



Originally published as:

De Lucia, M., Pilz, P., Liebscher, A., Kühn, M. (2015): Measurements of H₂ Solubility in Saline Solutions under Reservoir Conditions: Preliminary Results from Project H₂STORE. - *Energy Procedia*, 76, p. 487-494.

DOI: <http://doi.org/10.1016/j.egypro.2015.07.892>



European Geosciences Union General Assembly 2015, EGU

Division Energy, Resources & the Environment, ERE

Measurements of H₂ solubility in saline solutions under reservoir conditions: preliminary results from project H2STORE

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Abstract

A high-pressure/high-temperature reactor has been used to lead PVT and H₂-solubility experiments in saline solutions covering conditions for which no data are available in literature: salinity up to halite concentration, pressure up to 200 bar and temperature up to 373 K. The hereby presented preliminary results show significant deviations from theoretical models. Further analysis and more measurements are needed to assess precision and reproducibility of these measurements; however they pinpoint the importance of experimental work to reliably constrain predictive models.

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Peer-review under responsibility of the GFZ German Research Centre for Geosciences

Keywords: Hydrogen Storage, Solubility, Fluid-fluid interactions

1. Introduction

Underground gas storage is increasingly regarded as a technically viable option for meeting environmental targets and energy demand through storage in form of H₂ or CH₄, i.e. resulting from excess wind energy. Gas storage in salt caverns is nowadays a mature technology; in regions where favorable geologic structures such as salt diapires are not available, however, gas storage can only be implemented in porous media such as depleted gas and oil reservoirs or suitable saline aquifers. In such settings, a significant amount of in-situ gas components such as CO₂, CH₄ (and N₂) will always be present, making the CO₂/CH₄/H₂ system of particular interest. A precise estimation of the impact of their gas mixtures on the mineralogical, geochemical and petrophysical properties of specific reservoirs and caprocks is therefore crucial for site selection and optimization of storage depth.

In the framework of the collaborative research project H2STORE, the feasibility of industrial-scale gas storage in porous media in several potential siliciclastic depleted gas and oil reservoirs or suitable saline aquifers is being investigated by means of experiments and modeling on actual core materials from the evaluated sites. Among them are the Altmark depleted gas reservoir in Saxony-Anhalt and the Ketzin pilot site for CO₂ storage in Brandenburg (Germany).

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Further sites are located in the Molasse basin in South Germany and Austria. In particular, two work packages hosted at the German Research Centre for Geosciences (GFZ) focus on the fluid-fluid and fluid-rock interactions triggered H_2 and H_2 mixtures.

To this aim, a high P -high T reactor suitable for H_2 experiments has been built to expose core samples to H_2 and H_2/CO_2 mixtures under site-specific conditions: temperatures up to 200 °C and pressure up to 300 bar. The apparatus is detailed in section 3. A preliminary literature research for experimental data about H_2 solubility in aqueous, saline solutions has determined that no actual data are available at higher P , T and salinity, as illustrated in section 2. For this reason, we proceeded to perform PVT and solubility experiments in order to fill such gap and achieve more reliable predictions of fluid-fluid interactions.

2. State of the art: available solubility data and Equation Of State

A preliminary literature review has been performed in order to assess the available data for H_2 and its solubility in saline solutions under expected reservoir conditions. The data concerning solubility, in particular, are scarce and quite dated, stemming from the late seventies. Either only measurements at low pressure (1 bar) for salinity up to seawater (4% NaCl) [1] or for pressure up to 150 bar and 150 °C [2] are available. No actual data for higher ionic strengths have been found. Figure 1 gives an overview of the experimental data cited above, as long as the calculation of solubility performed through geochemical modeling following the expression of equation 1 using the established PHREEQC simulator [3] together with the `llnl.dat` thermodynamic database.

