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Modelling of Liquid-Vapour Equilibria in the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ and $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{NaCl}$ Systems to 270°C

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Résumé — Modélisation des équilibres liquide-vapeur dans les systèmes $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ et $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{NaCl}$ jusqu'à 270°C — Cet article présente un modèle thermodynamique dissymétrique d'équilibre liquide-vapeur dans les systèmes $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ et $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{NaCl}$ en dessous du point critique de l'eau (250°C pour H_2S , 270°C pour CO_2). La phase vapeur est décrite par une équation d'état cubique. L'eau et les composants gazeux de la phase aqueuse liquide sont respectivement décrits par la loi de Raoult et la loi de Henry combinées avec un modèle de Redlich-Kister de solutions régulières, permettant de calculer les coefficients d'activité. Après une analyse de la base de données expérimentales, plus de 80 % pour CO_2 et 92 % pour H_2S des pressions calculées des isoplethes concernant les solutions aqueuses diffèrent de moins de 5% des données expérimentales, ce qui est comparable à l'incertitude expérimentale. Bien que le modèle ne soit pas optimisé sur la composition de la phase vapeur, les compositions calculées sont correctes au-dessus de 100°C . L'effet du sel est modélisé en combinant le modèle de Pitzer pour le calcul du coefficient d'activité de l'eau dans la solution aqueuse et une extension de la loi de Setchenow. Les hypothèses à la base de ce modèle induisent sa validité pour des pressions inférieures à 300 bar.

Abstract — Modelling of Liquid-Vapour Equilibria in the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ and $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{NaCl}$ Systems to 270°C — An unsymmetric thermodynamic model for the liquid-vapour equilibria in the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ and $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{NaCl}$ systems for temperatures below the critical point of water (250°C for H_2S , 270°C for CO_2) is presented. The vapour phase is described by a cubic Equation of state. The water and gas components in the liquid aqueous phase are respectively described by Raoult's law and Henry's law combined with a Redlich-Kister's model of regular solutions for the activity coefficients of these two components. After an analysis of the experimental data base, more than 80% for CO_2 and 92% for H_2S of predicted pressures of aqueous isopleths deviate less than 5%, which is comparable to experimental uncertainty. Although the model is not fitted on the composition of the vapour phase, the predicted values are correct above 100°C . The salt effect is modelled by a combination of the model of Pitzer for the water activity and an extension of Setchenow's law. The hypotheses behind this model makes it applicable at pressures below 300 bar.

INTRODUCTION

The high value of the critical point of water (374.15°C) combined with the salting-out effect result in the existence of a large field in the P-T space of coexistence of two fluid phases. The temperature range up to 250°C corresponds to different geological environments of the upper crust such as sedimentary basins, geothermal and epithermal systems, and incipient metamorphism. Fluid inclusions may also provide invaluable information on the P-T conditions of trapping if immiscibility is identified (Pichavant *et al.*, 1982; Ramboz *et al.*, 1982). A calibration of the Raman techniques in H₂O-gas-salt systems at the homogenisation temperature using synthetic fluid inclusions, made using the aqueous phase coexisting with a vapour phase, and the subsequent use of these data for natural fluid inclusions is possible if the gas solubility in the aqueous phase is well known (Dubessy *et al.*, 2001; Guillaume *et al.*, 2003). The calculation of liquid-vapour equilibria in H₂O-gas-salt systems is also important in various contexts of waste confinement into subsurface reservoirs. The storage of acid gases in deep oil reservoirs will produce fluid phase equilibria in the water-gas-salt system. In addition to the heat budget, several phenomena accompany the immiscibility process from a single fluid phase and were summarised by several authors (Reed and Spycher, 1985; Drummond and Ohmoto, 1985; Shmulovich *et al.*, 1995):

- the increase in pH of the residual liquid phase by CO₂ or H₂S fractionation to the vapour phase with consequences on the hydrolysis and speciation of metals;
- the phase separation and different migration properties of the liquid and vapour phases;
- the frequent increase of the redox state resulting in the removal of H₂, CH₄ and H₂S from the system;
- the change of the mineral solubility due to the variations of all these parameters.

Therefore, the calculation of liquid-vapour equilibria in H₂O-gas-salt systems is important for many geological processes occurring in the upper crust.

There are essentially two ways for modelling liquid-vapour equilibria. The first one consists in using a single Equation of state to represent the thermodynamic properties of both phases. This approach is used for systems with non polar molecules or at least without electrolytes. However, there is no satisfactory Equation of state both for the water-rich salt-bearing aqueous phase and the gas-rich phase free of salts. Therefore, the approach chosen for this work consisted to use an unsymmetric model based on Henry's and Raoult's limiting laws for describing the liquid aqueous phase and a cubic Equation of state for the gas-rich phase.

This work has two aims:

- to write the Equations describing the liquid-vapour equilibrium in the H₂O-gas-salt system;

- to develop a software program enabling the calculation of the isopleths (lines at fixed composition in a temperature-pressure diagram) of the aqueous phase, coexisting with the vapour phase, and the composition of this vapour phase in the range 50-270°C and for NaCl concentrations up to 6 molal.

Three phase liquid-liquid-gas equilibria are not considered in this work.

1 THEORY

1.1 Calculation of Isopleths of the Liquid Phase

Two-phase equilibrium between an aqueous liquid phase and a vapour phase in a two component system (no salt) is fully described by the following set of Equations (1):

$$\begin{aligned} T^{\text{vap}} &= T^{\text{aq}} ; & P^{\text{vap}} &= P^{\text{aq}} ; \\ \mu_{\text{H}_2\text{O}}^{\text{vap}} &= \mu_{\text{H}_2\text{O}}^{\text{aq}} ; & \mu_{\text{gas}}^{\text{vap}} &= \mu_{\text{gas}}^{\text{aq}} \end{aligned} \quad (1)$$

Assuming thermal and mechanical equilibrium and using the fugacity instead of the chemical potential, the equilibrium Equations are:

$$f_{\text{H}_2\text{O}}^{\text{vap}} = f_{\text{H}_2\text{O}}^{\text{aq}} ; \quad f_{\text{gas}}^{\text{vap}} = f_{\text{gas}}^{\text{aq}} \quad (2)$$

According to the phase rule ($v = c + 2 - \phi$), the variance of a liquid-vapour equilibrium (two phases: $\phi = 2$) for a two component ($c = 2$) system is two. This means that there are two independent parameters among x_i^{aq} , y_i^{vap} , P and T , where x_i^{aq} is the mole fraction of component i in the aqueous phase, and y_i^{vap} is the mole fraction of component i in the vapour phase. Therefore, two of these intensive properties must be specified for the determination of the two remaining ones (Prausnitz *et al.*, 1986). In the case of the calculation of the projection of an isopleth in the space P - T , the temperature and the composition of the liquid aqueous phase (x_i^{aq}) are specified. The remaining variables are the pressure and the composition of the vapour phase (y_i^{vap}), which are the solutions of Equations (2). At this step, there are three ways to calculate aqueous isopleths depending on the method used for the calculation of the composition of the vapour phase. All the Equations given below are written for a specific temperature, corresponding to a point along the liquid aqueous isopleth.

First case: $y_{\text{H}_2\text{O}}^{\text{vap}} = 0$

With this hypothesis, the vapour phase is made exclusively of the gas component. As the concentration of one component is specified $y_{\text{H}_2\text{O}}^{\text{vap}} = 0$ or $y_{\text{gas}}^{\text{vap}} = 1$, the number of independent intensive variables of the system decreases to one. Thus, the only variable to be determined is the pressure and only one Equation remains to be solved:

$$f_{\text{gas}}^{\text{vap}} = f_{\text{gas}}^{\text{aq}} \quad (3)$$

The fugacity of the gas component in the vapour phase is calculated from the Equation:

$$f_{\text{gas}}^{\text{vap}} = (y_{\text{gas}}^{\text{vap}} = 1) \cdot \phi_{\text{gas}}^{\text{vap}}(P) \cdot P \quad (4)$$

where $\phi_{\text{gas}}^{\text{vap}}(P)$ is the fugacity coefficient of the gas component inside the pure vapour phase, calculated with an Equation of state, which depends only on P as T is fixed.

