility of active forms give solubility products that are higher than those of the inactive forms. Inactive solid phases with ordered crystals are also formed from solutions that are only slightly oversaturated. Precipitates are frequently formed from strongly oversaturated solutions. The conditions of precipitation of the incipient active compound are often of primary interest. Most solubility products measured refer to the most active component. The solubility products for active solid compounds are, because of their time dependence, not equilibrium constants. They are of operational value to estimate the conditions under which precipitation occurs [m].

In order to test whether a solution is over- or under-saturated, the free energy of dissolution of the solid phase has to be inquired, whether it is positive, negative or zero.
For a salt AB the K_{s0};

$$AB(s) = A^{+}(aq) + B^{-}(aq) \qquad \textbf{(2-33)}$$

The Gibbs energy for a salt in equilibrium is defined as;

$$\Delta G = 0 = \Delta G^{0}{}_{eq} + RT\ln\left(K_{s0,eq}\right) \qquad \textbf{(2-34)}$$

Thus;

$$\Delta G^{0}{}_{eq} = -RT\ln\left(K_{s0,eq}\right) \qquad \textbf{(2-35)}$$

Combining the both equations gives;

$$\Delta G = -RT\ln\left(K_{s0,eq}\right) + RT\ln\left(K_{s0,act}\right) \qquad \textbf{(2-36)}$$

with

$$K_{s0,act} = \Pi(a_i^{\upsilon_i}) \qquad \textbf{(2-37)}$$

Within a solution with an oversaturated concentration $\Delta G \neq 0 = \Delta G^{0}{}_{eq} + RT\ln\left(\Pi(a_i^{\upsilon_i})\right)_{act}$.
Combining this wit equations 2-35 and equation 2-37, it can also be written as;

$$\Delta G = RT\ln\left(\frac{\Pi(a_i^{\upsilon_i})}{K_{s0,eq}}\right) \qquad \textbf{(2-38)}$$

With $a_i^{\upsilon_i}$ calculated as explained in equation 2-25.
Hence, the free energy of dissolution is given by;

$$\Delta G = RT\ln\frac{Q}{K_{s0}} \qquad \textbf{(2-39)}$$

Here $Q = \left(\Pi a_i^{\upsilon_i}\right)_{act}$ and $K_{s0} = \left(\Pi a_i^{\upsilon_i}\right)_{eq}$.
Applying this to the salt AB we get

$$\Delta G = RT\ln\frac{\left\{A^{+}\right\}_{act}\left\{B^{-}\right\}_{act}}{\left\{A^{+}\right\}_{eq}\left\{B^{-}\right\}_{eq}} = RT\ln\frac{IAP}{K_{s0}} \qquad \textbf{(2-40)}$$

A^+ and B^- are given either in concentration or in molality. IAP stands for the actual Ion Activity Product.

Since $\{A^+\}_{eq}\{B^-\}_{eq}$ are in equilibrium state, they are equal to one, and can be ousted. Hence;

$$\Delta G = RT\ln\{A^+\}_{act}\{B^-\}_{act} = RT\ln\frac{IAP}{K_{s0}} \qquad \textbf{(2-41)}$$

The state of saturation of a solution with respect to a solid is defined as follows:

$$\begin{aligned} &IAP > K_{s0}(oversaturated) \\ &IAP = K_{s0}(equilibrium, saturated) \\ &IAP < K_{s0}(undersaturated) \end{aligned} \qquad \textbf{(2-42)}$$

By comparing the internal energy, Q, with K, the state of saturation for all reactions that involve a solid phase can be defined. When a saturation is oversaturated, the salt AB will precipitate.

As already explained in chapter 2.1.1, the expansion of the gas takes along a cooling down of the temperature of the gas and hence the liquid cooling down as well. Therefore the liquid becomes oversaturated and salts may precipitate. This can cause clogging within the well or at surface.

2.3 The Effect of a Porous Medium

It is known that the phase behaviour of a system in a bulk phase is different than if present in porous media. This is due to the fact, that the interface between the two coexisting phases is more bent in porous media then in the bulk phase. It has influence on the surface tension due to the changed inertial forces. E.g. reservoir water is captured in small pores of the reservoir matrix. As a consequence the water is present as small droplets with a strongly curved meniscus. The smaller the pores, the greater the curving of the interface. As it is known from the Young-Laplace equation [t], $\Delta p = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$,the pressure at different sides of a curved interface is different.

W. Thomson, later Lord Kelvin, developed an equation which implied that the vapour pressure of a component or solution over a curved interface differs from that over a plane interface.

2.3.1 Pure water

The influence of pore size on the evaporation-condensation process is described by the so-called Kelvin equation as follows [u];

$$\ln\left(\frac{p(r)}{p_0}\right) = -\frac{2\sigma v_L^0}{rRT}\cos\varphi \qquad \textbf{(2-43)}$$

where $p(r)$ is the equilibrium partial pressure of water vapour at the temperature T (K) with a curved interface with radius r. p_0 is the vapour pressure of water with a flat interface, σ is the surface tension, v_L^0 is the liquid molar volume of water, φ is the contact angle between the interface and the solid (pore), r is the radius describing the curvature of the radius interface, R is the gas constant. If p_0 is smaller than $p(r)$ it means that in porous medium the pressure within an isothermal condition, at which water starts boiling is higher. From the equation Young-Laplace it can be concluded that with decreasing radius, the vapour pressure, $p(r)$, increases and water evaporates.
This Kelvin formula has been derived for water and cannot be used for other components.

The relative humidity (RH given in fractions) gives the ratio of the partial pressure of water, $p(r)$, over the vapour pressure, p_0, at the same temperature. Including this in equation 2-43 results in [u];

$$RH = \exp\left(\frac{-2\sigma v_L^0 \cos\varphi}{rRT}\right) \qquad \textbf{(2-44)}$$

The evaporation process within different kinds of geometries is described in appendix 0

2.3.2 Aqueous solutions

When the formation water contains soluble salts, the Kelvin Equation can be rewritten adding a term accounting for the presence of dissolved ions, which depend on the kind of salts and its concentration [6];

$$\ln\left(\frac{p_0(r)}{p_0}\right)=-\frac{2\sigma v_L^0}{rRT}\cos\varphi-\upsilon\phi\frac{m_S M_A}{m_A M_S} \qquad \textbf{(2-45)}$$

Here υ is the number of ions into which a salt molecule dissociates if dissolved in water, ϕ is the osmotic coefficient approaching 1 for sufficiently dilute solutions, m is the mass of pure water or salt and M is the molecular weight of either water or salt.

A simple view of a porous rock can be described as a bundle of pore throats and chambers. The pore chamber is placed between the pore throats (Figure 2-16). By definition, the pore throat is smaller than the pore chamber. Thus, it is reasonable to expect the evaporation-condensation process to be limited mainly by the pore throats. Hence, the pore chamber does not regulate the flow properties. However, it does influence the porosity significantly and thus the capacity of the rock.

The evaporation process can now be distinguished into two sub-processes (Figure 2-15). The first stage of evaporation corresponds to surface evaporation of the water and is linear versus time. This stage depends mainly on the capillary forces and the nature of the solution. The second stage is the drying process during which water vapor diffuses from the porous media towards the surface. The rate of evaporation in the second stage is much slower than for the first stage. Not all water is evaporated along the second part. This is called the residual water content and stays as a film along the grains [r].

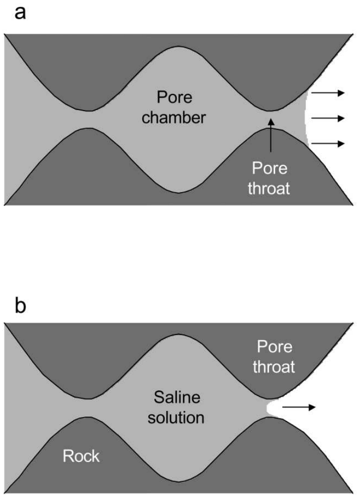

Figure 2-16 Evaporation process in a pore chamber (a); and in the pore throat (b), of which the porous structure is described as a combination of pore throats and chambers [u]

---

[6] Also Köhler(1921,1926), Wright(1936), Mason(1957), Byers(1965) and Low(1969) made similar expressions

Gibbs-free energy difference

The Gibbs free energy describing the evaporation at a given temperature and pressure, $\Delta G_{l\to v}$, can be defined by the water activity, a_w, the equilibrium partial pressure of the water vapour at the temperature T (K), the pressure $p(r)$ and the vapour pressure, p_0, of the bulk phase (flat interface) as follows;

$$\Delta G_{l\to v} = RT \ln \frac{a_w}{p/p_0} = RT \ln \frac{a_w}{RH_{env}} \tag{2-46}$$

where R is the gas constant per mole, T is the temperature (K) and RH_{env} is the environmental relative humidity, which is defined as; $RH_{env} = \frac{p_w^{air}}{p_w^{sat,water}}$

However, in a pore, the saturated vapour pressure in the water meniscus depends on the surface. Thus, given that an interface is present, it is necessary to *add* an energetic term using the Kelvin Equation (equation 2-43). Adding equation 2-43 to equation 2-46, the Gibbs free energy change in a pore, $\Delta G_{l\to v}(r)$, can be written as;

$$\Delta G_{l\to v}(r) = RT\left(\ln \frac{a_w}{RH_{env}}\right) + \frac{2\sigma v_l^0}{r}\cos\varphi \tag{2-47}$$

The second term on the right-hand side of equation 2-48 is accounting for the presence of a meniscus (interface gas-liquid). For a saline solution with $r = \infty$, the equation reduces to

$$\lim_{r\to\infty} \Delta G_{l\to v}(r) = RT \ln a_w = \Delta G_{l\to v} \tag{2-48}$$

Wetting plays an important role in the evaporation process. In a water-wet rock, the evaporation process is thermodynamically restrained, whereas an oil-wet rock, evaporation is easier.

Dealing with a water-wet rock, $\varphi = 0°$ equation 2-48 can be therefore written as;

$$\Delta G_{l\to v}(r) = RT\left(\ln \frac{a_w}{RH_{env}}\right) + \frac{2\sigma v_l^0}{r} \tag{2-49}$$

This evaporation model is defined for a cylindrical pore. In order to apply this model to a porous rock it is necessary to link the cylindrical pore to the porous media of rock. The connection can be made using the mean pore throat radius, r.