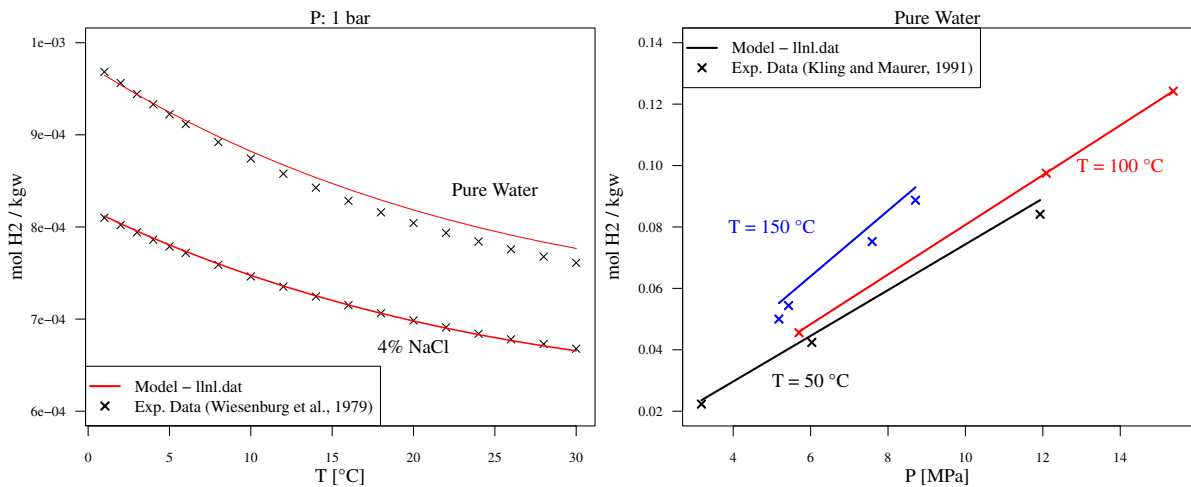


Fig. 1: Overview of the scarce solubility data available in literature, compared with the solubility calculated by geochemical model combined with the SR EOS with equation 1.

The solubility of a real gas in an aqueous solution can namely be calculated correcting for non-ideal behavior the Henry's law as in the following expression:

$$a_{H_2(aq)} = \frac{\varphi_{H_2} P_{H_2}}{K_H} \cdot \exp \left\{ -\frac{\bar{v}_{H_2}}{RT} (P_{H_2} - 1) \right\} \quad (1)$$

where $a_{H_2(aq)}$ is the activity of dissolved H_2 , P_{H_2} its partial pressure, \bar{v}_{H_2} the average apparent molar volume of H_2 in the pressure range $[1, P]$, φ_{H_2} the fugacity coefficient and K_H the Henry's constant.

The fugacity coefficient φ_{H_2} must be calculated with an Equation Of State (Abbreviated EOS in the following), which is a much better covered matter in literature, especially for high P , T . For the purpose of geochemical modeling, the third order virial EOS of Spycher and Reed [4] proved to be very accurate, if compared with the very recent

measurements of Sakoda et al. [5]. The form of this EOS for pure H₂ is:

$$\frac{P\hat{v}}{RT} = Z = 1 + (a/T^2 + b/T + c)P + (d/T^2 + e/T + f)P^2 \quad (2)$$

where $\hat{v} = V/n$ is the specific molar volume, and the numeric values for the six parameters are given in the first column of table (1). This EOS (abbreviated “SR” in the following) is a third order virial equation explicit in pressure, which has the advantage of being accurate in density. This allows a very easy derivation of fugacity coefficients, which is convenient for geochemical modeling and solubility calculations, as explained above.

From figure 1 it is clear that, for low salinity and low P, T , the models have acceptable accuracy. However, the absence of experimental data for higher salinity is striking. In the following sections we describe the set of experiments we performed and the preliminary results.

3. H₂ reactor and experimental setup

The experimental apparatus is constituted by a Büchi-MidiClave H₂-Reactor System certified for pressure up to 350 bar and temperature up to 250 °C. An overview of the system is showed in figure 2. The reactor vessel has a nominal volume of 1.0 liter (Type 3, CrNiMoTi-steel). A Büchi 1500 watt electric heating system with integrated water circuit cares for the temperature control of the reactor. The system integrates a Büchi pressflow gas controller with working pressures up to 400 bar, including a gas feed regulator; a Büchi Temperature–Cascade controller and a “Cyclone75” magnetic stirrer with “cc075” regulation complete the reactor. The apparatus can be controlled and data acquired through the “bls 2” software.