The fugacity of the gas component inside the aqueous liquid phase is represented by Henry's law, a limiting law, allowing the calculation of the concentration of a solute in a liquid phase at equilibrium with a vapour phase if the solute concentration is small. Its formulation is the Equation (5):

$$K_{\text{gas,aq}}^{P_{\text{sat}}} = \lim_{x_{\text{gas}}^{\text{aq}} \rightarrow 0} \left(\frac{f_{\text{gas}}^{\text{aq}}}{x_{\text{gas}}^{\text{aq}}} \right) \quad (5)$$

where $f_{\text{gas}}^{\text{aq}}$ is the fugacity of gas component in the aqueous phase, and P_{sat} is the saturation pressure of the pure solvent at the considered temperature (Prausnitz *et al.*, 1986). For the calculation, the limiting condition is no longer written although it stands. If the concentration of the solute deviates significantly from zero, the pressure P is no longer equal to the saturation pressure of the pure solvent. Therefore, an integration of Equation (5) is necessary from P_{sat} to P and results in Equation (6) called the Equation of Krichevsky and Kasarnovsky (Prausnitz *et al.*, 1986):

$$\begin{aligned} \ln \left(\frac{f_{\text{gas}}^{\text{aq}}}{x_{\text{gas}}^{\text{aq}}} \right) &= \ln K_{\text{gas,aq}}^{P_{\text{sat}}} + \frac{P_{\text{sat}}}{RT} \int_{P_{\text{sat}}}^P \frac{1}{v_{\text{gas}}^{\infty}} dP \\ &= \ln K_{\text{gas,aq}}^{P_{\text{sat}}} + \frac{\overline{v_{\text{gas}}^{\infty}} \cdot (P - P_{\text{sat}})}{RT} \end{aligned} \quad (6)$$

where $\overline{v_{\text{gas}}^{\infty}}$ is the molar volume at infinite dilution of the gas solute in the aqueous solvent at temperature T . The variations of $\overline{v_{\text{gas}}^{\infty}}$ with temperature along the saturation curve are taken into account using the model of Plyasunov *et al.* (2000a). However the change with pressure of $\overline{v_{\text{gas}}^{\infty}}$ above 330°C precludes its integration with pressure considering it is constant as done in Equation (6). Therefore the model is limited in temperature to 300°C. Moreover Equation (6) shows that the only unknown is pressure for the calculation of an isopleth (T and $x_{\text{gas}}^{\text{aq}}$ are specified for the calculation of an isopleth):

$$f_{\text{gas}}^{\text{aq}} = \Psi_H(P) \quad (7)$$

Therefore using Equation (4), the equilibrium condition is written:

$$\phi_{\text{gas}}^{\text{vap}}(P) \cdot P = \Psi_H(P) \quad (8)$$

This Equation with only one unknown, P , is solved by an iterative procedure. This procedure is convenient for pressure-temperature conditions far from the critical line of the H₂O-gas system to satisfy the physical assumption of a quasi water-free vapour phase. This approach was used by Duan *et al.* (1992) in the CH₄-H₂O-NaCl system up to 250°C, with the liquid phase modelled by Pitzer's model. However, the water content inside the vapour phase cannot be neglected.

Second case: $y_{\text{H}_2\text{O}}^{\text{vap}} \neq 0$ and addition of partial pressure of gases and water in the vapour phase.

This case, taking into account the presence of water molecules in the vapour phase, was treated previously in two ways. In the first one, the composition of the vapour phase is directly linked to pressure according to Equation (9):

$$y_{\text{gas}}^{\text{vap}} = \frac{P - P_{\text{sat}}}{P} \quad (9)$$

This approach was used by Drummond (1981) in his PhD Thesis. It is valid only for weak vapour phase density and low pressure. The fugacity coefficient of the gas component in the vapour phase ($\phi_{\text{gas}}^{\text{vap}}$) depends on the composition of the vapour phase if the vapour phase is not considered as ideal. This dependence is a function of pressure according to Equation (9), and thus equilibrium is described by Equation (10) with P as the only unknown, as in the first case:

$$\begin{aligned} y_{\text{gas}}^{\text{vap}} \cdot \phi_{\text{gas}}^{\text{vap}}(P) \cdot P &= \Psi_H(P) \text{ or} \\ \left(\frac{P - P_{\text{sat}}}{P} \right) \cdot \phi_{\text{gas}}^{\text{vap}}(P) \cdot P &= \Psi_H(P) \end{aligned} \quad (10)$$

Third case: no hypothesis on the composition of the vapour phase. This is the correct and theoretically well founded approach. A second Equation is required dealing with the water component:

$$f_{\text{H}_2\text{O}}^{\text{vap}} = f_{\text{H}_2\text{O}}^{\text{aq}} \quad (11)$$

Both the water and gas fugacities inside the vapour phase are calculated with the same Equation of state that describes the vapour phase. The fugacity of water in the liquid aqueous phase is deduced from Raoult's law Equation and takes into account the effect of pressure via the Poynting correction (Prausnitz *et al.*, 1986):

$$f_{\text{H}_2\text{O}}^{\text{aq}} = (1 - x_{\text{gas}}^{\text{aq}}) \cdot P_{\text{sat}} \cdot \phi_{\text{H}_2\text{O}}^{\text{sat}} \cdot \exp \left[\int_{P_{\text{sat}}}^P \frac{V_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP \right] \quad (12)$$

where $\phi_{\text{H}_2\text{O}}^{\text{sat}}$ is the fugacity coefficient of water at saturation pressure for pure water which is calculated with the Equation of state for the vapour phase; $\overline{V_{\text{H}_2\text{O}}^{\text{liq}}}$ is the molar volume of pure water.

The vapour composition and pressure are solutions to the set of two following Equations:

$$\begin{aligned}
 f_{\text{H}_2\text{O}}^{\text{aq}} &= f_{\text{H}_2\text{O}}^{\text{vap}} \text{ or } (1 - x_{\text{gas}}^{\text{aq}}) \cdot P_{\text{sat}} \cdot \phi_{\text{H}_2\text{O}}^{\text{sat}} \\
 &\cdot \exp \left[\int_{P_{\text{sat}}}^P \frac{V_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP \right] = (1 - y_{\text{gas}}^{\text{vap}}) \cdot P \cdot \phi_{\text{H}_2\text{O}}^{\text{vap}} \\
 f_{\text{gas}}^{\text{aq}} &= f_{\text{gas}}^{\text{vap}} \text{ or } K_{\text{gas, aq}}^{P_{\text{sat}}} \cdot x_{\text{gas}}^{\text{aq}} \\
 &\cdot \exp \left(\frac{v_{\text{gas}}^{\infty} \cdot (P - P_{\text{sat}})}{RT} \right) = y_{\text{gas}}^{\text{vap}} \cdot P \cdot \phi_{\text{gas}}^{\text{vap}}
 \end{aligned} \quad (13)$$

where the fugacity coefficients of components in the vapour phase ($\phi_{\text{H}_2\text{O}}^{\text{sat}}$ and $\phi_{\text{gas}}^{\text{vap}}$) are calculated with the Equation of state of the vapour phase and depend on pressure and the composition of the vapour phase.

At this step of the thermodynamic model, the aqueous solution containing water and gas is assumed to be ideal, which results in activity coefficients of the solute and of the solvent in the aqueous phase equal to one. For highly insoluble gases such as methane or nitrogen at low temperature this hypothesis could be valid because the perturbations of the structure of the liquid remain very weak and because the interactions between two gas molecules are unlikely due to their large average distance. However, this assumption does not stand at least for aqueous solutions containing gases with higher solubilities such as carbon dioxide or hydrogen sulfide (Caroll and Mather, 1992, 1993) and the correct system of Equations is the following (14):

$$\begin{aligned}
 \gamma_{\text{H}_2\text{O}}^{\text{aq}} \cdot (1 - x_{\text{gas}}^{\text{aq}}) \cdot P_{\text{sat}} \cdot \phi_{\text{H}_2\text{O}}^{\text{sat}} \cdot \exp \left[\int_{P_{\text{sat}}}^P \frac{V_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP \right] \\
 = (1 - y_{\text{gas}}^{\text{vap}}) \cdot P \cdot \phi_{\text{H}_2\text{O}}^{\text{vap}}
 \end{aligned} \quad (14)$$

$$\gamma_{\text{gas}}^{\text{aq}*} \cdot K_{\text{gas, aq}}^{P_{\text{sat}}} \cdot x_{\text{gas}}^{\text{aq}} \cdot \exp \left(\frac{v_{\text{gas}}^{\infty} \cdot (P - P_{\text{sat}})}{RT} \right) = y_{\text{gas}}^{\text{vap}} \cdot P \cdot \phi_{\text{gas}}^{\text{vap}}$$

where $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$ and $\gamma_{\text{gas}}^{\text{aq}*}$ and are respectively the activity coefficients of water and the gas solute in the aqueous liquid phase which requires to be modelled at least as a function of temperature and composition. The superscript * points out the different normalisation conditions of these two activity coefficients:

$$\gamma_{\text{gas}}^{\text{aq}*} \rightarrow 1 \text{ when } x_{\text{gas}}^{\text{aq}} \rightarrow 0 \text{ and } \gamma_{\text{H}_2\text{O}}^{\text{aq}} \rightarrow 1 \text{ when } x_{\text{H}_2\text{O}}^{\text{aq}} \rightarrow 1$$

According to Prausnitz *et al.* (1986), the superscript* designates the activity coefficient defined with respect to a reference of an ideal dilute solution in the sense of Henry's

law whereas the activity coefficient $\gamma_{\text{gas}}^{\text{aq}}$ is defined with respect to a reference state of an ideal solution in the sense of Raoult's law. $\gamma_{\text{gas}}^{\text{aq}}$ is related to $\gamma_{\text{gas}}^{\text{aq}*}$ by Equation (15):

$$\frac{\gamma_{\text{gas}}^{\text{aq}}}{\gamma_{\text{gas}}^{\text{aq}*}} = \lim \gamma_{\text{gas}}^{\text{aq}} \text{ when } x_{\text{gas}}^{\text{aq}} \rightarrow 0 \text{ or } \frac{\gamma_{\text{gas}}^{\text{aq}}}{\gamma_{\text{gas}}^{\text{aq}*}} = \gamma_{\text{gas}}^{\infty, \text{aq}} \quad (15)$$

where $\gamma_{\text{gas}}^{\infty, \text{aq}}$ is the activity coefficient at infinite dilution of the gas in the aqueous phase.