The system is at equilibrium when $\Delta G_{l\to v}(r)$ is equal to 0. From equation 2-50 a critical value of the relative humidity, RH(r), can be obtained as follows;

$$RH_{eq}(r) = a_w \cdot \exp\left(\frac{-2\sigma v_l^0}{rRT}\right) \tag{2-50}$$

$RH_{eq}(r)$ is the relative humidity at equilibrium with the saline solution in a pore. Comparing $RH_{eq}(r)$ with the environmental relative humidity, RH_{env}, it is possible to predict when the evaporation (or condensation) occurs. Thus, if $RH_{env} < RH_{eq}(r)$, evaporation will occur, meanwhile if $RH_{env} > RH_{eq}(r)$ condensation will take place.

To predict the tendency for the solutes to precipitate, the following parameters are necessary; the water activity of the solution and the critical relative humidity for evaporation. Also the molar volume of the solution, v_l^0, and the surface tension, σ, are required. The molar volume

of the solution can be written as the sum of its partial molar quantities for each component in the system, such as $H_2O(l)$, $Na^+(aq)$ and $Cl^-(aq)$ assuming ideal behaviour.
However, during evaporation the saline solution becomes more concentrated, since water evaporates. Thus, the water activity decreases until $RH_{eq}(r) = RH_{env}$. As evaporation continues, the halite saturated solution is reached and precipitation will occur.

2.3.3 Dissolved Components in Formation Water

The most frequently occurring component dissolved in formation/reservoir water is calcium carbonate originating from limestone strata, sandstones with calcium binders, marls etc. Water which passed through dolomite strata often contains magnesium carbonate. Further, readily soluble salts, such as common salt and magnesium sulphate, are often present in reservoir water, due to a possible salt cap of the reservoir. Also gypsum (calcium sulphate) is frequently found [f].

3 Results and Discussion

The following graphs are obtained from Matlab files. The program code can be found in the appendix.

3.1 Description of Phase Behaviour of Pure Water

From temperature to pressure

The first m-file which was made was the Antoine Equation, in two different ranges [v]. Hereby the following equation was used;

$$\log_{10}(p) = A - \left(\frac{B}{T + C - 273.15}\right) \qquad \textbf{(3-1)}$$

With the Boundary Conditions; `T=273-473K, p=0-16 bar`

For water, the parameters are;

```
A = 5.11564
B = 1687.537
C = 230.17
```

With equation 3-1 the values of the vapour pressure were calculated in bar, with an input of the temperature [K]. The programme also had the opportunity to make a graph. This graph consisted of temperature starting from 273.2 K to 473.2 K. The graph can be seen in Figure 3-1.

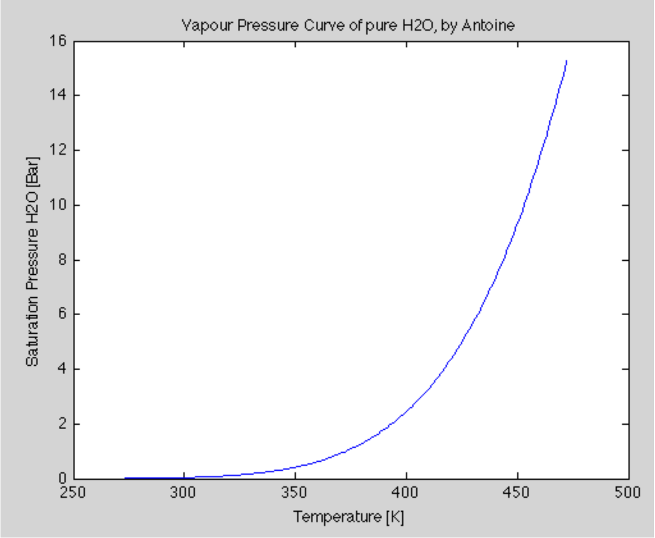

Figure 3-1 Smaller range of pressure and temperature[v]

Since reservoir pressures have higher pressures, a modification of the Antoine Equation with a larger range had to be searched for. The Wagner Equation satisfied these, which was given by the following equation;

$$\ln(p) = \ln p_c + \left(\frac{T_c}{T}\right)(a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6) \qquad \textbf{(3-2)}$$

with

$$\tau = \left(1 - \frac{T}{T_c}\right) \qquad \textbf{(3-3)}$$

Here the Boundary Conditions are; `T=273.2-648.2K, p=0-221 bar`

The parameters for water are;

```
a = -7.77224;
b = 1.45684;
c = -2.71942;
d = -1.41336;
p_c = 220.64;
T_c = 647.3;
```

Again the programme was provides the user a choice whether to see a graph or give a temperature to which the vapour pressure needs to be calculated for. The graph can be seen in Figure 3-2.

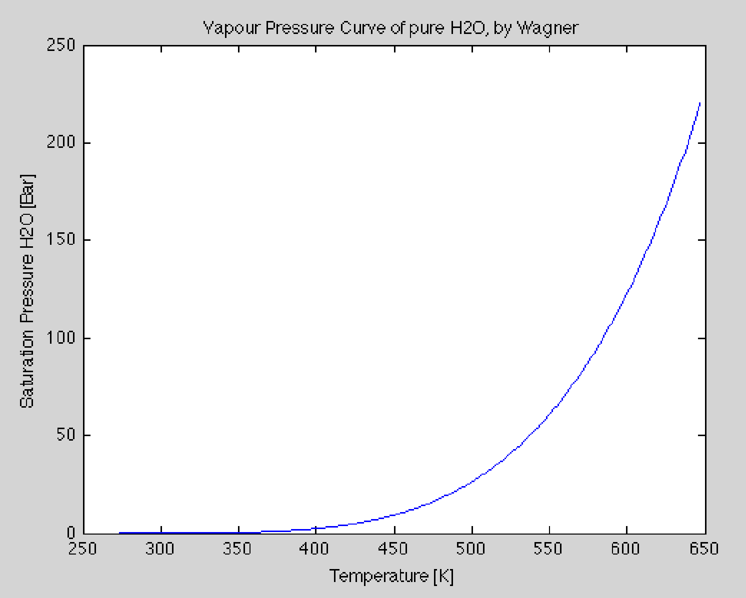

Figure 3-2 Larger range of pressure and temperature [v]

From pressure to boiling temperature

The Antoine Equation provides us to calculate the saturation pressure at a certain temperature. But by rewriting the equation, also the other way around could be calculated. Now the pressure is the input and it will say at which temperature the dew-point can be found. Equation 3-1 is now rewritten to;

$$T = \left(\frac{B}{(A - \log_{10}(p))} \right) - C + 273.15 \tag{3-4}$$

To rewrite the Wagner Equation, the calculation was more complicated. Since the temperature is a function of the pressure, it had to be iterated. Here I allowed a maximum iteration of 10,000 or otherwise an error of less than 1E-06. The output gave the maximum number of iterations, the error, the given pressure p, the calculated saturation pressure, and the actual pressure at which this boiling temperature was calculated. This I did in order to see how much the pressure differed from the given pressure. For the exact programming of this function I refer to Annex 2 ‘Reversed_Function.m’

3.2 Description of Aqueous Solutions (Non Electrolyte)

3.2.1 Temperature

To see how much the boiling temperature of liquid water changes due to dissolved solutes, the program 'Increase_T_b.m' was made.

Again the user has a choice between showing a graph or to calculation the new boiling temperature at a certain concentration. It was all calculated for standard conditions, thus, a pressure of 1 atm. For the calculation, the user has to give the mole fractions of water as an input. Since concentrations in reservoir water will not be more than 20%, the user is asked to give the mole fraction of water which differs between 0.8 and 1.0. Pure water means x_i is 1.0, and as more solutes are dissolved, x_i will decrease. With the decrease of the mole fraction of liquid water, the new boiling temperature increases. The theory behind this phenomenon is explained in appendix 0 'Elevation of Boiling Point'. The graph of this program can be seen in Figure 3-3.

For this programme, the following equation was used.

$$T_b(x) = \frac{\Delta H_{H_2O}^{vap}}{R \cdot \log(x_{H_2O}^L) + \frac{\Delta H_{H_2O}^{vap}}{T_b}} \qquad \textbf{(3-5)}$$

With $\Delta H_{H_2O}^{vap} = 40660$ J/mol

The output at this programme also involved the temperature difference, which was calculated with respect to the boiling temperature of 373 at 1 atm.

$\Delta T = T_b(x) - T_b$

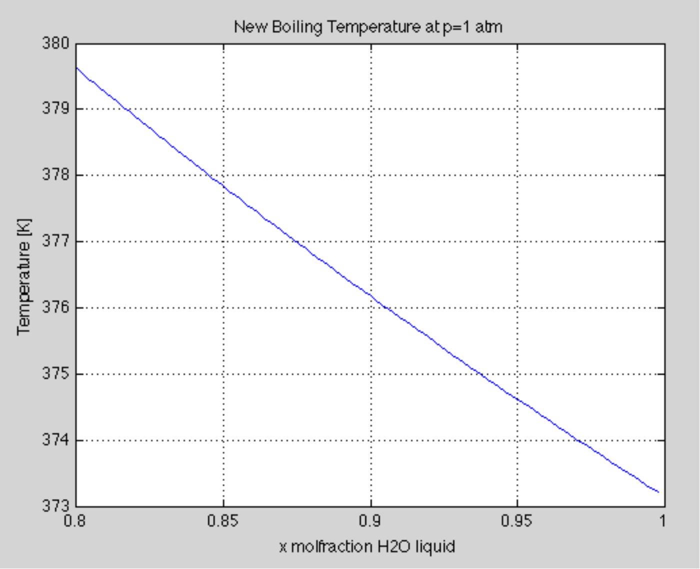

Figure 3-3 As the mole fraction of water is decreasing, the boiling temperature increases [w]

3.2.2 Vapour Pressure

Due to dissolved solutes, also the vapour pressure changes. The new vapour pressures were calculated by using the Wagner Equation (second part of 3.1), multiplied by the mole fraction of liquid water;

$$p_{sat}(x) = p_{vapour\_pressure} \cdot x^{L}_{H_2O}$$

The plots from this programme are seen in Figure 3-4 until Figure 3-9. These hold mole fractions of water from 1.0 – 0.8 [-] with steps of 0.05.