The gas feeds available for the experiments are H₂-Alphagaz1 by Air liquid (M: 2.02 g/mol, 99.999 mol% purity) and N₂-Alphagaz1 by Air liquid (M: 28.01 g/mol, 99.999 mol% purity). As for the synthetic reservoir fluids, double deionised water has been mixed with 20.0% NaCl (M: 58.44 g/mol, >99.8 mol% purity).

This reactor has been designed for long-term fluid-rock experiments and therefore its dimensions and control system are probably not best suited for PVT and solubility measurement, which would require high precision instruments and small control volumes. Nevertheless we conducted two sets of experiments, one with pure hydrogen in the reactor and one with hydrogen and saline solution (pure water or 20% NaCl) in order to measure, at least indirectly, solubility. The idea of the experiments is that measuring the pressure registered by the apparatus and knowing the total mass of H₂ injected in the otherwise closed system would suffice to determine the amount of gaseous and dissolved hydrogen in the reactor at equilibrium. Several hypotheses and assumptions are necessary for this evaluation, as will be discussed in subsection 4.2.

In the first pure-H₂ experiment, vacuum was pumped in the reactor and subsequently a well-defined amount of H₂ injected in several steps. Upon reaching a stationary state, a further amount of gas has been injected. The pressure increase due to the amount of injected hydrogen is the observable used in the analysis. The experiment has been repeated at 25, 50, 75 and 100 °C.

The solubility experiments have been conducted filling the vessel with a accurately weighted amount of solution, either pure water or 20 % NaCl solution. Then the reactor has been sealed and purged four times with nitrogen (approx 4 bar). The nitrogen has been subsequently evacuated, without pumping vacuum in the system to prevent a significant loss of aqueous solution, as observed in the first runs. Instead, by opening an outlet valve, atmospheric pressure has been reached. All the data from these experiment have been accordingly corrected taking into account the remaining partial pressure of nitrogen in the system and the differential with atmospheric pressure. After closing again the reactor, it was heated to reach the desired temperature and finally a step-wise injection of H₂ initiated. After each injection step, an appropriated time has been waited, with intermittent stirring of the solution, until a stationary reading of pressure was reached. This required up to several hours in these solubility experiments. The final P , amount of injected H₂ together with the known volume of the reactor and amount of solution constitute the experimental observation evaluated in the following section.