As the concentration of the gas remains small in the aqueous phase, less than 2 mol%, the aqueous solution of gas and water can be considered as a regular or slightly non ideal solution for which Margules' Equations are relevant (Anderson and Crerar, 1993). The Redlich-Kister's form of the excess energy G^E of a mixture can be written as a function of the mole fraction of components 1 and 2 (x_1 and x_2 with $x_1 + x_2 = 1$) following Equation (16):

$$\frac{G^E}{RT} = x_1 x_2 (B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots) \quad (16)$$

In this work, parameter D is considered to be zero. Using the classical Equations relating the activity coefficient γ_i of component i to the excess energy (17),

$$\ln \gamma_i = \frac{\partial (nG^E/RT)}{\partial n_i} \quad (17)$$

the activity coefficients of the gas component, the solute, and of the solvent (water) are given by Equations (18) and (19):

$$\ln \gamma_{\text{H}_2\text{O}}^{\text{aq}} = (B - C + 4Cx_{\text{gas}}^{\text{aq}})(x_{\text{gas}}^{\text{aq}})^2 \quad (18)$$

$$\ln \gamma_{\text{gas}}^{\text{aq}} = (B + C - 4Cx_{\text{gas}}^{\text{aq}})(x_{\text{H}_2\text{O}}^{\text{aq}})^2 \quad (19)$$

Equation (19) shows that $\gamma_{\text{gas}}^{\infty, \text{aq}} = \exp(B + C)$. Therefore:

$$\frac{\gamma_{\text{gas}}^{\text{aq}}}{\gamma_{\text{gas}}^{\text{aq}*}} = \exp(B + C) \text{ when } x_{\text{gas}}^{\text{aq}} \rightarrow 0$$

Therefore the Equation giving $\gamma_{\text{gas}}^{\text{aq}*}$ is the following:

$$\ln \gamma_{\text{gas}}^{\text{aq}*} = -x_{\text{gas}}^{\text{aq}} \cdot ((B + C)(x_{\text{H}_2\text{O}}^{\text{aq}} + 1) + 4C(x_{\text{H}_2\text{O}}^{\text{aq}})^2) \quad (20)$$

1.2 Presence of Salts

If NaCl is present, the vapour phase can be considered to be free of salt in this temperature range below the critical point of water. Therefore no additional equilibrium Equations are

required since the concentration of NaCl is fixed in the aqueous phase. The modifications of Equations (19) are detailed below:

- The calculations of P_{sat} and of the partial molar volume of water in the aqueous solution $\overline{V}_{\text{H}_2\text{O}}^{\text{liq}}$ are carried out in the H₂O-NaCl system at the considered temperature from Haas (1976). $\overline{V}_{\text{H}_2\text{O}}^{\text{liq}}$ is considered to be independent of pressure between P_{sat} and P .
- The effect of salt concentration on the molar volumes at infinite dilution of the gas v_{gas}^∞ is assumed to be independent of salt concentration, because there are no data or very few data.
- The activity coefficient of solute gases is assumed to be independent of salt concentration as a first assumption:

$$\gamma_{\text{gas}}^{\text{aq,NaCl}} = \gamma_{\text{gas}}^{\text{aq,NaCl}=0} \quad (21)$$

- The activity coefficient of water is considered to be the result of the effect of gas and salt according to Equation (22):

$$\gamma_{\text{H}_2\text{O}}^{\text{aq(gas,NaCl)}} = \gamma_{\text{H}_2\text{O}}^{\text{aq,NaCl}} \cdot \gamma_{\text{H}_2\text{O}}^{\text{aq,gas}} \quad (22)$$

where $\gamma_{\text{H}_2\text{O}}^{\text{aq,NaCl}}$ is calculated from the model of Pitzer (Silvester and Pitzer, 1977) and $\gamma_{\text{H}_2\text{O}}^{\text{aq,gas}}$ is calculated using Equation (18) as a function of the pseudo gas mole fraction $z_{\text{H}_2\text{O}}^{\text{aq}}$ in the pseudo binary H₂O-gas:

$$z_{\text{H}_2\text{O}}^{\text{aq}} = \frac{x_{\text{gas}}^{\text{aq}}}{x_{\text{gas}}^{\text{aq}} + x_{\text{H}_2\text{O}}^{\text{aq}}} \quad (23)$$

- The effect of salt concentration on the Henry's constants $K_{\text{gas,aq}}^{\text{Psat}}$, called the salting-out effect, is often modelled using the Setchenow relationships (Lewis *et al.*, 1961):

$$\log_{10}\left(S_{\text{gas,aq}}^\circ / S_{\text{gas,aq}}^{\text{NaCl}}\right) = k_s \cdot c_{\text{NaCl}} \quad (24)$$

where $S_{\text{gas,aq}}^\circ$ and $S_{\text{gas,aq}}^{\text{NaCl}}$ are respectively the solubility of the gas in the NaCl-free aqueous solvent and the solubility of the gas in the NaCl-bearing aqueous solvent; k_s is the Setchenow coefficient and c_{NaCl} is the salt concentration. This Equation can be rewritten with the Henry's constants as a function of salt concentration m_{NaCl} in the molality scale:

$$K_{\text{gas,aq},m_{\text{NaCl}}}^{\text{Psat}} = K_{\text{gas,aq}}^{\text{Psat}} \cdot 10^{m_{\text{NaCl}}} \quad (25)$$

This Equation is valid at one temperature. However, the salting-out effect is dependent on temperature and the temperature effect is usually modelled according to Equations (26).

$$K_{\text{gas,aq},m_{\text{NaCl}}}^{\text{Psat}} = K_{\text{gas,aq}}^{\text{Psat}} \cdot 10^{m_{\text{NaCl}} \cdot \beta(T)} \text{ or} \\ \log\left(\frac{K_{\text{gas,aq},m_{\text{NaCl}}}^{\text{Psat}}}{K_{\text{gas,aq}}^{\text{Psat}}}\right) = m_{\text{NaCl}} \cdot \beta(T) \quad (26)$$

Regression of experimental data on the H₂O-CO₂-NaCl and H₂O-H₂S-NaCl systems was not satisfactory using Equations (26). Therefore, we proposed a new formulation by Equation (27):

$$\log\left(\frac{K_{\text{gas,aq},m_{\text{NaCl}}}^{\text{Psat}}}{K_{\text{gas,aq}}^{\text{Psat}}}\right) = m_{\text{NaCl}}\beta_1(T) + m_{\text{NaCl}}^2\beta_2(T) \\ + m_{\text{NaCl}}^3\beta_3(T) \quad (27)$$

Finally this results in the following system of two Equations with two unknowns:

$$\gamma_{\text{H}_2\text{O}}^{\text{aq,NaCl}} \cdot \gamma_{\text{H}_2\text{O}}^{\text{aq,gas}} (1 - x_{\text{gas}}^{\text{aq}} - x_{\text{NaCl}}^{\text{aq}}) P_{\text{sat}} \cdot \phi_{\text{H}_2\text{O}}^{\text{sat}} \\ \cdot \exp\left[\int_{P_{\text{sat}}}^P \frac{\overline{V}_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP\right] = (1 - y_{\text{gas}}^{\text{vap}}) \cdot P \cdot \phi_{\text{H}_2\text{O}}^{\text{vap}} \\ \gamma_{\text{gas}}^{\text{aq}*} \cdot K_{\text{gas,aq},m_{\text{NaCl}}}^{\text{Psat}} \cdot x_{\text{gas}}^{\text{aq}} \cdot \exp\left(\frac{v_{\text{gas}}^\infty \cdot (P - P_{\text{sat}})}{RT}\right) \\ = y_{\text{gas}}^{\text{vap}} \cdot P \cdot \phi_{\text{gas}}^{\text{vap}} \quad (28)$$

2 EQUATIONS AND ALGORITHMS

2.1 The Equation of State of the Nonaqueous Phase

The Stryjek and Vera's Equation of state (Stryjek and Vera, 1986a, 1986b, 1986c) is chosen to model the fugacity coefficients of the different components inside the gas phase and the water fugacity of pure water along the saturation vapour phase. This is a cubic Equation of state derived from the Peng and Robinson's Equation that is recommended by Crovetto (1991) and Prini and Crovetto (1989).

2.2 Henry's Constants

The literature contains several formulations for the Henry's constants describing the solubility of simple gases in pure water. Plyasunov *et al.* (2000b) has developed a new model enabling the calculation of the Henry's constants up to the critical point of water with a high accuracy. For our purpose, we are interested for lower temperatures (< 300°C). Therefore, we used the correlation proposed by Harvey (1996) for many gases (Table 1).

2.3 Properties of the Aqueous Solution

The molar volumes of gases at infinite dilution ($\overline{v}_{\text{gas}}^\infty$) were calculated along the saturation curve of water (Plyasunov *et al.*, 2000a). They are assumed to be independent of pressure as the pressure used in these calculations is below 500 bar

and fitted as a function of temperature. Values of the Equation parameters for CO₂ and H₂S are given in Table 2. The saturation pressure and molar volume of the liquid phase along the liquid-vapour coexistence curve of the H₂O-NaCl system is calculated from Haas (1976).