For both the calculation and the plot, the programme needs the mole fraction of water as an input. Next to this mole fraction input, also the temperature input is required for the calculation at which the vapour pressure decrease needs to be calculated.

It can be seen that as the mole fraction of water decreases, the vapour pressure of the solution also decreases. The blue line reflects the vapour pressure of pure water. The red line reflects the vapour pressure of the aqueous solution.

It can be seen that at higher temperatures, the result of the deviation with respect to the pure solvent is greater.

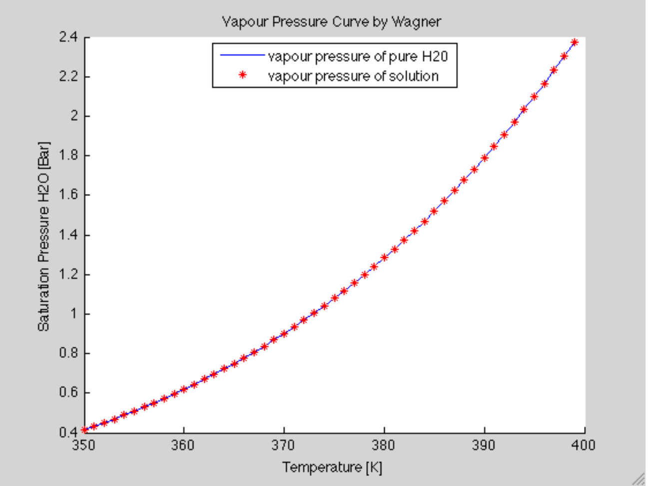

Figure 3-4 P,T-diagram with mole fraction of water = 1.00 [x]

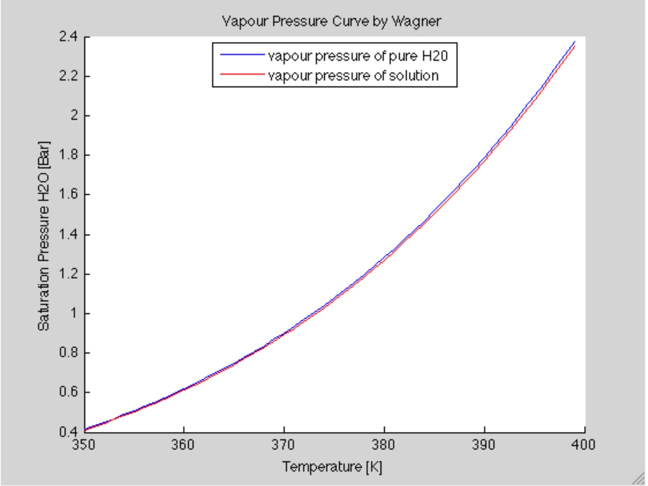

Figure 3-5 P-T-diagram with mole fraction of water = 0.99 [x]

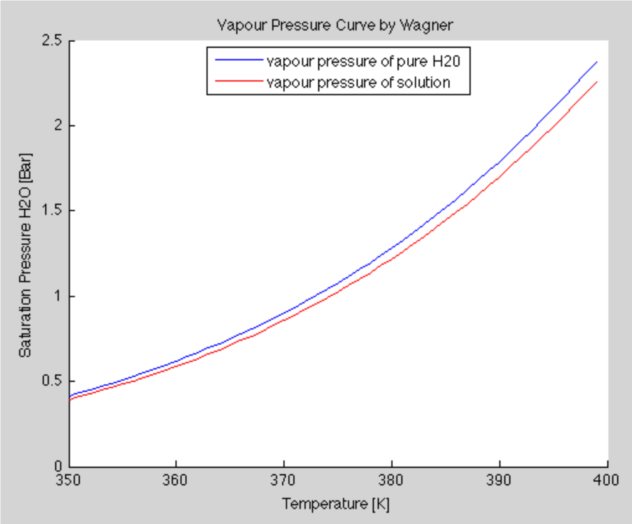

Figure 3-6 P,T-diagram with mole fraction of water = 0.95 [x]

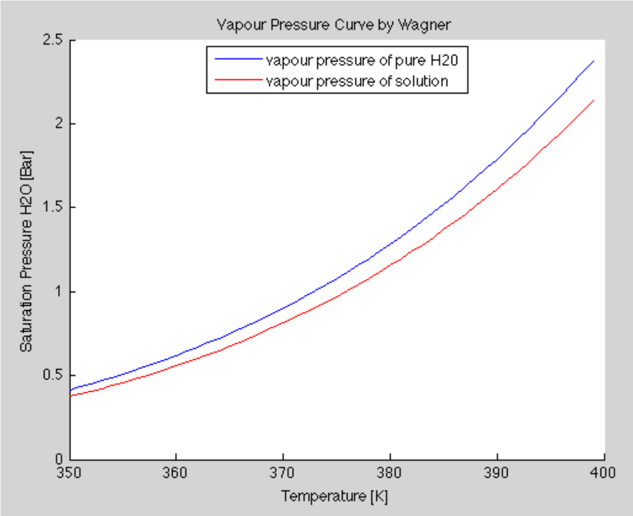

Figure 3-7 P,T-diagram with mole fraction of water = 0.90 [x]

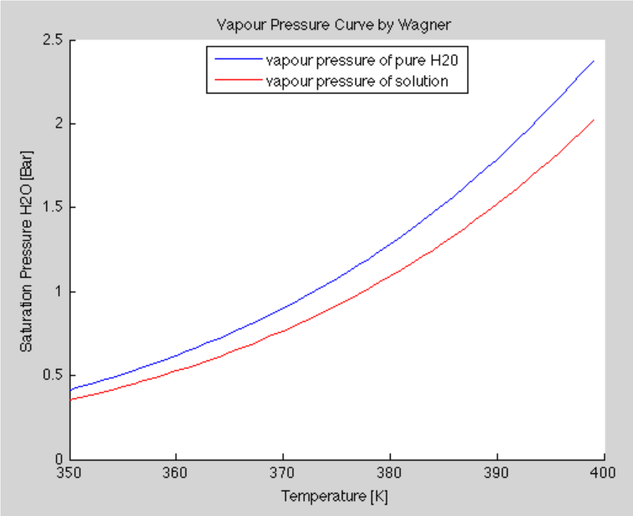

Figure 3-8 P,T-diagram with mole fraction of water = 0.85 [x]

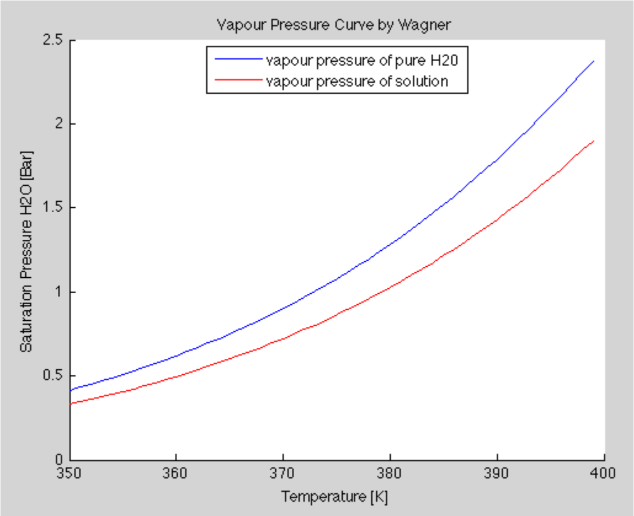

Figure 3-9 P,T-diagram with mole fraction of water = 0.80 [x]

3.3 Description of Aqueous Electrolyte Solutions

3.3.1 Debye-Hückel Theory

The Debye-Hückel theory gives an insight of the effects of different kinds of solutes. According to the theory, the activity coefficient decreases with increasing concentration ionic strength (Figure 3-10 and Figure 0-1). As this is not the case, the Debye-Hückel theory is only valid until an ionic strength until 0.042 M. This can be seen in Figure 3-11. Pay attention here, that the x-axis is given here in the square root of the ionic strength, and that the activity coefficient is given in the base10 logarithm.
From the graphs, it can be seen that, the valance of the ions has impact on the activity coefficient.

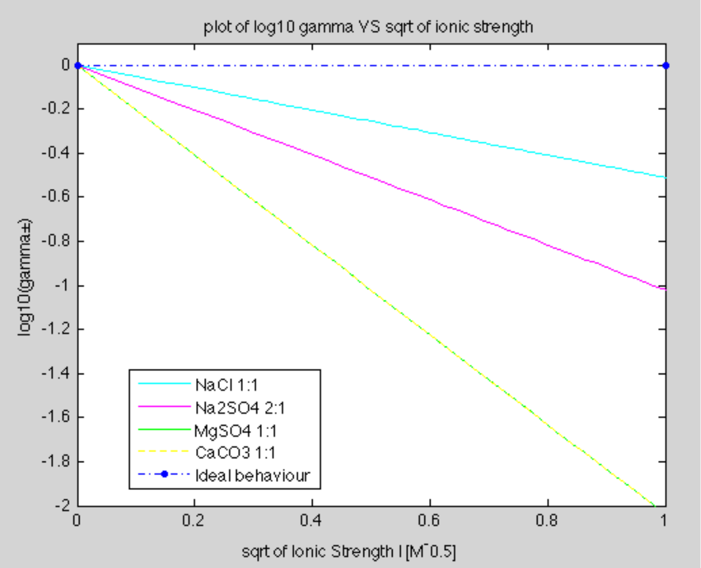

Figure 3-10 Concentration from 0.0 to 1.0 [mol/L] [y]

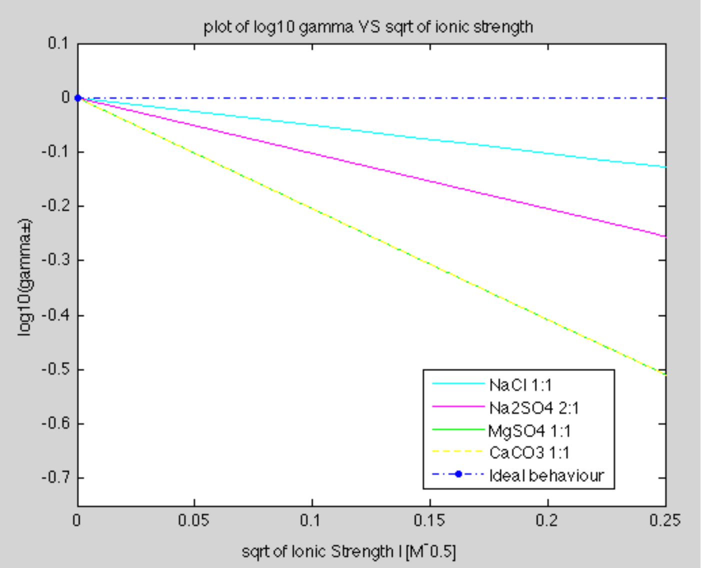

Figure 3-11 Zoom on concentration from 0.0 to 0.25 [mol/L] [y]

4 Conclusion

It is obviously that temperature and pressure are crucial parameters which have a direct effect on the behaviour of water. Due to the dissolved solutes, the vapour pressure is decreased. In addition also the curved interface decreases the vapour pressure of reservoir water. However, due to the production process, the reservoir water will cross the vapour pressure, which results in evaporation.
Since the solutes are not volatile, they will stay in the remained reservoir water, which increases the concentration as is monitored. The water will proceed its way to surface as steam. At a certain point, the produced gas will expand, and will cool down. Due to this cool down, together with lower temperatures at surface, the steam will condensate back to liquid water. This liquid water will add to the watercut, but since the steam did not take along any solutes, the concentration monitored at surface remains more or less constant.