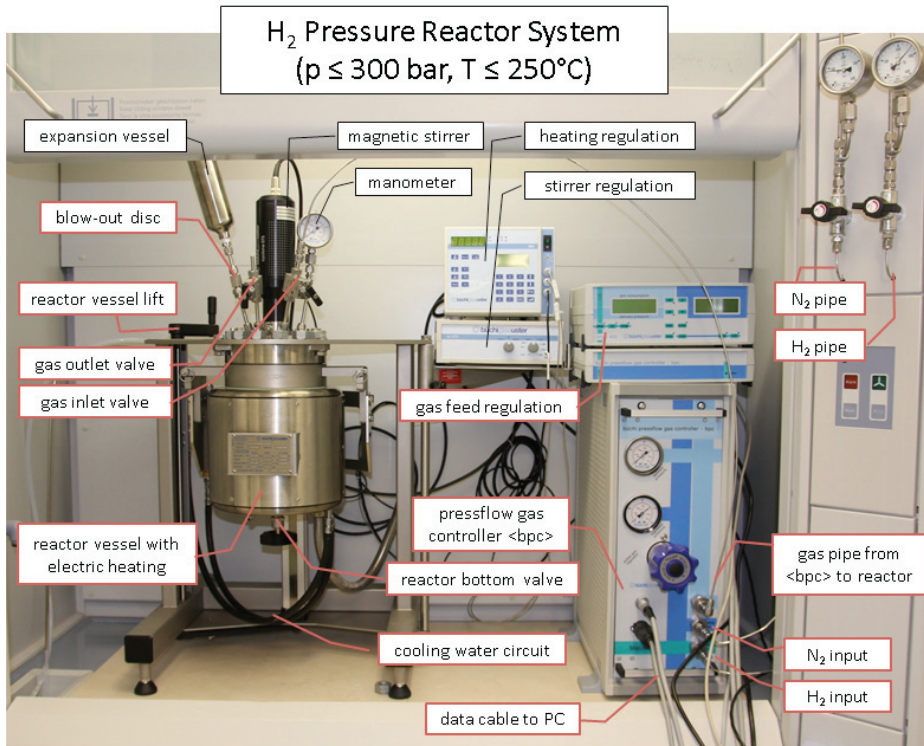


Fig. 2: The high P / high T Büchi reactor used for the experiments.

4. Preliminary results

4.1. Pure H_2 : EOS and dead volume determination

The first batch of experiments with pure H_2 has been used to measure the total volume of the system (main vessel and dead space) as well as to obtain PVT data for H_2 at low P and T . To do so, an indirect evaluation of the pressure reading through an equation of state is necessary. Rewriting equation 2 in terms of volume, it reads:

$$V = \frac{nRT}{P} \left(1 + a \frac{P}{T^2} + b \frac{P}{T} + cP + d \frac{P^2}{T^2} + e \frac{P^2}{T} + fP^2 \right) \quad (3)$$

An *a priori* knowledge of the total volume V occupied by the gas is not needed: it suffices to subtract member-wise two equations (3) written for two distinct states i and j from the pool of measurements. Developing such an expression we have:

$$V_i - V_j = \frac{n_i RT_i}{P_i} \left(1 + aP_i/T_i^2 + bP_i/T_i + cP_i + dP_i^2/T_i^2 + eP_i^2/T_i + fP_i^2 \right) - \frac{n_j RT_j}{P_j} \left(1 + aP_j/T_j^2 + bP_j/T_j + cP_j + dP_j^2/T_j^2 + eP_j^2/T_j + fP_j^2 \right) \quad (4)$$

which can be rearranged and simplified obtaining:

$$\frac{V_i - V_j}{R} = \frac{n_i T_i}{P_i} - \frac{n_j T_j}{P_j} + a \left(\frac{n_i}{T_i} - \frac{n_j}{T_j} \right) + b (n_i - n_j) + c (n_i T_i - n_j T_j) + d \left(\frac{n_i P_i}{T_i} - \frac{n_j P_j}{T_j} \right) + e (n_i P_i - n_j P_j) + f (n_i P_i T_i - n_j P_j T_j) \quad (5)$$

and finally:

$$\frac{V_i - V_j}{R} - \frac{n_j T_j}{P_j} - \frac{n_i T_i}{P_i} = a \left(\frac{n_i}{T_i} - \frac{n_j}{T_j} \right) + b (n_i - n_j) + c (n_i T_i - n_j T_j) + d \left(\frac{n_i P_i}{T_i} - \frac{n_j P_j}{T_j} \right) + e (n_i P_i - n_j P_j) + f (n_i P_i T_i - n_j P_j T_j) \quad (6)$$

The form of equation 5 is suitable to regress the apparent dependence of V to P and T (elastic and thermal dilation at larger P and T) using the a, b, c, d, e, f parameters from the SR EOS. In form of equation 6, after subtracting the previously calculated volumetric term on the left hand side of the equation, it is suitable to directly regress the parameters a, b, c, d, e, f against **pairs** of (P, T, n) of measured data, without explicit knowledge of the volume of the apparatus. The left-hand side of equation (6) is taken as observation points for the regressions.

The results of this procedure are given in table 1. The central column of the table displays the parameters fitted considering only the experimental points produced in the pure- H_2 experiments of this work. For this reason, it is only valid up to 100 °C and 150 bar, whereas, given that only few points are available at 100 °C, the precision actually rapidly declines after 75 °C. However, this form actually smooths or better filters out the systematic measurement errors and artifacts due to the employed experimental system and, for this reason, can be employed for the evaluation of solubility experiments, as will be showed in the next section. The third, rightmost column of table 1 displays the values obtained considering our data together with density measurements from [5] in the regression. This second regression can be regarded as proof of the mathematical procedure outlined above and as inclusion of lower T, P data into the dataset of [5], which is oriented towards higher P and T . It achieves excellent agreement with the published data, comparable to the SR EOS, and it is a little better at lower P ranges, as displayed in figure 3. Only density data have been considered here, so no comparison relative to, i.e., fugacity or virial coefficients has been performed.