TABLE 1

Parameters of the Henry's constant in the formalism of Harvey (1996):

$$\ln K_{\text{gas, aq}}^{\text{Psat}} = \ln P_{\text{sat}} + A_{\text{gas}}/T^* + B_{\text{gas}} \cdot (1-T^*)^{0.335}/T^* + C_{\text{gas}} \cdot (T^*)^{-0.41} \exp(1-T^*)$$

Solute	A_{gas}	B_{gas}	C_{gas}
CO ₂	-9.4234	4.0087	10.3199
H ₂ S	-5.7131	5.3727	5.4227

2.4 Estimation of the B and C Parameters of the Margules-Redlich-Kister's Equation

The B and C parameters are fitted *versus* temperature according to Equations (29):

$$B = a + bT + cT^2 + dT^3 \quad \text{and} \quad C = e + fT + gT^2 + hT^3 \quad (29)$$

For each temperature and gas concentration in the liquid aqueous phase, the activity coefficient $\gamma_{\text{gas}}^{\text{aq}}$ and $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$ are calculated iteratively in order to reproduce the experimental pressure and then the fitting parameters are adjusted over the experimental values (Appendix 1).

2.5 The Salt Effect

At each temperature, for a given isopleth (fixed gas and salt concentration in the aqueous phase), the Henry's constant, $K_{\text{gas, aq, m}_{\text{NaCl}}}^{\text{Psat}}$ is calculated iteratively according to the procedure described in Appendix 2. Then the values are fitted with a polynomial as suggested by Battistelli *et al.* (1997).

3 EXPERIMENTAL DATA BASE AND PARAMETERS OF THE MODEL

All the experimental solubility data of the gases in the liquid aqueous phase are given in different units in the literature. They were all converted into the molality and mole fraction scales.

3.1 Experimental Data of the H₂O-CO₂-NaCl System

Experimental data concern mainly the composition of the aqueous phase in terms of gas concentration at given pressure and temperature. Data are very rare for the non aqueous phase. The data source is the following: Bamberger *et al.* (2000), Briones *et al.* (1987), Dhorn *et al.* (1993), Drummond (1981), D'Souza *et al.* (1998), Gillepsie and Wilson (1982), King *et al.* (1992), Malinin and Savelyeva (1972), Malinin and Kurovskova (1975), Matous *et al.* (1969), Müller *et al.* (1988), Nighswander *et al.* (1989), Prutton and Savage (1945), Sako *et al.* (1991), Takenouchi and Kennedy (1964), Tödheide and Franck (1963), Wiebe and Gaddy (1939, 1941), Zawisza and Malesinska (1981), Zel'vinskii (1937). Values are reported in Table 3. Diamond and Akinfiyev (2003) have discussed in detail the criteria to discriminate experimental data. First, we did not take into account data below the critical point of pure carbon dioxide because our model does not calculate three phase equilibria (liquid aqueous solution, liquid carbon dioxide, vapour carbon dioxide). All the experimental data were plotted as isotherms in diagrams of total pressure *versus* carbon dioxide solubility in the aqueous phase. These diagrams allow the elimination of discontinuities and conflicting values. After this first selection, the model was fitted over the experimental data. Then the predictions of the model were compared with the experimental data and experimental data deviating by more than 15% were removed. These data correspond usually to high pressures, above 300 bar, and so to high density fluids of the "non"-aqueous phase. The total number of experimental data points used is 257. Ninety percent of calculated pressures differ by less than 8% from the experimental values.

Data of Rumpf *et al.* (1994) above 80°C are not consistent with the data of Drummond (1981), which cover the largest range of P-T-X conditions. In the absence of more experimental data, we did not take into account the data of Rumpf *et al.* (1994) without making a judgement on the quality of these data. In addition, Drummond (1981) obtained experimental data in two steps, first at increasing and then decreasing temperatures. For concentrations around 6 molal, the Henry's constants deduced from these two sets of experimental data are not consistent. It is worth noting that the spread of Henry's constants between the two sets of experimental data of Drummond (1981) covers the variations given by Rumpf *et al.*

TABLE 2

Regression of the data of Plyasunov *et al.* (2000a) using the fitting Equation:

$$\frac{1}{v_{\text{gas } i}^{\text{sat}}} = \sum_{j=0}^{j=4} v_{i,j} \cdot T^j$$

Gas i	$v_{i,0} \cdot 10^2$	$v_{i,1} \cdot 10^4$	$v_{i,2} \cdot 10^6$	$v_{i,3} \cdot 10^9$	$v_{i,4} \cdot 10^{12}$
CO ₂	2.439488129	5.790665261	-2.122757825	3.1918934075	-1.862906530
H ₂ S	-7.987367136	11.17890399	-4.091393094	6.3421129256	-3.701657751

(1994). For the H₂O-CO₂-NaCl system (Table 4), Drummond (1981) does not mention any formation of siderite which could modify the solubility of carbon dioxide. Did some unnoticed phenomenon occur which could modify liquid-vapour equilibrium and explain such conflicting values? The question remains open and underlines the need for more experimental data.

TABLE 3
Experimental data for the H₂O-CO₂ system

Reference	<i>P</i> (bar) ^a	<i>T</i> (°C)	Data
[1]	40.5-141.1	50-80	29, 23*
[2]	68.2-176.8	50	8, 0*
[3]	101.3-152	50-75	4, 0*
[4]	101-301	50	3, 0*
[5]	40.2-211.7	36.3-318.5	53, 42*
[6]	6.9-101.4	31.05-93.3	16, 7*
[7]	48.1-48.3	50-75	2, 2*
[8]	49-52.7	100-150	2, 2*
[9]	50-80	10-40	9, 9*
[10]	3.25-81.1	100-200	49, 46*
[11]	21.1-102.1	79.7-198.1	33, 4*
[12]	23-703	101-120	26, 0*
[13]	101.8-197.2	75.15-148.25	7, 0*
[14]	100-250	110-300	8, 4*
[15]	200	200-300	5, 3*
[16]	50-300	50-100	29, 21*
[17]	25-300	31.04-40	25, 15*
[18]	1.54-53.9	50-200	33, 28
[19]	19-95	50-100	55, 50*

a: range of selected temperatures or pressures; * number of data points selected.
[1]: Bamberger *et al.* (2000); [2]: Briones *et al.* (1987); [3]: D'Souza *et al.* (1998); [4]: Dhorn *et al.* (1993); [5]: Drummond (1981); [6]: Gillespie and Wilson (1982); [7]: Malinin and Savelyeva (1972); [8]: Malinin and Kurovskova (1975); [9]: Matous *et al.* (1969); [10]: Müller *et al.* (1988); [11]: Nighswander *et al.* (1989); [12]: Prutton and Savage (1945); [13]: Sako *et al.* (1991); [14]: Takenouchi and Kennedy (1964); [15]: Tödheide and Franck (1963); [16]: Wiebe and Gaddy (1939); [17]: Wiebe and Gaddy (1941); [18]: Zawisza and Malesinska (1981); [19]: Zel'vinskii (1937).

3.2 Experimental Data of the H₂O-H₂S-NaCl System

The experimental data base is shown in Table 5 for the NaCl free system. All the data above 270°C were not taken into account because the binary interaction parameters between H₂O and H₂S are determined for temperatures only up to 240°C. Most of the data are consistent. As suggested by Duan *et al.* (1996), data of Kozintseva (1964) underestimate solubility of H₂S compared to other data and thus were discarded. In general, the concentration of H₂S in the aqueous phase determined by Drummond (1981) is a little higher than the values given by Suleimenov and Krupp (1994) whilst the relationship is inverted above 240°C. In addition, the values of the Henry's constant calculated by Drummond (1981) are based on the assumption that the vapour phase behaves like a perfect gas, which explains the important discrepancy in the values of the Henry's constants. Some data from Barret *et al.* (1988) and Wright and Maas (1932) are not self-consistent and conflict with data from other sources: they were discarded. Data of Selleck *et al.* (1952) are considered only along the liquid-gas curve. Their data above 2 molal and data at high concentrations of Lee and Mather (1977) could not be included (above 1.8 molal) because the model could not converge for the determination of the activity coefficients in the aqueous phase for the following reasons:

- the condition of low gas concentration in the aqueous phase required both for the model of the activity coefficients in the aqueous phase and the validity of Henry's law is not fulfilled;
- the existence of a three phase equilibrium (liquid-liquid-vapour) is not included in our model.

After a first fitting of activity coefficients, some data were removed when the deviation in the calculation of pressure exceeded 15%.

For the H₂O-H₂S-NaCl system (Table 6), data of Drummond (1981) obtained at decreasing temperature were removed because the author noticed formation of pyrrhotite and H₂ due to corrosion of the stainless steel vessel. After a first fitting of the extended Setchenow's law, some values, which are not consistent with the model fitted over the set of experimental data, were removed.

TABLE 4
Experimental data for the H₂O-CO₂-NaCl system

Reference	<i>P</i> (bar)	<i>T</i> (°C)	<i>m</i> (NaCl)	Data
[1]	37-290	35-345	0.99-6.28	396, 287*
[2]	48.35-48.51	50-75	0.358-4.458	10, 10*
[3]	48.975-52.709	100-150	0.9978-5.9158	9, 8*
[4]	6.02-92.01	40.07-159.93	5.999	28, 25*
[5]	4.67-96.37	39.99-159.83	3.997-4.001	35, 22*

[1]: Drummond (1981); [2]: Malinin and Savelyeva (1972); [3]: Malinin and Kurovskova (1975); [4]: Nighswander *et al.* (1989); [5]: Rumpf *et al.* (1994).
* : number of selected data points.