When the maximum saturation has been reached in the reservoir water down-hole, the solutes will start to precipitate. This precipitation can take place within the pores but also within the production well. It will affect the permeability, and at a certain moment it can clog the pores and form scaling within the well. Simultaneously with the lower temperatures at pressures also the still available liquid water will become oversaturated within the tube, since the maximum solubility is a function of temperature. The precipitation of salts has a decreasing effect on the tubing head pressure.

Although from the Kelvin model it can be assumed that evaporation within reservoirs with smaller pores is less favourable, I expect that the evaporation has more influence than evaporation within reservoirs with larger pores. This is because the evaporation occurs more gradually over a larger area, whereas in the smaller pores it takes along all the solutes towards the production well. Since the pores are also smaller, less precipitation is needed to clog the pores.

Appendix

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VAPOUR PRESSURE DECREASE 47

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Elevation of Boiling Point

As was shown in Figure 2-8, the boiling point of a mixture rises due to the presence of solutes according to an isobaric condition. This colligative property is called ‘Elevation of boiling point’ and is related to the amount of solute.

In order to calculate the change of the boiling temperature with respect to the boiling temperature of the pure solvent, again the initial condition must be subtracted from the final condition.
The vapour pressure equilibrium condition for a mixture, thus the final condition has a new boiling temperature, $T_{b,S}$, but has the same pressure p, thus now it holds for the solution with solvent A:

$$\mu_A^L\left(T_{b,S}, p\right) = \mu_A^G\left(T_{b,S}, p\right) \qquad \textbf{(1)}$$

Combining equations 2-7 and 2-21, gives therefore the elevation of boiling point with respect to the original temperature of the boiling point:

$$\mu_A^L\left(T_{b,S}, p\right) - \mu_A^{\bullet,L}\left(T_{b,A}^{\bullet}, p\right) = \mu_A^G\left(T_{b,S}, p\right) - \mu_A^{\bullet,G}\left(T_{b,A}^{\bullet}, p\right) \qquad \textbf{(2)}$$

The chemical potential of a mixture can be expressed in terms of the standard chemical potential of the pure component and the activity due to the added solutes (see equation 2-3). This activity is expressed in terms of composition of the molecules of the solvent. It describes the deviation of the interactions between the molecules of the pure solvent, due to the addition of the dissolved molecules to the solvent. For a liquid, the activity at boiling point is related by the activity coefficient γ_A and actual concentration x_A of component A;

$$\mu_A^L\left(T_{b,S}, p\right) = \mu_A^{\bullet,L}\left(T_{b,S}, p\right) + RT_{b,S}\ln\left(x_A\gamma_A\right)^L \qquad \textbf{(3)}$$

Please not that the boiling temperature which is used here, is not the boiling temperature of the pure solvent A, but the boiling temperature of the mixture S; $T_{b,S}$.

For a vapour, the activity and concentration are related by the fugacity coefficient ϕ_A , the concentration y_A and the vapour pressure p. Combined with equation 2-3 the chemical potential of a gaseous mixture is given by;

$$\mu_A^G\left(T_{b,S}, p\right) = \mu_A^{\bullet,G}\left(T_{b,S}, p\right) + RT_{b,S}\ln\left(x_A\gamma_A\right)^G \qquad \textbf{(4)}$$

Again, using the boiling temperature of the mixture, $T_{b,S}$.

A non-volatile solute is only present in the liquid phase. Therefore the vapour phase only consists of pure solvent and thus y_A =1. For simplicity it was also assumed that the vapour behaved like ideal gas and thus $\gamma_A = 1$ (page 14). Now the term $RT_{b,S}\ln\left(x_A\gamma_A\right)^G$ drops out and thus from equation 4 will only remain;

$$\mu_A^G\left(T_{b,S},p\right) = \mu_A^{\bullet,G}\left(T_{b,S},p\right) \tag{5}$$

By substituting equations 3 and 5 into equation 2 one can find:

$$\underbrace{\underbrace{\mu_A^{\bullet,L}\left(T_{b,S},p\right)}_{st.potential} + \underbrace{RT_{b,S}\ln\left(x_A\gamma_A\right)^L}_{deviation}}_{final\_liquid\_condition} - \underbrace{\underbrace{\mu_A^{\bullet,L}\left(T_{b,A}^{\bullet},p\right)}_{pure\_comp.}}_{ini\_liquid\_condition} = \underbrace{\underbrace{\mu_A^{\bullet,G}\left(T_{b,S},p\right)}_{st.potential}}_{final\_gaseous\_condition} - \underbrace{\underbrace{\mu_A^{\bullet,G}\left(T_{b,A}^{\bullet},p\right)}_{pure\_comp.}}_{initial\_gaseous\_condition} \tag{6}$$

By rewriting and separating the chemical potentials from the term which describes the deviation due to the effect of dissolution, the following equation is obtained;

$$\underbrace{\left(\mu_A^{\bullet,L}\left(T_{b,S},p\right) - \mu_A^{\bullet,G}\left(T_{b,S},p\right)\right)}_{mixture} + \underbrace{\left(-\mu_A^{\bullet,L}\left(T_{b,A}^{\bullet},p\right) + \mu_A^{\bullet,G}\left(T_{b,A}^{\bullet},p\right)\right)}_{pure\_component} = -RT_{b,S}\ln\left(x_A\gamma_A\right)^L \tag{7}$$

The first term on the left-hand side describes the chemical potential difference between the gas and the liquid phase of the pure component A at the bubble-point of the solution, whereas the second term on the left-hand side describes the chemical potential difference on the vapour pressure curve of the pure component A.
Since the vapour pressure curve describes equilibrium between the liquid and vapour phase, the chemical potentials of equation 7 must be equal, the second term becomes zero;

$$\mu_A^{\bullet,L}\left(T_{b,S},p\right) - \mu_A^{\bullet,G}\left(T_{b,S},p\right) = -RT_{b,S}\ln\left(x_A\gamma_A\right)^L \tag{8}$$

The second term of the left hand side of equation 7 will also become 0, applying equation 2-19. $T_{b,A}^{\bullet}$ will be divided by $T_{b,A}$ and results in one, hence the enthalpy must be multiplied with 0. As the enthalpy is used, equation 8 can now be rewritten to;

$$\Delta\overline{H_{A,trans}^{\bullet}}(T_{b,S},p)\cdot\left(1-\frac{T_{b,S}}{T_{b,A}}\right) = -RT_{b,S}\ln\left(x_A\gamma_A\right)^L \tag{9}$$

Since equation 8 goes out from a starting position of a gaseous phase towards a liquid phase, the enthalpy sign is thus as if it is condensing!
Since it is preferred to use the enthalpy of evaporation, rather than the enthalpy of condensation, this can be changed by a minus sign on the right hand side;

$$\Delta\overline{H_{A,vap}^{\bullet}}(T_{b,S},p)\cdot\left(1-\frac{T_{b,S}}{T_{b,A}}\right) = RT_{b,S}\ln\left(x_A\gamma_A\right)^L \tag{10}$$

A simple rewriting gives;

$$T_{b,A} - T_{b,S} = \frac{\left(RT_{b,S}\ln\left(x_A\gamma_A\right)^L\right)}{\Delta\overline{H_{A,vap}^{\bullet}}(T_{b,S},p)}\cdot T_{b,A} \tag{11}$$

Here a boiling temperature difference is stated between a mixture (begin) and a pure solvent (end), thus the evaporation of the boiling point of a mixture with respect to the pure solvent can be calculated by:

$$\Delta T_b = T_{b,S} - T_{b,A} = \frac{-\left(RT_{b,A}T_{b,S}\left(\ln\left(x_A\gamma_A\right)^L\right)\right)}{\Delta\overline{H_{A,vap}^{\bullet}}(T_{b,S},p)} \tag{12a}$$

Here, x_A is the concentration / mole fraction of the pure solvent. Since it is more useful to know what the effect is of the addition of a *specific amount of weight* to the solution the formula needs to obtain x_S, the mole fraction of the solute.