Table 1: Parameters of the original virial EOS from [4], those fitted regressing only the data obtained in this study, and those fitted including also density data from [5].

	Spycher and Reed, 1988	This work - eq. (6)	This work - incl. data from [5]
a	-12.5908	$8.773\ 31 \times 10^3$	$-1.158\ 30 \times 10^2$
b	0.259 78	$-5.570\ 18 \times 10^1$	$7.230\ 62 \times 10^{-1}$
c	$-7.247\ 30 \times 10^{-5}$	$8.904\ 92 \times 10^{-2}$	$-5.951\ 11 \times 10^{-4}$
d	$0.471\ 94 \times 10^{-2}$	$-1.470\ 18 \times 10^2$	$1.219\ 98 \times 10^{-1}$
e	$-2.699\ 62 \times 10^{-5}$	$9.416\ 03 \times 10^{-1}$	$-5.606\ 51 \times 10^{-4}$
f	$2.156\ 22 \times 10^{-8}$	$-1.507\ 81 \times 10^{-3}$	$6.317\ 37 \times 10^{-7}$

It is important to stress out the fact that all the measurements at this point must be considered as preliminary. Further corrections and experiment repeats are to be performed in the future as we gather more and more experience and data with our laboratory setup. For this reason, the precise numerical results of the regression as well as the actual experimental readings are not included in this paper, since they will most probably undergo review and changes in the future.

4.2. Solubility experiments

The evaluation of these data requires the calculation of the volume occupied by the gaseous phase at equilibrium and consequently the amount of gaseous H_2 in the reactor. The difference between total injected hydrogen and that in the gas phase gives the amount of dissolved hydrogen.

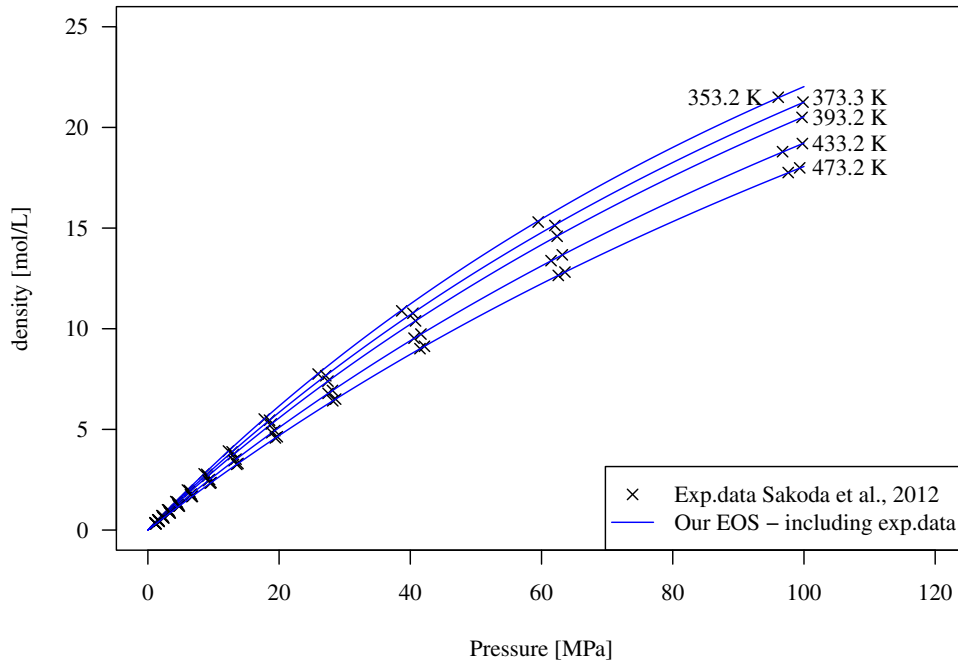


Fig. 3: Comparison of the newly fitted EOS combining the experimental data of this work and density data from [5]. The precision of the newly fitted EOS is comparable to the original expression of Spycher and Reed [4].