TABLE 5
Experimental data for the H₂O-H₂S system

Reference	P (bar) ^a	T (°C) ^a	Data
[1]	1.01	23.5-94.5	39, 35*
[2]	0.47-0.95	0-49.987	36, 36*
[3]	1.01	2.1-29.82	14, 14*
[4]	8.21-52.28	41-241	75, 73*
[5]	1.01	25	1, 1*
[6]	$0.84-2.07 + P_{\text{sat atm}}$	160-330	14, 0*
[7]	1.548-66.704	10-180	325, 288*
[8]	3.93-138.61	20.8-321	49, 42*
[9]	0.37-2.24	37.78-171.11	66, 27*
[10]	6.90-68.95	5-60	26, 22*

a: range of selected temperatures or pressures; * number of data points selected
[1]: Barrett *et al.* (1988); [2]: Clarke and Glew (1971); [3]: Douabul and Riley (1979); [4]: Drummond (1981); [5]: Kendall and Andrews (1921); [6]: Kozintseva (1964); [7]: Lee and Mather (1977); [8]: Suleimenov and Krupp (1994); [9]: Wright and Maas (1932); [10]: Selleck *et al.* (1952).

TABLE 6
Experimental data for the H₂O-H₂S-NaCl system

Reference	P (bar)	T (°C)	m (NaCl)	Data
[1]	1.01	59.5-96.5	1-5	182, 177*
[2]	1.01	2.1-29.82	0.559-2.314	42, 42*
[3]	6.97-55.18	41-242	1-6.04	207, 151*
[4]	1.01	25	0.5-3	9, 9*
[5]	11.96-138.42	155.2-320.4	0.235-2.656	23, 15*

[1]: Barrett *et al.* (1988); [2]: Douabul and Riley (1979); [3]: Drummond (1981); [4]: Gamsjäger and Schindler (1969); [5]: Suleimenov and Krupp (1994).
*: number of selected data points.

TABLE 7
Fitting parameters of the B and C parameters of the Margules-Redlich-Kister Equation (29)

	CO ₂	H ₂ S
B		
a	-1127.63016458677	-2407.93265898133
b	11.8665759834639	16.9917300698207
c	-0.0363815939147719	-0.0369144016195112
d	0.0000344533889448619	0.0000244723762962793
C		
e	359.662899252007	823.685566149131
f	-3.88804875551428	-5.85727510585188
g	0.0120996653413114	0.0128724402817956
h	-0.0000115603635771203	-0.0000086802035546012
R^2	0.66	0.85

4 RESULTS

4.1 The H₂O-CO₂-NaCl System

Values of the fitting parameters of the Redlich-Kister's model (Eqs. 18, 20 and 29) are given in Table 7. The reproducibility of the experimental data for the pressure is

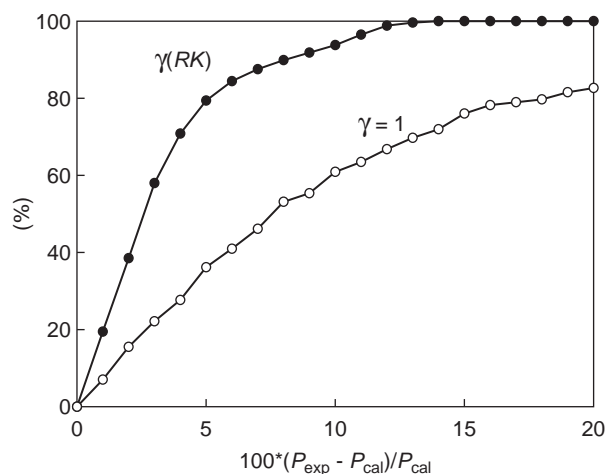


Figure 1

System H₂O-CO₂: percentage of pressure data reproduced with errors expressed by $100*(P_{\text{exp}} - P_{\text{cal}})/P_{\text{cal}}$ where P_{exp} and P_{cal} are respectively the experimental and calculated pressures. $\gamma(RK)$ curve is calculated using the fitted model (non-ideal behaviour of the aqueous solution and pressure calculated with Equation (14); $\gamma = 1$ curve corresponds to the ideal behaviour of aqueous solution (pressure calculated with Equation (13)).

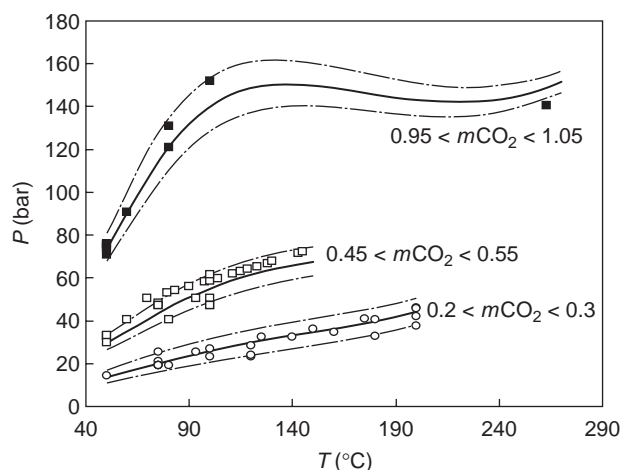


Figure 2

System H₂O-CO₂: comparison of experimental data and the calculated values with the model. As the CO₂ concentrations are not exactly identical within each set of data, three isopleths bracketing the compositions were calculated for each set of values. The lines represent the calculated isopleths with the concentration of CO₂ in molal.

significantly improved when the activity coefficients of water and CO₂ in the aqueous phase are taken into account (Fig. 1). More than 79 and 93% of the calculated pressure differ respectively by less than 5 and 10% from the experimental

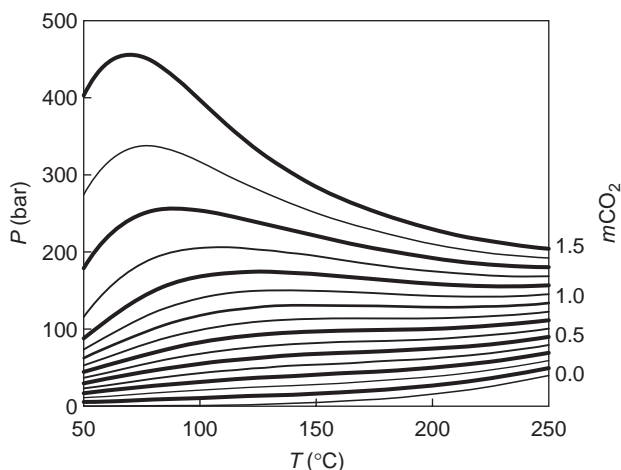


Figure 3

Isoleths in the system H_2O-CO_2 for mCO_2 between 0 and 1.5 molal by steps of 0.1 molal and for $mNaCl = 0$.

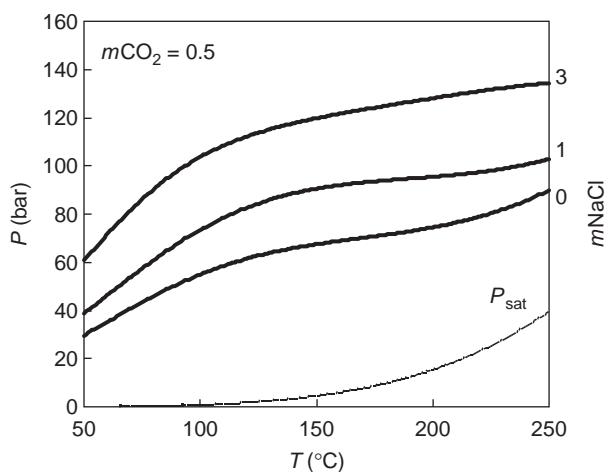


Figure 4

Isoleth of the liquid aqueous phase in the system H_2O-CO_2-NaCl for $mCO_2 = 0.5$ molal and for different NaCl concentrations between 0 and 3 molal. P_{sat} is the saturation line of pure water.

values with this model whereas the proportion falls at 36% at 5% accuracy with the assumptions $\gamma_{H_2O}^{aq} = \gamma_{CO_2}^{aq} = 1$. A comparison between experimental data and the model is illustrated in the pressure-temperature plane (Fig. 2). The isopleths in the $P-T$ plane are given in Figure 3. The model was not constrained using the vapour composition. To verify the model, the estimation of the composition of the vapour phase is compared with respect to the experimental data (Table 8). Up

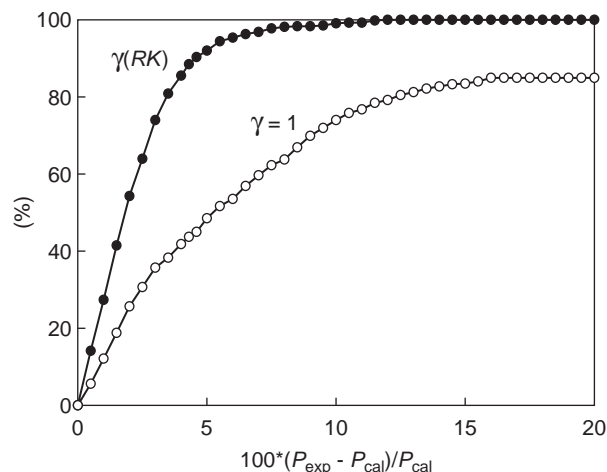


Figure 5

System H_2O-H_2S : percentage of pressure data reproduced with errors expressed by $100(P_{exp} - P_{cal})/P_{cal}$ where P_{exp} and P_{cal} are respectively the experimental and calculated pressures. $\gamma(RK)$ curve is calculated using the fitted model (non ideal behaviour of the aqueous solution and pressure calculated with Equation (14)); $\gamma = 1$ curve corresponds to the ideal behaviour of aqueous solution (pressure calculated with Equation (13)).

to 100°C and above 100 bar, the model overestimates the concentration of water in the gaseous phase. However the predictions are acceptable above 120°C. More data will be required to optimise the binary interaction parameters between H_2O and CO_2 in the vapour phase, which was not within the scope of this work.