In terms of the solute

With a dilution, the amount of dissolved matter is very small in comparison to the amount of solvent. Actually, for simplicity it could be stated that the mixture consists of solvent, e.g. dropping a sugar cube into a bath tube. Thus it can be written that $x_A^L \rightarrow 1$. Because the pure solvent reaches one, it can be said that the activity coefficient approaches one, thus $\gamma_i \rightarrow 1$. With these assumptions the term in the numerator of equation 12a becomes:

$$-RT_{b,A}T_{b,S} \cdot \ln\left(x_A\right)^L \qquad \textbf{(12b)}$$

x_A can be replaced by a term which contains x_S, namely $x_A = \left(1 - x_S\right)$. It is known from mathematics that $\ln\left(1-x\right)$ can be described by the series $\ln\left(1-x\right) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4}$, the expression $\ln\left(1-x_S\right)$ of a diluted solution with $x_S \rightarrow 0$, reduces therefore to the limiting value of

$$\lim_{x\rightarrow 0}(\ln(1-x_S)) \cong -x_S \qquad \textbf{(13)}$$

Combining this with equation 12, the minus sign drops out and gives;

$$\Delta T_b = \frac{RT_{b,A}T_{b,S} \cdot \ln\left(x_S\right)^L}{\overline{\Delta H^{\bullet}_{A,vap}}(T_{b,S}, p)} \qquad \textbf{(14)}$$

If this same mathematical theory is applied to equation 10 and the minus sign is put in front, the following is obtained;

$$\overline{\Delta H^{\bullet}_{A,vap}}(T^{\bullet}_{b,A}, p) \cdot \left(1 - \frac{T_{b,S}}{T^{\bullet}_{b,A}}\right) = -RT_{b,S}\ \ln(x_S)^L \qquad \textbf{(15)}$$

Hence, it can be stated that the boiling temperature of the solution, $T_{b,S}$, must be greater than the boiling temperature of the pure solvent, $T^{\bullet}_{b,A}$, since the ratio of the temperatures must be larger than 1, as the molar enthalpy of vaporization, $\overline{\Delta H^{\bullet}_{vap,A}}$, has a positive value and the left side of the equation is negative. This proves the elevation of boiling point.■

In terms of the added mass of the solute

In order to relate changes in temperature to the molality (mol per kg solution) the mole fractions need to be converted;

$$x_S = \frac{n_S}{n_S + n_A} = \frac{m_S}{m_S + \frac{1000}{M_A}} \qquad \textbf{(16)}$$

x_S is the mole fraction of the solute S, as is used in equation 15. n_S is the amount of moles of the solute S and n_A the amount of moles of solvent A. m_S is the molality of the solute added per kilogram solution of A and M_A is the molar mass of solvent A given gram per mole. Since molality is per *kilo*gram and the molar mass is in grams, a factor thousand is added.

In a diluted solution the mass of the dissolved solute is small compared to the mass solvent. It can thus be assumed that the mass of the solution is equal to the mass of solvent. Equation 16 will therefore become:

$$x_S = \frac{m_S \cdot M_A}{1000} \tag{17}$$

Combining equation 15 with equation 2-17 gives;

$$\Delta \overline{H^\bullet_{vap,A}}\left(T^\bullet_{b,A}, p\right) \cdot \left(1 - \frac{T_{b,S}}{T^\bullet_{b,A}}\right) \approx -R \cdot T_{b,S} \cdot m_S \cdot \frac{M_A}{1000} \tag{18}$$

In order to calculate ΔT_b, all terms of boiling temperatures need to be separated from the other terms, thus;

$$-\left(\frac{1}{T_{b,S}} - \frac{1}{T^\bullet_{b,A}}\right) \approx \frac{R \cdot m_S}{\Delta \overline{H^\bullet_{vap,A}}\left(T^\bullet_{b,A}, p\right)} \cdot \frac{M_A}{1000} \tag{19}$$

And for simplicity;

$$-\left(\frac{T^\bullet_{b,A} - T_{b,S}}{T_{b,S} \cdot T^\bullet_{b,A}}\right) \approx \frac{R \cdot m_S}{\Delta \overline{H^\bullet_{vap,A}}\left(T^\bullet_{b,A}, p\right)} \cdot \frac{M_A}{1000} \tag{20}$$

If it can be further assumed that $T^\bullet_{b,A} \approx T_{b,S}$, the temperature $T_{b,S}$ in the denominator can be replaced by $T^\bullet_{b,A}$. The minus sign is helpful to change the begin and end condition in the numerator and thus can be stated that;

$$\Delta T_b = T_{b,S} - T^\bullet_{b,A} \approx \frac{R \cdot \left(T^\bullet_{b,A}\right)^2 \cdot m_S}{\Delta \overline{H^\bullet_{vap,A}}\left(T^\bullet_{b,A}, p\right)} \cdot \frac{M_A}{1000} \tag{21}$$

With this equation the boiling temperature can be calculated based on the amount of added solute. As can be seen, it does not differ very much from equation 14.

Vapour Pressure Decrease

In contrary to the elevation of boiling temperature, where an isobaric condition is described, it is also required to calculate the effect on the vapour pressure at isothermal conditions.
The initial condition is the pure solvent A at the temperature $T^{\bullet}_{b,A}$ and its respective vapour pressure $p^{\bullet}_{A}$. The final state is the dilute solution at the same temperature $T^{\bullet}_{b,A}$, but now at the pressure p_S the vapour pressure of the solution.
To calculate the pressure difference, the initial condition is subtracted from the final condition;

$$\Delta p = p_i\,(T) - x_i \gamma_i p_i\,(T) \qquad \textbf{(22)}$$

In general, a gas-liquid equilibrium can be described by the modified law of Raoult.
Using the boiling point temperature of the pure solvent gives;

$$x_i \gamma_i p_i^{sat}(T) = y_i \phi_i p_i(T) \qquad \textbf{(23)}$$

.

x_i represents the mole fraction of component i in the liquid phase. y_i the mole fraction of component i in the gas phase. p_i^{sat} is the vapour pressure of the pure component i at given temperature (also called saturation pressure), ϕ_i is the fugacity coefficient of component i in the gas phase.
At initial condition, the liquid phase exists only of pure solvent, so $x_A = 1$ and the pure component standard state is used, also $\gamma_A = 1$. Also the gas phase consists solely of pure solvent, and thus $y_A = 1$. Again it is assumed that the vapour will behave as an ideal gas, and hence $\phi_A = 1$. At the initial conditions the pressure is equal to the vapour pressure of the pure solvent A at the given temperature;

$$p_i(T) = p^{\bullet}_A(T) \qquad \textbf{(24)}$$

At the final state the gas phase still only consists of pure solvent A because the solute is non-volatile, and thus $y_A = 1$ and $\phi_A = 1$. However the liquid phase consists of both solute and solvent and thus equation 23 becomes;

$$x_A \gamma_A p^{\bullet}_A(T) = p_A^{sat}(T) \qquad \textbf{(25)}$$

where x_A represents the mole fraction of the solvent A. Often it is assumed that the liquid phase behaves ideally so that $\gamma_A = 1$ (same assumptions as on page 43), hence;

$$x_A p^{\bullet}_A(T) = p_A^{sat}(T) \qquad \textbf{(26)}$$

From this equation it can be concluded that the bubble point pressure of the solution, $p_A^{sat}(T)$, is smaller than the vapour pressure of the pure solvent A, $p^{\bullet}_A(T)$, as the mole fractions is always smaller than one $x_A < 1$

To calculate the difference in vapour pressure decline, equation 22 has to be combined with equations 24 and 26. This gives;

$$\Delta p = x_A p^{\bullet}_A(T) - p^{\bullet}_A(T) \Rightarrow (x_A - 1)\cdot p^{\bullet}_A(T) \qquad \textbf{(27)}$$

Furthermore $x_A = (1 - x_S)$, hence;

$$\Delta p = -x_S \cdot p^{\bullet}_A(T) \qquad \textbf{(28)}$$

Since the pressure and mole fraction are both positive, the vapour pressure difference must be negative, with respect to the vapour pressure of the pure component A■

The difference in vapour pressure difference can also be calculated based on the amount of added solute. Therefore x_S must be replaced by the molality;

$$\Delta p = -\frac{M_A}{1000} \cdot m_S \cdot p_A^{\bullet}(T) \tag{29}$$

Debye-Hückel Theory

The amount of salt that can be dissolved depends on the kind of salt but also whether there are already other ions in the solution present.
Whereas calculating electrostatic interactions in a crystal is straightforward, the interactions in liquid solutions are dynamic with ions continuously changing their positions. A completely random distribution of ions in the solution results in a neutral solution, no net attractive or repulsive interactions because the average separations of like-charged and oppositely charged ions are the same. However, it is now known that the distribution of ions in the solution is not random due to the charges of the ions and this ‘structure’ has to be taken into account.

The solubility equilibrium is influenced by the ionic strength of the solution. For fresh water conditions, the Debye-Hückel theory (or the Günthelberg or Davies Equation) may be used to convert the solubility equilibrium constant [m].
According to the Debye-Hückel theory, the mean activity coefficient, γ, of an dissolved electrolyte is given by

$$\log_{10}\gamma_{+/-} = -A\left|z_x \cdot z_y\right|\sqrt{I} \qquad \textbf{(30)}$$

A is a constant incorporating the properties of the solvent; for an aqueous solution at 298 K, A is equal to $0.51\mathrm{M}^{-0.5}$.
I is the ionic strength of the solution and is given by

$$I = \frac{1}{2}\sum_j c_j z_{+/-,j}^2 \qquad \textbf{(31)}$$

where c_j is the concentration and $z_{+/-,j}$ is the charge of the j^{th} ionic species. The summation is taken over all dissolved ions.
For consistency c_j can be rewritten in terms of molality, thus;

$$I = \frac{1}{2}\sum_j \left\{ \left(\frac{\upsilon m_j M_A}{1000} \right) \cdot z_j^2 \right\} \qquad \textbf{(32)}$$

It is not possible to experimentally determine the activity coefficient of a single ion without the presence of its counter ion; it is not possible to add a positive ion to the solution without a balancing negative ion. Therefore, the mean activity coefficient is usually determined.

These predictions are confirmed by experiments for ion strengths less than ≈ 0.042M, as can be seen in Figure 0-1 It demonstrates the validity of the Debye-Hückel model only for dilute ionic solutions.