The volumes respectively occupied by the gas and the liquid (water) phase equals at all time the total volume of the system, which is a function of P, T :

$$V_{tot} = V_{gas} + V_{wat}$$

The volume of water equals the mass of solution M_{sol} multiplied by its specific volume v_s : $V_{sol} = v_s \cdot M_{sol}$. v_s is calculated through the correlation given by [6] as function of T, P and salinity. Assuming that through the dissolution of H_2 no relevant volume change in the water phase occurs, the volume of gas at the given experimental P and T can therefore be calculated. A further assumption is that the gas phase is composed by gaseous hydrogen and water vapor, whose vapor pressure is subtracted from the total pressure P_{abs} read by the apparatus. However, this contribution is rather small and with no evident impact on the results. Once the volume occupied by gas is calculated, its density and therefore its amount in moles is calculated through an EOS. Using the virial EOS we have:

$$n_{gas} = \frac{V_{gas}}{R} \cdot \left(\frac{T}{P_{H_2}} + \frac{a}{T} + b + c \cdot T + d \cdot \frac{P_{H_2}}{T} + e \cdot P_{H_2} + f \cdot P_{H_2} \cdot T \right)^{-1} \quad (7)$$

where P_{H_2} indicates the partial pressure of gaseous H_2 . From this equation is clear that the total amount x of dissolved H_2 in molal units can now be calculated as the difference from the total H_2 injected in the system, N_{total} , divided by the mass of water in solution m_{H_2O} : $x = (N_{total} - n_{gas})/m_{H_2O}$.

Figure 4 displays the interpretation of the experimental data using different EOS for the density of the gas phase, compared with the solubility calculated by geochemical models with PHREEQC, as well as the comparison between modeled and experimental solubility for the whole dataset (temperature up to 75 °C and salinity 0 and 20 %). Using the EOS fitted in this work matches best the data at 25 °C, certainly because of its smoothing of systematic errors in the measurements. However, these data do not match well the predictions if density of gas phase is calculated through the SR EOS or the EOS fitted including the data from [5]. Moreover, when looking at the discrepancy between

interpreted data and model predictions for 20% salinity on the right side of image 4, it is clear that the models predict a significantly smaller solubility than our data interpretation suggests.

Such discrepancy may have many reasons: systematic reading error from the pressure or temperature sensors; significant temperature deviation in the gas and aqueous phase at the moment of measurement; temperature gradients in the apparatus, i.e. in the pipes linking the reactor to the gas controller or the outlet valves. Further experiments are being conducted aimed at gathering more data, to ameliorate the knowledge of the experimental system on one hand and on the other to ensure the reproducibility of these measurements, which can not be assumed at the moment. At this time of writing it is not possible to further discriminate between experimental and interpretation errors; however, our preliminary dataset suggests that under the tested P, T and salinity the models are underestimating hydrogen solubility. More work is thus necessary to explain and validate the observations.