Parameters used to model the salting-out effect of Equation (26) are given in Table 9. Some isopleths with the same gas concentration and different salt concentrations are shown in Figure 4.

4.2 The $H_2O-H_2S-NaCl$ System

The values of the fitting parameters of the Redlich-Kister's model are given in Table 7. The reproducibility of the experimental data for the pressure is significantly improved when the activity coefficients of water and H_2S in the aqueous phase are taken into account (Fig. 5). More than 92% of the calculated pressures differ less than 5% from the experimental with this model whereas it is only 50% with the assumptions $\gamma_{H_2O}^{aq} = \gamma_{H_2S}^{aq} = 1$. A comparison between experimental data and the model is illustrated in the pressure-temperature plane (Fig. 6). Different isopleths of the H_2O-H_2S system are plotted in Figure 7. As for the CO_2-H_2O system, the fitting of the model was not optimised using the composition of the

TABLE 8

Experimental and calculated composition of the vapour phase in the system H₂O-CO₂.

P_{exp} : experimental pressure; P_{calc} : calculated pressure; $m\text{CO}_2$: concentration (molality) of CO₂ in the aqueous phase;
 $y\text{H}_2\text{O}_{\text{exp}}$ (%): experimental concentration of water in mole per mil; $y\text{H}_2\text{O}_{\text{calc}}$ (%) calculated concentration of water in mole per mil;
 $\Delta y/y(\%) = 100*(y\text{H}_2\text{O}_{\text{exp}}-y\text{H}_2\text{O}_{\text{calc}})/y\text{H}_2\text{O}_{\text{exp}}$

Ref. [1]						
T (°C)	P_{exp} (bar)	$m\text{CO}_2$	$y\text{H}_2\text{O}_{\text{exp}}$ (%)	P_{calc} (bar)	$y\text{H}_2\text{O}_{\text{calc}}$ (%)	$\Delta y/y$ (%)
50	25.3	0.433	6.20	25.12	6.81	-9.91
50	50.7	0.769	3.83	50.12	5.06	-32.14
50	76	1.005	3.50	74.13	5.64	-61.12
50	101.3	1.143	4.49	96.61	9.60	-113.71
75	25.3	0.304	18.16	24.90	19.95	-9.83
75	101.3	0.92	8.29	98.14	13.67	-64.85
75	152	1.097	9.56	140.64	21.72	-127.22
Ref. [2]						
T (°C)	P_{exp} (bar)	$m\text{CO}_2$	$y\text{H}_2\text{O}_{\text{exp}}$ (%)	P_{calc} (bar)	$y\text{H}_2\text{O}_{\text{calc}}$ (%)	$\Delta y/y$ (%)
75	25.3	0.302	18.16	24.73	20.05	-10.40
75	50.7	0.564	10.87	50.09	13.28	-22.17
93.3	25.3	0.242	34.71	23.73	40.90	-17.84
93.3	50.7	0.473	19.7	48.94	25.21	-27.97
93.3	101.4	0.816	13.74	97.27	21.62	-57.35
Ref. [3]						
T (°C)	P_{exp} (bar)	$m\text{CO}_2$	$y\text{H}_2\text{O}_{\text{exp}}$ (%)	P_{calc} (bar)	$y\text{H}_2\text{O}_{\text{calc}}$ (%)	$\Delta y/y$ (%)
100	3.25	0.025	288	3.37	306.23	-6.33
100	6	0.054	155	6.15	171.92	-10.91
100	9.2	0.088	107	9.45	114.92	-7.40
100	11.91	0.116	77	12.21	90.99	-18.16
100	14.52	0.145	69	15.10	75.31	-9.15
100	18.16	0.183	54	18.97	61.94	-14.71
100	23.07	0.231	45	23.97	51.15	-13.67
120	5.99	0.039	337	6.13	333.93	0.91
120	9.39	0.071	205	9.57	218.90	-6.78
120	12.65	0.101	160	12.84	166.90	-4.31
120	16.31	0.133	122	16.38	134.15	-9.96
120	19.95	0.166	102	20.09	112.32	-10.12
120	24.12	0.202	83	24.19	96.04	-15.71
120	28.48	0.239	74	28.49	84.13	-13.69
140	6.5	0.022	569	6.10	602.58	-5.90
140	9.26	0.047	406	8.94	418.22	-3.01
140	11.93	0.073	317	11.92	319.32	-0.73
140	16.03	0.103	242	15.39	252.49	-4.34
140	20.1	0.139	200	19.62	203.29	-1.65
140	32.47	0.242	128	32.03	134.34	-4.96
160	8.78	0.022	732	8.72	719.14	1.76
160	11.44	0.047	579	11.63	548.06	5.34
160	14.17	0.073	476	14.68	441.49	7.25
160	17.77	0.103	388	18.23	362.38	6.60
160	21.83	0.139	323	22.53	299.99	7.12
160	25.88	0.171	275	26.39	261.38	4.95
160	34.08	0.242	211	35.10	205.80	2.47
180	14.39	0.045	728	15.21	677.24	6.97
180	21.01	0.103	522	21.98	484.38	7.21
180	26.15	0.150	431	27.53	396.92	7.91
180	32.8	0.208	359	34.48	327.38	8.81
180	40.7	0.275	300	42.65	274.95	8.35
180	49.1	0.343	257	51.10	238.70	7.12
200	20.0	0.038	767	19.79	802.00	-4.56
200	24.94	0.087	629	25.31	642.92	-2.21
200	31	0.143	514	31.68	527.83	-2.69
200	37.6	0.208	426	39.18	440.44	-3.39
200	45.7	0.279	365	47.51	376.02	-3.02
200	60.4	0.398	292	61.80	306.60	-5.00
200	20.27	0.051	755	21.25	751.99	0.40
200	26.38	0.109	592	27.80	591.60	0.07
200	34.0	0.178	471	35.71	476.35	-1.13
200	42.0	0.250	392	44.09	399.48	-1.91
200	51.2	0.327	332	53.22	343.67	-3.52
200	65.2	0.441	276	67.08	288.69	-4.60
200	81.1	0.579	238	84.49	246.32	-3.50

[1]: Wiebe and Gaddy (1939); [2]: Gillespie and Wilson (1982); [3]: Müller *et al.* (1988).

TABLE 9

Fitting parameters for the calculation of the salting out effect on the Henry's constants in the systems H₂O-CO₂-NaCl and H₂O-H₂S-NaCl. The values of $K_{\text{gas,aq},m\text{NaCl}}^{\text{Psat}}$ are fitted to the Equation:

$$\log K_{\text{gas,aq},m\text{NaCl}}^{\text{Psat}} = \log K_{\text{gas,a}}^{\text{Psat}} + m_{\text{NaCl}} \cdot \beta_1(T) + (m_{\text{NaCl}})^2 \cdot \beta_2(T) + (m_{\text{NaCl}})^3 \cdot \beta_3(T) \quad \text{with } \beta_i^j(T) = \sum_{i=0}^4 B_i^j \cdot (T)^j$$

H ₂ O-CO ₂ -NaCl R ² = 0.83	B _i ⁰	B _i ¹ * 10 ²	B _i ² * 10 ⁴	B _i ³ * 10 ⁸	B _i ⁴ * 10 ¹¹
β ₁ (T)	3.114712456	-2.7655585	0.9176713976	-12.78795941	6.2704268351
β ₂ (T)	-2.05637458	2.081980200	-0.765857702	12.011325315	-6.790343083
β ₃ (T)	0.253424331	-0.26047432	0.0972580216	-1.551654794	0.8948557284
H ₂ O-H ₂ S-NaCl R ² = 0.74	B _i ⁰	B _i ¹ * 10 ²	B _i ² * 10 ⁴	B _i ³ * 10 ⁷	B _i ⁴ * 10 ¹⁰
β ₁ (T)	-12.4617636	12.69373100	-4.791540697	7.9817223650	-4.931093145
β ₂ (T)	5.327383011	-5.82779828	2.3650333285	-4.207913036	2.7628521914
β ₃ (T)	-0.75715275	0.831927411	-0.338668040	0.6037602785	-0.397049836

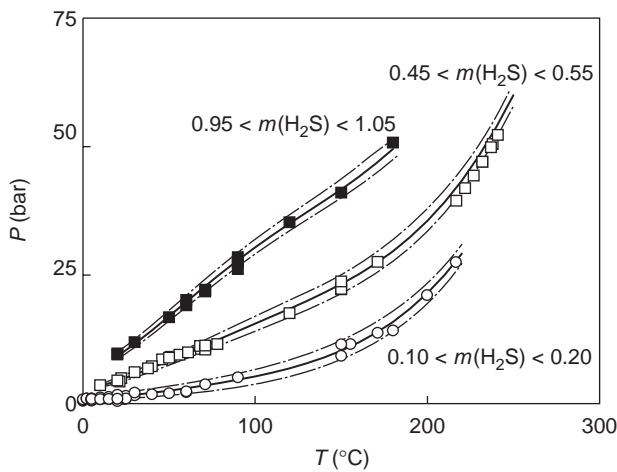


Figure 6

System H₂O-H₂S. Comparison of experimental data and the calculated values with the model. Experimental data are the different symbols. As the H₂S concentrations are not exactly identical within each set of data, three isopleths bracketing the compositions were calculated for each set of values. The lines represent the calculated isopleths with the concentration of H₂S in molal.