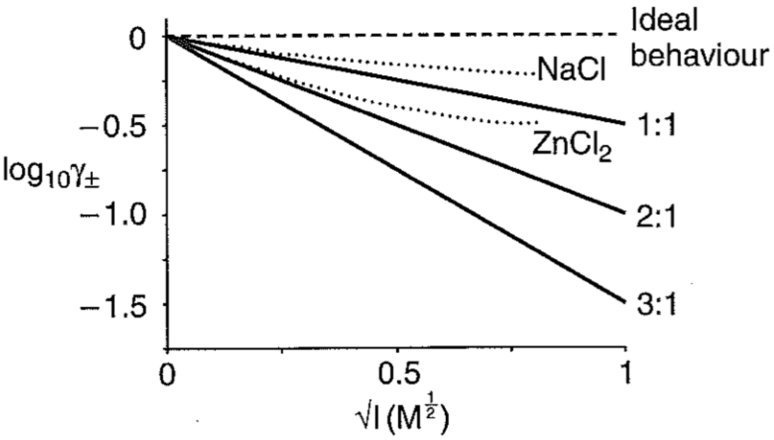

Figure 0-1 Calculated plots of $\log_{10}\gamma_x$ versus $\sqrt{I}$
The experimental data for NaCl and ZnCl$_2$ are shown as dotted lines [q]

At higher values of ionic strength, the Debye-Hückel theory can no longer match the experimental data. In fact, the Debye-Hückel theory predicts that $\gamma_\pm$ will continue decreasing at high values of the ionic strength, whereas the experimental data (Figure 0-1), show that $\gamma_\pm$ reaches a minimum and then increases to be eventually greater than 1 (as is shown in Figure 2-14). In order to be able to describe also the behaviour of concentrated solutions other models such as the Pitzer model or the Chen-NRTL model need to be applied
Therefore a modified Debye-Hückel theory is obtained, but will not be further discussed here [y].

Evaporation Process within a Pore

The evaporation of water of the pores during decreasing RH is not symmetrical to the adsorption phase during increasing RH. Some hypotheses have been conceived in order to explain the hysteresis loop. One of them is based on the different geometry of the meniscus; e.g. cylindrical during condensation into capillaries and spherical during evaporation [7]. Another theory which is first proposed by Kraemer (1931) is the 'ink bottle' geometry. This theory states that in a pore system composed of two cylindrical cavities, like an ink bottle, the condensation occurs filling first of all the wider cavity, as in a bottle, and then the narrow neck. As a consequence, the environmental RH determining the loop width can be calculated by means of equation 2-42, by considering the radius of the wide body for the condensation and the radius of the neck for the evaporation.

The pore and capillary geometry influence both the critical RH -as computed with the so-called equilibrium of equation 2-40 and the following processes. Imagine that the water filling by condensation occurs reversibly, in equilibrium with the increasing RH. In the latter it is irreversibly triggered by the critical value of RH, given by the same equation, but now representing an unstable equilibrium. The geometry plays a very important role here. Therefore the cases of a single pore or capillary differ from a combination of them together.

A hemispheric pore with radius r_s (Figure 0-2) faces a larger cavity or the external environment. When RH reaches RH_S, the water molecules of the flat water surface (cavity) will be evaporated until $r=r_S$. This includes water out of the pore, forming a curved meniscus in the pore. Now, due to the more curved meniscus, a higher water surface tension is obtained. Therefore RH needs to decrease until RH_0 for further evaporation of the water out of the pore.

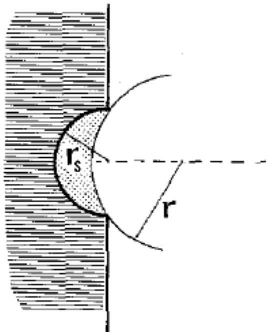

Figure 0-2 Evaporation in a hemispheric cavity with radius r_s; r is the radius of the meniscus in equilibrium with the Kelvin formula [u]

In case of a spherical pore with a radius r_s which is open to the environment through a small hole with radius r_0 (Figure 0-3), the pore remains filled and evaporation starts as soon as RH reaches the value RH_0 given by equation 2-40 for $r=r_0$. Since the meniscus with radius r is in equilibrium with RH $>RH_0$, the latter value constitutes again a critical unstable limit to the system and triggers the evaporation of the cavity.

In contrast to the case of the hemisphere which is characterized by equilibrium between RH and r, so that the shrinkage curve is continuous with RH, the case of a nearly complete sphere is typical of unstable equilibrium and the evaporation is now triggered by two critical values RH_s and RH_0.

---

[7] Cohan(1944)[u]

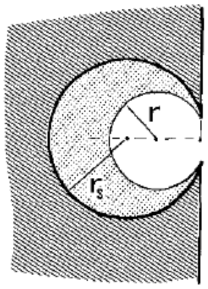

Figure 0-3 Condensation in a spherical cavity with radius r_s, open to the environment through a small hole with radius r_0 [u]

For evaporation in a capillary the evaporation takes place at both the open ends of the cylinder with two hemispherical menisci which remain practically at the same curvature during all the evaporation process. In this case the RH required for the evaporation is RH_e as obtained from equation 2-40 for $r=r_e$, i.e. $RH = \frac{(RH_c)^2}{100}$. Lower values of RH correspond to more curved menisci, so that a small droplet in the environmental RH causes the complete evaporation of the cylinder. In conclusion, the evaporation occurs at RH_e with the meniscus unchanged but drawn back, so that it represents a condition of neutral equilibrium, and the evaporation is possible only with an outward flux of moisture which reduces RH near the meniscus.

With reference to a spherical pore connected to the environment through a capillary, three cases can be distinguished depending on the relationships between the radii of the capillary r_c and the sphere r_s, namely:

1. In the cases $2r_c>r_s$ (Figure 0-4), evaporation begins at the free end of the capillary in conditions of neutral equilibrium. Here fore RH is equal to RH_e. When the capillary is completely emptied, the same RH_e is critical for the spherical pore which evaporates as in case of a spherical pore.

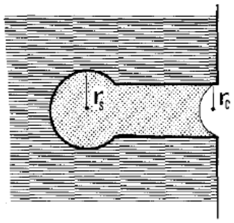

Figure 0-4 Evaporation of a pore (radius r_s) connected to the environment through a capillary (radius $r_c>r_s/2$). Evaporation occurs in two steps: first capillary and then the pore [u]

2. When $2r_c=r_s$, like in Figure 0-5, evaporation occurs as in the preceding case at RH_e

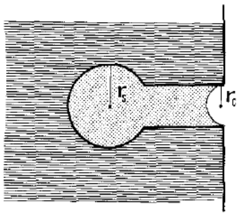

Figure 0-5 As in Figure 0-4 except for $r_c=r_s/2$ [u]

3. In the case that $2r_c<r_s$ (Figure 0-6), again evaporation takes place when RH_e is reached, starting from the open base of the cylinder, communicating with the surroundings.

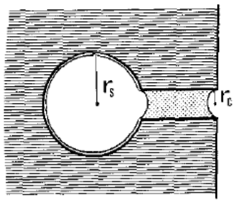

Figure 0-6 As in Figure 0-4 except for $r_c<r_s/2$ [u]

Now two adjoining spherical pores can be considered.

1. When the arrangement of the pores is as sketched in Figure 0-7 the evaporation is accomplished in two steps triggered by the size of the holes. When the pores are equal, the evaporation is again triggered by RH_0 as in case of a spherical pore and occurs first in the external pore and then in the internal one.

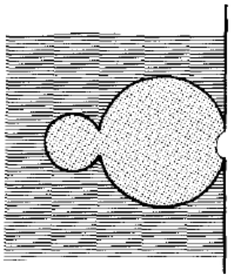

Figure 0-7 Evaporation into tow contiguous pores where the larger is external. The evaporation occurs in two steps: first the external, then the internal [u]

2. When the pores are arranged as in Figure 0-8, usually the larger pore is empty, due to the drainage process, where the smaller pore was filled first, insulating the larger one from the environment. Therefore the filled air remained captured.

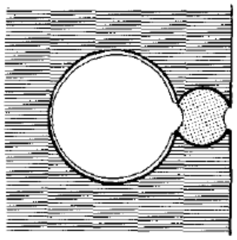

Figure 0-8 As in Figure 0-7 except for the relative position of the two pores [u]

3. In the case of the ‘ink bottle’ with a narrow neck (Figure 0-9) again the same problem arises as in the previous case.

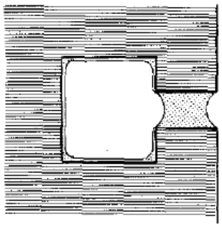

Figure 0-9 Evaporation into two capillaries forming an ‘ink bottle’. The evaporation occurs into the narrower neck [u]

The only way these larger pores got filled was if the situation was once that the porous body was submerged into liquid water (water level arising), after the air could escape. Another way is that, by the overburden, temperature got increased and the pressure of the air in the inner pores pushed the water outside the mouth, i.e. the smaller external pore or capillary. Therefore, the latter could also be emptied by expelling liquid water instead of evaporating it. On the contrary, a drop in temperature may cause some water to be sucked into the inner pore. So, besides the condensation-evaporation cycles in history, variations in temperature or pressure are also responsible for migration of water into porous bodies.

Bibliography

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[a] Dorp, Q. Van, Salt precipitation in gas reservoirs
[b] Tang, R. and Etzion, Y., Comparative studies on the water evaporation rate from a wetted surface and that from a free water surface, 2003
[c] Jahn, F., Cook, M., Graham, M., Hydrocarbon Exploration and Production
[d] http://liteoilinvestments.com/fundamentals.html, March 2010
[e] http://www.chem.ufl.edu/~itl/2045/lectures/lec_f.html, April 2010
[f] Debski, K., Continental hydrology. Vol 2. Physics of water, atmospheric precipitation and evaporation, 1966
[g] Chemical Thermodynamics and Kinetics - p36
[h] http://www.chem.arizona.edu/~salzmanr/480a/480ants/fugacity/fugacity.html, March 2010
[i] http://en.wikipedia.org/wiki/Phase_diagram.html, February 2010
[j] http://serc.carleton.edu/NAGTWorkshops/geochemistry/table_contents.html
[k] Sandwijk, Mijnbouwchemie, 2003
[l] http://depts.uwc.edu/chemistry/, February 2010
[m] Aquatic Chemistry_ 349_359
[n] http://en.wikipedia.org/wiki/Electrolyte, April 2010
[o] http://dqb.unl.edu/Teacher/NSF/C01/C01Mats/Salts/SaltSol.html, February 2010
[p] http://www.abdn.ac.uk/rhynie/sinter.htm, February 2010
[q] Price, N.C. et al, Principles and problems in physical chemistry for biochemics, 3rd edition
[r] Benavente, D, García del Cura, M.A., Ordóñez S., Salt influence on evaporation from porous building rocks, 2002
[s] McQuarrie and Donald A., Molecular Thermodynamics; p459, eq 11.44
[t] http://en.wikipedia.org/wiki/Young-Laplace_equation, February 2010
[u] Camuffo, D.; Condensation-Evaporation Cycles in pore and capillary systems according to the Kelvin model, 1982
[v] Antoine_Combi.m
[w] Increase_T_b.m
[x] Decrease_P_vap.m
[y] Debye_Huckel.m
[z] Activity_Coefficient_Iteration.m
[aa] Sawamura, S., Solubility of sodium chloride in water under high pressure
[ab] http://www.thermexcel.com/english/tables/eau_atm.htm, February 2010
[ac] Application of a modified Debye-Hückel theory to fully ionized gases, Kidder, R.E., DeWitt, H.E., 1961