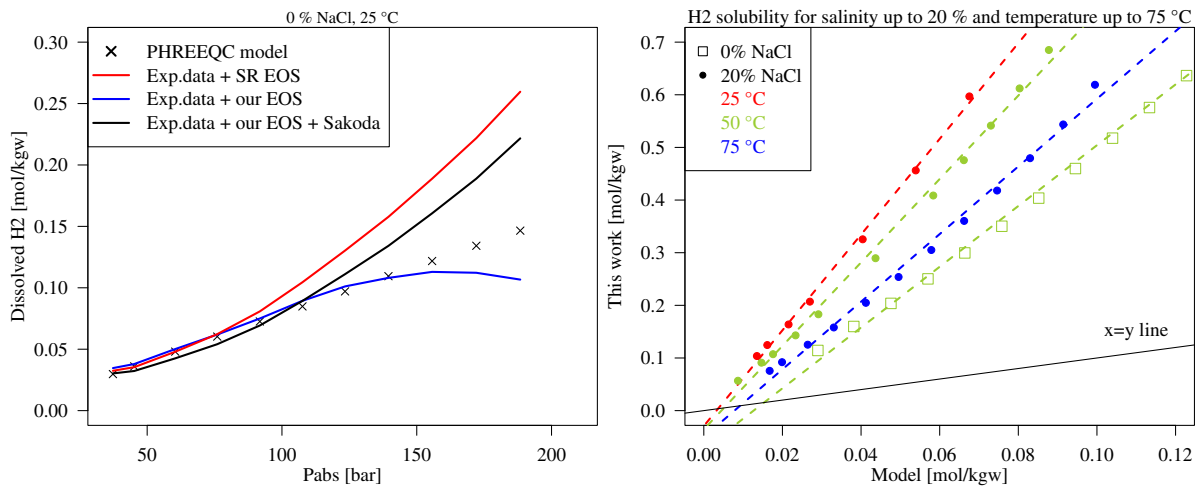


Fig. 4: Interpretation of the solubility data for pure water and 25 °C. Left, the influence of the employed EOS on the outcome of the evaluation for the run with pure water and 25 °C. On the right, the overview of the discrepancy between models and our preliminary data.

5. Summary and outlook

PVT and solubility measurements for H₂ in saline solutions under high P - high T conditions are being conducted at the German Research Centre for Geosciences. There is namely a lack of such data in the literature, and these experiments are required to reliably constrain predictive models of fluid-fluid and fluid-rock interactions.

In this contribution an evaluation method has been outlined to obtain PVT data and to interpret the solubility data obtained by the experimental apparatus. While the PVT data are in good agreement with literature and allow to obtain new regression values for the parameters of a third order virial Equation Of State, the solubility data are in disagreement with the theoretical predictions of the models. In particular, the interpretation of the experimental observations lay significantly above the solubility predicted by theoretical models. At the moment it is not possible to ascertain, from the preliminary data in our possession, whether the data are affected by excessive experimental errors, or the precision of the apparatus is insufficient for solubility measurements, or the employed models and interpretation procedure are wrong. More data and more analysis are therefore needed to deepen the understanding of the system.

Current and future experiments will extend the investigated temperature range up to 150 °C, reaching halite saturation and pressure up to 200 bar, and will also consider H₂ mixtures. The ultimate goal of this work is to better constrain geochemical and reactive transport models for feasibility assessment of H₂-storage in porous media.

Acknowledgments

H2STORE is part of the research and development program “Energiespeicher” funded by the German Federal Ministry of Education and Research (BMBF), grant n. 03SF0434B – GFZ Postdam. We thank E.on Gas Storage GmbH, GDF SUEZ E&P DEUTSCHLAND GmbH, Rohöl Aufsuchungs Aktiengesellschaft (RAG) Austria and RWE Gasspeicher GmbH for support and sample supply.

References

- [1] Wiesenburg D, Guinasso N. Equilibrium Solubilities of Methane, Carbon Monoxide, and Hydrogen in Water and Sea Water. *J Chem Eng Data* 1979;24(4):356-360.
- [2] Kling G, Maurer G. The solubility of hydrogen in water and in 2-aminoethanol at temperatures between 323 K and 423 K and pressures up to 16 MPa. *J Chem Thermodyn* 1991;23:531-541.
- [3] Parkhurst D, Appelo C. Users guide to PHREEQC (version 2). Tech. rep., U.S. Geological Survey, 1999.
- [4] Spycher N, Reed M. Fugacity coefficients of H₂, CO₂, CH₄, H₂O and of H₂O-CO₂-CH₄ mixtures: A virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling. *Geochim Cosmochim Acta* 1988;52:739-749.
- [5] Sakoda N, Shindo K, Motomura K, Shinzato K, Kohno M, Takata Y, Fujii M. Burnett PVT Measurements of Hydrogen and the Development of a Virial Equation of State at Pressures up to 100 MPa. *Int J Thermophys* 2012;33:381–395, doi:10.1007/s10765-012-1168-2.
- [6] Rowe AM, Chou JCS. Pressure–volume–temperature– concentration relation of aqueous NaCl solutions. *J. Chem. Eng. Data* 1970;15:61–66.