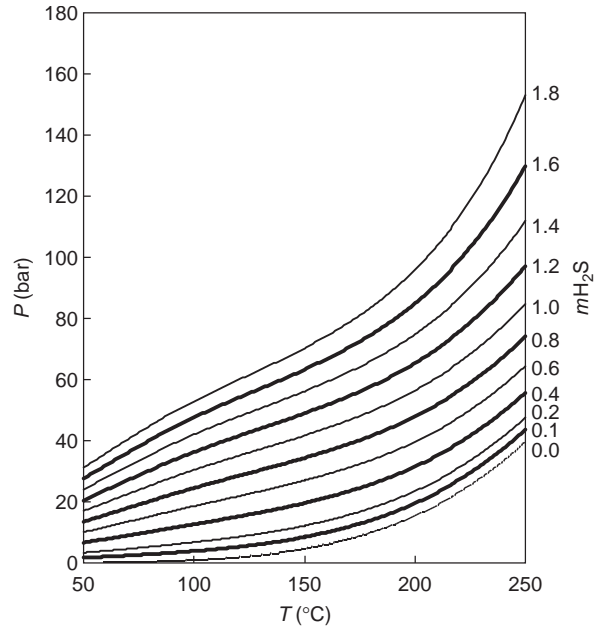


Figure 7

Isopleths in the system H₂O-H₂S for mH₂S between 0 (saturation pressure of pure H₂O) and 1.8 molal and for mNaCl = 0.

vapour phase since few data were available. The prediction of the composition of our model was checked with respect to the experimental data of Clarke and Glew (1971). Results (Table 10) are satisfactory since the maximum overestimation of the concentration of water is c.a. 5% at the exception of seven experimental data over sixty three.

Parameters used to model the salting-out effect of Equation (26) are given in Table 9. Some isopleths with the

same gas concentration and different salt concentrations are shown in Figure 8.

CONCLUSIONS

An unsymmetric thermodynamic model is proposed to calculate the liquid-vapour equilibrium in the system H₂O-CO₂-NaCl system to 270°C and 300 bar and to 250°C and 150 bar

TABLE 10

Composition of the vapour phase in the system H₂O-H₂S. Experimental data from [1]: Clarke and Glew (1971);
 [2]: Selleck *et al.* (1952). P_{exp} : experimental pressure; P_{calc} : calculated pressure; m_{H_2S} : concentration (molality) of H₂S in the aqueous phase;
 $y_{H_2O_{exp}}$ (‰) experimental concentration of water in mole per mile; $y_{H_2O_{calc}}$ (‰) calculated concentration of water in mole per mile

$$\Delta y/y \% = 100*(y_{H_2O_{exp}}(\text{‰}) - y_{H_2O_{calc}}(\text{‰})) / y_{H_2O_{exp}}(\text{‰})$$

Ref. [1]						
T (°C)	P_{exp} (bar)	m_{H_2S}	$y_{H_2O_{exp}}$ (‰)	P_{calc} (bar)	$y_{H_2O_{calc}}$ (‰)	$\Delta y/y$ (%)
0.001	0.55	1123	11.36	0.56	10.95	-3.59
0.001	0.66	0.346	9.52	0.67	9.16	-3.81
0	0.83	0.1697	7.60	0.85	7.28	-4.18
4.956	0.50	0.0862	17.72	0.51	17.29	-2.44
4.958	0.58	0.1009	15.22	0.59	14.82	-2.61
4.955	0.70	0.1223	12.62	0.72	12.27	-2.79
4.955	0.90	0.1568	9.92	0.92	9.61	-3.15
10.019	0.47	0.0687	26.66	0.47	26.24	-1.58
10.018	0.55	0.0807	22.83	0.55	22.43	-1.73
10.019	0.67	0.0984	18.85	0.67	18.49	-1.90
10.019	0.86	0.1272	14.71	0.86	14.38	-2.21
15.008	0.58	0.0735	29.90	0.58	29.63	-0.90
15.008	0.71	0.0903	24.54	0.71	24.27	-1.10
15.006	0.92	0.1182	18.95	0.92	18.68	-1.43
20.01	0.50	0.0547	47.35	0.50	47.22	-0.27
20.011	0.59	0.0649	40.25	0.59	40.09	-0.39
20.011	0.73	0.0803	32.88	0.72	32.69	-0.58
20.009	0.95	0.1061	25.21	0.95	24.97	-0.94
25.018	0.56	0.0534	57.50	0.55	57.59	0.15
25.016	0.68	0.0652	47.73	0.67	47.73	0.00
25.015	0.86	0.0840	37.55	0.85	37.45	-0.26
25.018	0.59	0.0564	54.64	0.58	54.67	0.06
25.017	0.73	0.0704	44.43	0.72	44.38	-0.12
25.017	0.96	0.0940	33.80	0.95	33.65	-0.43
25.03	0.56	0.0536	57.41	0.56	57.45	0.07
25.029	0.69	0.0669	46.62	0.69	46.57	-0.10
25.031	0.92	0.0897	35.35	0.91	35.21	-0.40
29.995	0.58	0.0482	74.79	0.57	75.02	0.31
29.992	0.71	0.0606	60.58	0.70	60.66	0.14
29.995	0.95	0.0818	45.79	0.94	45.72	-0.15
39.991	0.50	0.0312	150.02	0.49	151.26	0.83
39.991	0.62	0.0402	120.57	0.61	121.44	0.73
39.992	0.84	0.0561	89.84	0.82	90.30	0.51
49.987	0.55	0.0267	225.01	0.55	226.42	0.63
49.984	0.70	0.0353	180.00	0.69	180.95	0.53
49.985	0.95	0.0507	133.13	0.93	133.57	0.33
Ref. [2]						
T (°C)	P_{exp} (bar)	m_{H_2S}	$y_{H_2O_{exp}}$ (‰)	P_{calc} (bar)	$y_{H_2O_{calc}}$ (‰)	$\Delta y/y$ (%)
37.78	6.90	0.4589	10.6	6.12	11.55	8.94
37.78	10.34	0.6912	7.5	9.32	7.92	5.55
37.78	13.79	0.9313	6.0	12.70	6.09	1.49
37.78	17.24	1.1733	6.0	16.17	5.03	-16.17
37.78	20.69	1.4233	4.6	19.81	4.34	-5.58
71.11	6.90	0.3351	59.2	7.67	45.75	-22.72
71.11	10.34	0.4251	35.2	9.69	36.94	4.94
71.11	13.79	0.5720	27.4	13.03	28.43	3.76
71.11	17.24	0.7767	22.9	17.74	21.95	-4.13
71.11	20.69	0.8682	19.9	19.85	20.07	0.87
71.11	27.58	1.1675	11.3	26.78	16.10	42.47
71.11	34.48	1.4701	14.4	33.72	13.93	-3.27
71.11	41.37	1.7758	13.5	40.53	12.71	-5.84
104.44	13.79	0.4307	95.4	14.11	92.61	-2.92
104.44	27.58	0.8797	52.3	27.82	52.49	0.36
104.44	41.37	1.3068	40.3	40.65	40.25	-0.12
104.44	55.16	1.7227	35.3	52.45	35.06	-0.67
137.78	13.79	0.3182	212.5	14.72	246.89	16.18
137.78	27.58	0.7140	141.1	28.83	137.47	-2.57
137.78	41.37	1.0809	101.6	41.78	103.29	1.66
137.78	55.16	1.4233	84.5	53.55	87.51	3.57
137.78	68.95	1.7345	75.2	63.82	79.32	5.48
171.11	13.79	0.1614	601.9	14.40	583.59	-3.04
171.11	27.58	0.5267	317.2	28.56	315.71	-0.47
171.11	41.37	0.8739	222.8	42.05	229.63	3.07
171.11	55.16	1.2138	177.6	55.39	187.15	5.38
171.11	68.95	1.5873	153.4	70.36	160.34	4.52

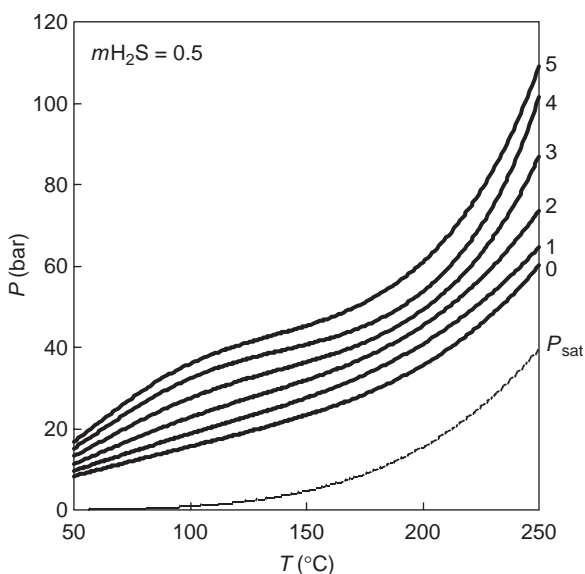


Figure 8

Isoleth of the liquid aqueous phase in the system H_2O - H_2S - $NaCl$ for $m_{H_2S} = 0.5$ molal and for different $NaCl$ concentrations between 0 and 5 molal labelled along the right y axis. P_{sat} is the saturation line of pure water.