Annex

ANTOINE COMBI.M 55

REVERSED FUNCTION.M 57

INCREASE T B.M 59

DECREASE_P_VAP.M 50

DEBYE HUCKEL.M 62

ACTIVITY_COEFFICIENT_ITERATION.M 67

1 Antoine_Combi.m

```
clc
clear all
close all

equation = input ('Equation 1(T=273-473K, p=0-16 bar) or
Equation 2(T=273-647K, p=0-221 bar)? ');

if equation==1
% This Antoine function is valid for the temperature range
between 273,20K
% to 473,20 K (so 0-200degC) and a pressure range of 0.01-16
bar. It
% calculates the vapour pressure curve through
% log10(p_Vp)=A-(B/(T+C-273.15)). T must be given in [K]
% source: properties of gases and liquids

A = 5.11564;
B = 1687.537;
C = 230.17;

choice = input ('Would you like a graph(1) or calculation(2)
');
 if choice == 1;

T = 273.20; % K

for i=1:200
    p_vp=10^(A-(B/(T+C-273.15)));
    Temp(i)=T;
    p_vp_sat(i)=p_vp;
    T=T+1;
end

% making plot
figure (1)
plot(Temp,p_vp_sat)
xlabel('Temperature [K]')
ylabel('Saturation Pressure H2O [Bar]')
title('Vapour Pressure Curve of pure H2O, by Antoine')
```

```
elseif choice == 2

T=input ('Temperature in [K] between 273.2 and 473.2: ');
p_vp=10^(A-(B/(T+C-273.15)))
end

elseif equation ==2
    % This Antoine function is valid for the temperature range
between 273.20K
% to 647.3 K (so 0-374.15degC), so until critical temperature,
and a pressure range of 0.01-221 bar. It
% calculates the vapour pressure curve through
% lnp=lnp_c+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6). T must
be given in [K]
% source: Bruce E. Poling, John M. Prausnitz, John P.
O'Connell, The properties of gases and liquids, 5th edition; p
A.59

a = -7.77224;
b = 1.45684;
c = -2.71942;
d = -1.41336;
p_c = 220.64; %bar
T_c = 647.3; %K

choice = input ('Would you like a graph(1) or calculation(2)
');

if choice == 1;

    T = 273.20; % K

    for i=1:375
            tau = (1-(T/T_c));

p_vp=exp(log(p_c)+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6));
            Temp(i)=T;
            p_vp_sat(i)=p_vp;
            T=T+1;
    end

    % making plot
    figure (1)
    plot(Temp,p_vp_sat)
    xlabel('Temperature [K]')
    ylabel('Saturation Pressure H2O [Bar]')
    title('Vapour Pressure Curve of pure H2O, by Wagner')

elseif choice == 2
        T=input ('Temperature in [K] between 273.2 and 647.3:
');
        tau = (1-(T/T_c));
        p_vp =
exp(log(p_c)+(T_c/T)*(a*tau+b*tau^3+d*tau^6))
end
end
```

2 Reversed_Function.m

```
clc
clear all
close all

equation = input ('Equation 1(T=273-473K, p=0-16 bar) or
Equation 2(T=273-647K, p=0-221 bar)? ');
p = input('At which pressure[bar] would you like to calculate
boiling Temperature?');

if equation==1
% This Antoine function is valid for the temperature range
between 273,20K
% to 473,20 K (so 0-200degC) and a pressure range of 0.01-16
bar. It
% calculates the vapour pressure curve through
% log10(p_Vp)=A-(B/(T+C-273.15)). T must be given in [K]
% source: properties of gases and liquids

A = 5.11564;
B = 1687.537;
C = 230.17;

new_boiling_temperature=(B/(A-log10(p)))+273.15-C


elseif equation == 2
     % This Antoine function is valid for the temperature
range between 273,20K
% to 647.3 K (so 0-374.15degC), so until critical temperature,
and a pressure range of 0.01-221 bar. It
% calculates the vapour pressure curve through
% lnp=lnp_c+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6). T must
be given in [K]
% source: Bruce E. Poling, John M. Prausnitz, John P.
O'Connell, The properties of gases and liquids, 5th edition; p
A.59

T0 =    647;    %[K]

max =   10000;    %maximum iterations
iter =  0;

a =     -7.77224;
b =     1.45684;
c =     -2.71942;
d =     -1.41336;
p_c =   220.64; %bar
T_c =   647.3;  %K

for i= 1:max;
    iter=iter+1; %iteration counter

    T_begin=T0;
    %Determine present guessed value of p_guess
```

```
        tau0    = (1-(T_begin/T_c)); %T_begin < T_c!
p_vp_begin   =
exp(log(p_c)+(T_c/T_begin)*(a*tau0+b*tau0^1.5+c*tau0^3+d*tau0^
6)); %logp_c=5.4, ()>1 so (a-d)tau-part must be neg)

       %Determine with (T+dT) next p
        dT  = 1.e-6; %[K]
        T1      = T_begin + dT;
        tau1    = (1-(T1/T_c));
        p_vp1      =
exp(log(p_c)+(T_c/T1)*(a*tau1+b*tau1^1.5+c*tau1^3+d*tau1^6));

        % Determine derivative FWD
        p_vp_prime = (p_vp1 - p_vp_begin) / dT;

        %Check if max allowed difference in p has been
exceeded;
        err = (p_vp_begin-p).^2;


        if (abs(err)<dT), break, end

        T1 = T_begin- (err / ((2*p_vp_begin-p)*p_vp_prime));
%Take Newton Raphson iteration step; % plus of maal dTx?

        T0=T1;
end
iter
err
p
p_vp_begin
new_boiling_temperature = T_begin
end
```

3 Increase_T_b.m

```
clear all
close all
clc

% GRAPH; on x-axis are molfracti of water in liquid phase
% between 0.8 en 1.0, with steps of 1/500. The following has
been used;
% dH_vap=-dH_cond=40,66kJ/mol, T_boiling=373,15 K.

% CALCULATION; give mole fraction of H2O. This input has to be
between 0.8 and 1.
% New boiling temperature gets calculated with formula and
shown afterwards, including dT.

choice = input ('Would you like a graph(1) or calculation(2)
')

    dH_H2O_vap = 40660;  % J/mol
    R = 8.314472;        % J/K/mol
    T_b = 373.15;        % boiling temperature in [K] at p=1
[atm]

if choice == 1;
     x = 0.8; % de grafiek loopt van 0.8 tot 1.0 molfractie
H2O.
for i=1:100


T=dH_H2O_vap/((R*log(x))+(dH_H2O_vap/T_b));
    x2(i)= x;
    T2(i)= T;

    x = x+(0.2/100);
end

figure (1)
plot(x2,T2)
xlabel('x mole fraction H2O liquid')
ylabel('Temperature [K]')
title('New Boiling Temperature at p=1 atm')
grid on
xlim([0.8 1.0])


elseif choice ==2;
mol_frac_l  =   input ('Mole fraction of H2O(l) between 0.8
and 1.0: ');
T_b_x = dH_H2O_vap/((R*log(mol_frac_l))+(dH_H2O_vap/T_b))

dT = T_b_x - T_b
end
```

4 Decrease_P_vap.m

```
clear all
close all
clc

     % This Antoine function is valid for the temperature
range between 273,20K
% to 647.3 K (so 0-374.15degC), so until critical temperature,
and a pressure range of 0.01-221 bar. It
% calculates the vapour pressure curve through
% lnp=lnp_c+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6). T must
be given in [K]
% source: Bruce E. Poling, John M. Prausnitz, John P.
O'Connell, The properties of gases and liquids, 5th edition; p
A.59

a = -7.77224;
b = 1.45684;
c = -2.71942;
d = -1.41336;
p_c = 220.64; %bar
T_c = 647.3; %K

choice = input ('Would you like a graph(1) or calculation(2)
');
mol_frac_l  =   input ('Mole fraction of H2O(l) between 0.8
and 1.0: ');

if choice == 1;
    T = 350; % K
    tau = (1-(T/T_c));
    for i=1:50
            tau = (1-(T/T_c));

p_vp=exp(log(p_c)+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6));

            %saving T and p_vp into vectors
            Temp(i)=T;
            p_vp_sat(i)=p_vp;
            p_vp_sat_x(i)=p_vp * mol_frac_l;

            T=T+1;

    end
    % making plot
    figure (1)
    hold;
    plot(Temp,p_vp_sat,'b', Temp, p_vp_sat_x, 'r')
    xlabel('Temperature [K]')
    ylabel('Saturation Pressure H20 [Bar]')
    title('Vapour Pressure Curve by Wagner')
   legend('vapour pressure of pure H20','vapour pressure of
solution','Location','Best')
 %  axis(273 ,320 ,0,3)
```

```
elseif choice == 2;
    T  =   input ('Calculate pressure decrease at Temperature
[K]: ');
   tau = (1-(T/T_c));


p_vp=exp(log(p_c)+(T_c/T)*(a*tau+b*tau^1.5+c*tau^3+d*tau^6));
            New_P_sat_x = p_vp * mol_frac_l
            dp= New_P_sat_x - p_vp
end
```

5 Debye_Huckel.m

```
clc
close all
clear all

% calculating log gamma ± by Debye-Huckel

% log10(gamma_x) =  -A*Z_x^2*sqrt(I)

% gamma_x   =     activity coefficient
% A         =     constant, 0.51 M^-(0.5) at 298K!
% I         =     ionic strength of solution given by 0.5
SUM(c_j*Z_j^2)
% c_j       =     concentration
% z_j       =     charge of ion j
% Summation within I is taken over all the ions in solution

A=0.51; %[M ^-.5]
choice = input('calculation(1) or plot(2)? ');

if choice==1
    solutechoice = input('NaCl (1) or Na2SO4 (2) MgSO4 (3)?
');

    if solutechoice==1;
        % 1 NaCl <--> 1 Na+ + 1 Cl-

        %charge of ions
        z_pos= 1; %Na+
        z_neg= -1; %Cl-
        conc= input('concentration in [mol]');

        %calculating concentration of ions
        c_Na =   1*conc ;
        c_Cl =   1*conc ;

        %calculating Ionic strength
        I=0.5*(c_Na*(z_pos^2)+c_Cl*(z_neg^2))

        %calculating activity coefficient
        gamma_Na=10^(-A*(z_pos^2)*sqrt(I))
        gamma_Cl=10^(-A*((z_neg)^2)*sqrt(I))
        gamma_NaCl=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I))


    elseif solutechoice==2
        %  1 Na2So4 <--> 2 Na+ + 1 SO4 (2-)

        %charge of ions
        z_pos= 1; %Na+
        z_neg= -2; %SO4 (2-)
        conc= input('concentration in [mol]');

        %calculating concentration of ions
        c_Na =   2*conc ;
```

```
        c_SO4 =   1*conc ;

        %calculating Ionic strength
        I=0.5*(c_Na*z_pos^2+c_SO4*(z_neg)^2)

        %calculating activity coefficient
        gamma_Na=10^(-A*(z_pos^2)*sqrt(I))
        gamma_SO4=10^(-A*((z_neg)^2)*sqrt(I))
        gamma_NaSO4=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I))

    elseif solutechoice==3

        % 1 MgSO4 <--> 1 Mg2+ + 1 SO4 (2-)

        %charge of ions
        z_pos= 2; %Mg2+
        z_neg= -2; %SO4 (2-)
        conc= input('concentration in [mol]');

        %calculating concentration of ions
        c_Mg =   1*conc ;
        c_SO4 =   1*conc ;

        %calculating Ionic strength
        I=0.5*(c_Mg*z_pos^2+c_SO4*z_neg^2)

        %calculating activity coefficient
        gamma_Mg=10^(-A*z_pos^2*sqrt(I))
        gamma_SO4=10^(-A*z_neg^2*sqrt(I))
        gamma_mgso4=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I))

    end

elseif choice==2

% 1 NaCl <--> 1 Na+ + 1 Cl-

%charge of ions
z_pos= 1; %Na+
z_neg= -1; %Cl-
conc=0.0;%concentration Mol/l

for i=1:101

    % calculating concentration of ions
    c_na =   1*conc ;
    c_cl =   1*conc ;

    % calculating Ionic strength
    I=0.5*(c_na*z_pos^2+c_cl*z_neg^2);

    % calculating activity coefficient
    gamma_na=10^(-A*z_pos^2*sqrt(I));
    gamma_cl=10^(-A*z_neg^2*sqrt(I));
    gamma_nacl=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I));
    log_gamma_nacl=(-A*abs(z_pos)*abs(z_neg)*sqrt(I));
```

```
    % save answers
    conc_saved(i,:)=conc;
    ionicstrength_NaCl(i,:)=I;
    wortelI_1(i,:) = sqrt(I);
    gamma_NaCl(i,:)=gamma_nacl;
    log_gamma_NaCl_saved(i,:)= log_gamma_nacl;
    conc = conc + 0.01;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    % 1 Na2So4 <--> 2 Na+ + 1 SO4 (2-)

    %charge of ions
    z_pos= 1; %Na+
    z_neg= -2; %SO4 (2-)
    conc= 0.0;%concentration Mol/l

for i=1:101

    %calculating concentration of ions
    c_Na2 =   2*conc ;
    c_SO4 =   1*conc ;

    %calculating Ionic strength
    I=0.5*(c_Na2*z_pos^2+c_SO4*z_neg^2);

    %calculating activity coefficient
    gamma_Na2=10^(-A*z_pos^2*sqrt(I));
    gamma_SO4=10^(-A*z_neg^2*sqrt(I));
    gamma_naso4=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I));
    log_gamma_naso4=(-A*abs(z_pos)*abs(z_neg)*sqrt(I));

    % save answers
    conc_saved2(i,:)=conc;
    ionicstrength_Na2SO4(i,:)=I;
    wortelI_2(i,:) = sqrt(I);
    gamma_Na2SO4(i,:)= gamma_naso4;
    log_gamma_Na2SO4_saved(i,:)= log_gamma_naso4;
    conc = conc + 0.01;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    % 1 MgSO4 <--> 1 MG2+ + 1 SO4 (2-)

    %charge of ions
    z_pos= 2; %Mg2+
    z_neg= -2; %SO4 (2-)
    conc= 0.0;%concentration Mol/l

for i=1:101

    %calculating concentration of ions
    c_Mg =   1*conc ;
    c_SO4 =   1*conc ;
```

```
    %calculating Ionic strength
    I=0.5*(c_Mg*z_pos^2+c_SO4*z_neg^2);

    %calculating activity coefficient
    gamma_Mg=10^(-A*z_pos^2*sqrt(I));
    gamma_SO4=10^(-A*z_neg^2*sqrt(I));
    gamma_mgso4=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I));
    log_gamma_mgso4=(-A*abs(z_pos)*abs(z_neg)*sqrt(I));

    % save answers
    conc_saved3(i,:)=conc;
    ionicstrength_MgSO4(i,:)=I;
    wortelI_3(i,:) = sqrt(I);
    gamma_MgSO4(i,:)= gamma_mgso4;
    log_gamma_MgSO4_saved(i,:)= log_gamma_mgso4;
    conc = conc + 0.01;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


    % 1 CaCO3 <--> 1 Ca2+ + 1 CO3 (2-)

    %charge of ions
    z_pos= 2; %Ca2+
    z_neg= -2; %CO3 (2-)
    conc= 0.0;%concentration Mol/l

for i=1:101

    %calculating concentration of ions
    c_Ca =   1*conc ;
    c_CO3 =   1*conc ;

    %calculating Ionic strength
    I=0.5*(c_Ca*z_pos^2+c_CO3*z_neg^2);

    %calculating activity coefficient
    gamma_Ca=10^(-A*z_pos^2*sqrt(I));
    gamma_CO3=10^(-A*z_neg^2*sqrt(I));
    gamma_caco3=10^(-A*abs(z_pos)*abs(z_neg)*sqrt(I));
    log_gamma_caco3=(-A*abs(z_pos)*abs(z_neg)*sqrt(I));

    % save answers
    conc_saved4(i,:)=conc;
    ionicstrength_CaCO3(i,:)=I;
    wortelI_4(i,:) = sqrt(I);
    gamma_CaCO3(i,:)= gamma_caco3;
    log_gamma_CaCO3_saved(i,:)= log_gamma_caco3;
    conc = conc + 0.01;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% ideal behaviour, when gamma = 1
wI=[0 1]';
ideal_behaviour=[0 0]';
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% making plot
figure (1)
plot(wortelI_1, log_gamma_NaCl_saved, 'c')
hold on
plot(wortelI_2, log_gamma_Na2SO4_saved, 'm')
hold on
plot(wortelI_3, log_gamma_MgSO4_saved, 'g')
hold on
plot(wortelI_4, log_gamma_CaCO3_saved, 'y--')
hold on
plot(wI, ideal_behaviour,'.-.')
 axis([0 0.25 -0.75 0.1])
legend ('NaCl 1:1', 'Na2SO4 2:1', 'MgSO4 1:1','CaCO3
1:1','Ideal behaviour', 'location','best')

xlabel('sqrt of Ionic Strength I [M^-0.5]')
ylabel('log10(gamma±)')
title('plot of log10 gamma VS sqrt of ionic strength')
end
```

6 Activity_Coefficient_Iteration.m

```
clc
clear all
close all


% Solubility product according to p 514

%NACl (s) <--> 1 NA+ (aq) + 1 CL- (aq)
%a_(Na+)^1*a_(Cl-)^1= K_sp = 37gr/100gr H2O
%a_Na^1*a_Cl^1=c_Na^1*c_Cl^1*gamma_±^2=K_sp

K_sp = (0.4755^2*(6.425*992.25)/1000)^2 %mol/L. 25.9 g/100mL
at 25deg; 39.1 g/100mL at 100deg(wikipedia); 6.425mol/kg
@313.15K 100mPa; solubility NACL at high pressures; rho_water
992.25kg/m3 @ 40deg (thermexcel); K=c_na*c_cl*gamma^2; assume
gamma=1)
c = input('Give concentration [mol/L] of NaCl ');
%concentration of NaCl mol/L
err= 1e-4; % maximum error

z_pos=1; % charge of positive (Na+)
z_neg=1; % charge of negative (Cl-)

n_pos = 1; % parts of positive (1 Na+)
n_neg = 1;% parts of negative (1 Cl-)
n_tot = n_pos +n_neg; % number of parts in which salt divides

s_0=(n_neg^n_neg)*(n_pos^n_pos);

% a_pos = ; % activity coefficient Na
% a_neg = ; % activity coefficient Cl

c_neg = n_neg*c; % concentration Cl-
c_pos = n_pos*c; % concentration Na+



gamma_old   = 1; % set gamma_± on 1
max         = 10; % maximum iterations
iter        = 0;

c = K_sp/(gamma_old^n_tot); % eq 12.72; this is c=(s)(2s)^2
s = (c/s_0)^(1/n_tot); % mol/L ; this is concentration s


for i = 1:max;
    iter        = iter +1; % iteration counter
    gamma_new   = gamma_old;

    % now calculate ionic strength using value of s. We need
the ionic
    % strength to put in equation 11.57 on page 464
    % ln (gamma)=-((1.73|z_pos*z_neg|(I)^0.5)/(1+(I)^0.5),
with I in mol/L
```

```
    % I=0.5(c_Na+c_Cl)


    I = 0.5*(s*n_pos*z_pos^2+s*n_neg*z_neg^2); % mol/L; eq.
11.52

    gamma_old = exp(-
((1.173*(z_pos*z_neg)*(I)^0.5)/(1+(I)^0.5))); % 11.57

    s = ((K_sp/(gamma_old^n_tot))/s_0)^(1/n_tot);



    er =(gamma_new-gamma_old).^2;
    if (abs(er)<err), break, end

end
iter
s
Activity_Coefficient=gamma_old
```