in the system H_2O - H_2S - $NaCl$. It is based on the description of the gaseous phase by the Stryjek and Vera's Equation of state, derived from the Peng-Robinson's Equation of state, and the combination of Henry's and Raoult's laws to describe the aqueous liquid phase. With respect to the gases, the deviation of the aqueous phase from ideality is taken into account using a Redlich-Kister's Equation. For salt-bearing aqueous solution, the effect of the salt is taken into account both via the Pitzer's formalism for the activity coefficient of water and via an extended Setchenow's law for the salting-out effect of the gases. The available experimental data checked for their consistency (temperature, composition of aqueous liquid phase, pressure) were fitted in order to best reproduce the experimental pressures for each system. The reproduction of experimental data is quite satisfactory. Furthermore, the composition of the vapour phase predicted for the model is correct for both system, but only above $100^\circ C$ for the H_2O - CO_2 system. The model is restricted by construction to low gas concentrations and total pressures below 500 bar for the following reasons:

- the use of Henry's and Raoult's formalisms which are two limiting laws;
- the hypothesis of non variation with pressure of the molar volume of water and the molar volume at infinite dilution of the gases;
- the use of the Pitzer's Equations which were fitted along the saturation curves of the H_2O - $NaCl$ system;

- the use of the Redlich-Kister's Equation with two parameters to model the activity coefficients of water and gases which requires two assumptions:
 - the nondependence on pressure of activity coefficients;
 - the calculation of the activity coefficient of gases γ_{gas}^{aq} from γ_{gas}^{aq*} and the activity coefficient at infinite dilution $\gamma_{gas}^{\infty,aq}$ (Eqs. 15, 19 and 20), a procedure which is valid only at low gas concentrations and consequently at low pressures.

Taking into account the hypotheses underlying this model, the model can be introduced in more general software for solving water-rock interactions with the assumptions that the $NaCl$ concentration is assumed equal to the ionic strength of the aqueous solution. This hypothesis is valid for dominantly $NaCl$ -bearing aqueous solutions but not for $CaCl_2$ dominant aqueous solutions. In addition, it is worth noting that the calculation takes into account only the dissolved gaseous species $CO_{2,aq}$ and $H_{2S,aq}$ but not the corresponding ionic species such as HCO_3^- , CO_3^{2-} , HS^- , S^{2-} .

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APPENDIX 1

Equations and Procedure for Calculating the Activity Coefficient of Gas and Water in the Aqueous Solution

The activity coefficients of the gas in the aqueous phase $\gamma_{\text{gas}}^{\text{aq}}$ is calculated from the following Equation:

$$\gamma_{\text{gas}}^{\text{aq}} = \frac{y_{\text{gas}}^{\text{aq, nid, } P_{\text{exp}}}}{y_{\text{gas}}^{\text{aq, id, } P_{\text{cal}}}} \frac{\phi_{\text{gas}}^{P_{\text{exp}}}}{\phi_{\text{gas}}^{P_{\text{cal}}}} \frac{P_{\text{exp}}}{P_{\text{cal}}} \exp\left(\frac{\bar{v}_{\text{gas}}^{\infty}}{RT} (P_{\text{cal}} - P_{\text{exp}})\right) \quad (\text{A1})$$

$y_{\text{gas}}^{\text{aq, id, } P_{\text{cal}}}$ is the mole fraction of the gas in the nonaqueous phase calculated assuming an ideal mixing between gas and water in the aqueous solution by solving the system of Equations (13).

$y_{\text{gas}}^{\text{aq, nid, } P_{\text{exp}}}$ is the mole fraction of the gas in the nonaqueous phase calculated considering that the activity coefficient of gas and water in aqueous solution are not equal to 1 by solving the system of Equations (16).

$\phi_{\text{gas}}^{P_{\text{exp}}}$ is the fugacity of the gas component in the nonaqueous phase calculated at $T, P_{\text{exp}}, y_{\text{gas}}^{\text{aq, nid, } P_{\text{exp}}}$.

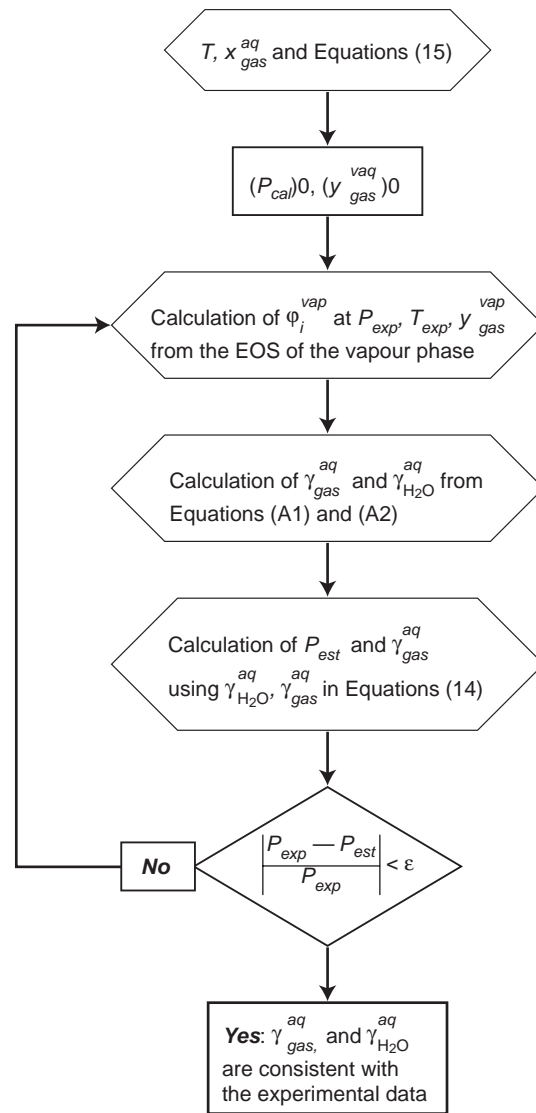
$\phi_{\text{gas}}^{P_{\text{cal}}}$ is the fugacity of the gas component in the nonaqueous phase calculated at $T, P_{\text{cal}}, y_{\text{gas}}^{\text{aq, id, } P_{\text{cal}}}$.

The activity coefficients of water in the aqueous phase $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$ is calculated from the following Equation:

$$\gamma_{\text{H}_2\text{O}}^{\text{aq}} = \frac{\left(1 - y_{\text{gas}}^{\text{aq, nid, } P_{\text{exp}}}\right) \phi_{\text{H}_2\text{O}}^{P_{\text{exp}}} P_{\text{exp}} \exp\left[\int_{P_{\text{sat}}}^{P_{\text{cal}}} \frac{V_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP\right]}{\left(1 - y_{\text{gas}}^{\text{aq, id, } P_{\text{cal}}}\right) \phi_{\text{H}_2\text{O}}^{P_{\text{cal}}} P_{\text{cal}} \exp\left[\int_{P_{\text{sat}}}^{P_{\text{exp}}} \frac{V_{\text{H}_2\text{O}}^{\text{liq}}}{RT} \cdot dP\right]} \quad (\text{A2})$$

The flowchart for the calculations of the activity coefficients of the gas component and water in the aqueous phase $\gamma_{\text{gas}}^{\text{aq}}$ and $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$ is illustrated below. ϵ is a number which measures the accuracy in pressure calculation. From the values of $\gamma_{\text{gas}}^{\text{aq}}$ and $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$ estimated from this procedure, the

parameters a, b, c, d , and e of Margules-Redlich-Kister's parameters B and C are estimated to best reproduce the activity coefficients according to Equations (18), (19) and (20) (values in Table 7).



Flowchart illustrating the procedure for estimating $\gamma_{\text{gas}}^{\text{aq}}$ and $\gamma_{\text{H}_2\text{O}}^{\text{aq}}$.

APPENDIX 2

Calculation of Henry Constant's for NaCl-Bearing Aqueous Solution

The composition of the aqueous phase and the pressure and temperature conditions are known. The only unknown in the Equation relative to the gas component is the composition of the vapour phase:

$$\gamma_{H_2O}^{aq} (1 - x_{gas}^{aq} - x_{NaCl}^{aq}) P_{sat} \cdot \phi_{H_2O}^{sat} \cdot \exp \left[\int_{P_{sat}}^P \frac{\overline{V}_{H_2O}^{liq}}{RT} \cdot dP \right] \\ = (1 - y_{gas}^{vap}) \cdot P \cdot \phi_{H_2O}^{vap}$$

Using this Equation, the gas concentration in the vapour phase y_{gas}^{vap} is calculated until convergence is obtained. Then the Henry's constant is derived with the following Equation at each temperature:

$$\gamma_{gas}^{aq*} \cdot K_{gas,aq,m_{NaCl}}^{P_{sat}} \cdot x_{gas}^{aq} \cdot \exp \left(\frac{\overline{v}_{gas}^{\infty} \cdot (P - P_{sat})}{RT} \right) \\ = y_{gas}^{vap} \cdot P \cdot \phi_{gas}^{vap}$$

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