

Thermodynamic data for modelling sequestration of acid gases in geological brines

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A flow calorimetric technique was developed to measure the heats of mixing of two fluids in the temperature range from 298 to 473 K at pressures up to 40 MPa using an isothermal differential heat flux calorimeter SETARAM BT 2.15 equipped with a customized cell made of stainless steel. Measuring the heat effect of gas dissolution in a liquid as a function of concentration allows also to determine the gas saturation limit from the change in the calorimetric signal. This technique was specifically adapted for the measurements with acid gases (H₂S, CO₂) in water and salt solutions and a new experimental arrangement was set up to provide safe conditions of experiments. The influence of pressure and the salt concentration is documented at temperature of 323 K by results on the heats of solution and the solubility limits of carbon dioxide in water and in aqueous NaCl solutions up to 3 molal at pressures from 5 to 20 MPa. The enthalpic and solubility values obtained were compared with available literature data. The reasonable agreement suggests that this technique, beside being a reliable source of enthalpic data, is also suitable for the indirect determination of solubility.

1. Introduction

This study is related to the treatment of acid gases resulting from the combustion of fossil fuels, *i.e.* oil or coal, or present as constituents of natural gas. The gases in question are carbon dioxide (CO₂) and hydrogen sulphide (H₂S), each of them being perilous for the environment. The carbon dioxide is the principal cause of the so-called greenhouse effect leading to global warming. Hydrogen sulphide is highly toxic and is also responsible for acid rain. The severe control and significant reduction of emissions of acid gases is vital for preserving our environment and the quality of life on earth. There are different ways how to achieve this objective. On a long term level the main options are to reduce the energy consumption in general, to increase the efficiency of energy utilisation, or to replace fossil fuels by other energy sources without acid gas emissions, such as nuclear power or renewable energies. On a short term level an efficient acid gas removal from effluents of fossil fuel combustion or from natural gas must be envisaged. This procedure involves the capture, the transport and finally the geological storage of acid gases in depleted oil or gas reservoirs, unminable coal beds or in deep saline aquifers. Each type of storage has its advantages; the acid gas injected into an oil reservoir can enhance oil recovery,

methane can be displaced by acid gas during storage in coal beds. The sequestration in deep saline reservoirs is, nevertheless, the storage option with the highest global capacity. The acid gases injected under high pressure will partially dissolve in an aquifer and will also react with minerals to form carbonates. A suitable aquifer has a cap rock system with very low permeability, so that the possibility of leakage is reduced.

In order to provide thermodynamic data necessary for modelling sequestration in saline aquifers, an experimental method was developed to study the enthalpic and solubility effects connected with the dissolution of acid gases in water and salt solutions. The technique allows the simultaneous determination of the heat (enthalpy) of solution, which has its own practical value and of the gas solubility in a liquid phase. This approach was previously used to study the solubility and heat effects of carbon dioxide in aqueous alkanolamine systems used for capture of acid gases by Mathonat *et al.* [1-2]. This time the gas dissolution experiments serve for modelling the sequestration process in saline aquifers. They have to be performed in concentrated salt solutions over a large range of temperatures and pressures; in this connection a special experimental arrangement had to be set up for preventing corrosion.

2. Experimental Method

2.1. Experimental Arrangement The measurements are carried out using a customized mixing flow unit adapted to SETARAM BT 2.15 heat conduction differential calorimeter of Calvet type. The overall experimental arrangement is depicted in Fig. 1. The two fluids are introduced into stainless steel tubes of 1.6 mm o.d. by two high-pressure pumps. The fluids enter the mixing unit where the gas dissolves in the aqueous phase inside the mixing cell in good thermal contact with the thermopile of the calorimeter. An ISCO 100 DM pump is used for an acid gas (solute) and an ISCO 230 D pump for an aqueous solution (solvent). Typically the flow rates for an acid gas and an aqueous phase are in the range 0.005 - 0.1 ml/min and 0.2 - 0.7 ml/min, respectively. The acid gas pump is connected to a nitrogen tank that enables the system to be flushed. The pumps are calibrated with water. The pressure in the system is maintained constant to 0.2 MPa using a Mity Mite backpressure regulator placed at the end of the high-pressure line. The pressure is measured by three KELLER pressure gauges with accuracy to 0.25% of the full-scale. They

are placed at the outlets of the acid gas and aqueous phase pumps, and between the mixing cell and the backpressure regulator. The fluids are thermostated before entering the mixing cell by three preheaters, one external to calorimeter and two internal. The flow lines are kept at a constant temperature above 308 K in order to avoid the formation of hydrogen sulphide hydrates. The temperature of the calorimeter is set and controlled within 0.01 K using a SETARAM G11 electronic control system. Safety of measurements with acid gases is insured by working with specially adapted valves and check valves. Excess acid gases are scrubbed from the line using an alkaline solution.

2.2. Mixing unit The calorimeter is equipped with a customized mixing unit depicted in Fig. 2. It was designed and manufactured in the Laboratory for operation with acid gases and salt solutions. Its main part is a mixing cell allowing dissolution of an acid gas in an aqueous phase and providing for quantitative transfer of heat between its outer surface and the thermopile of the calorimeter.

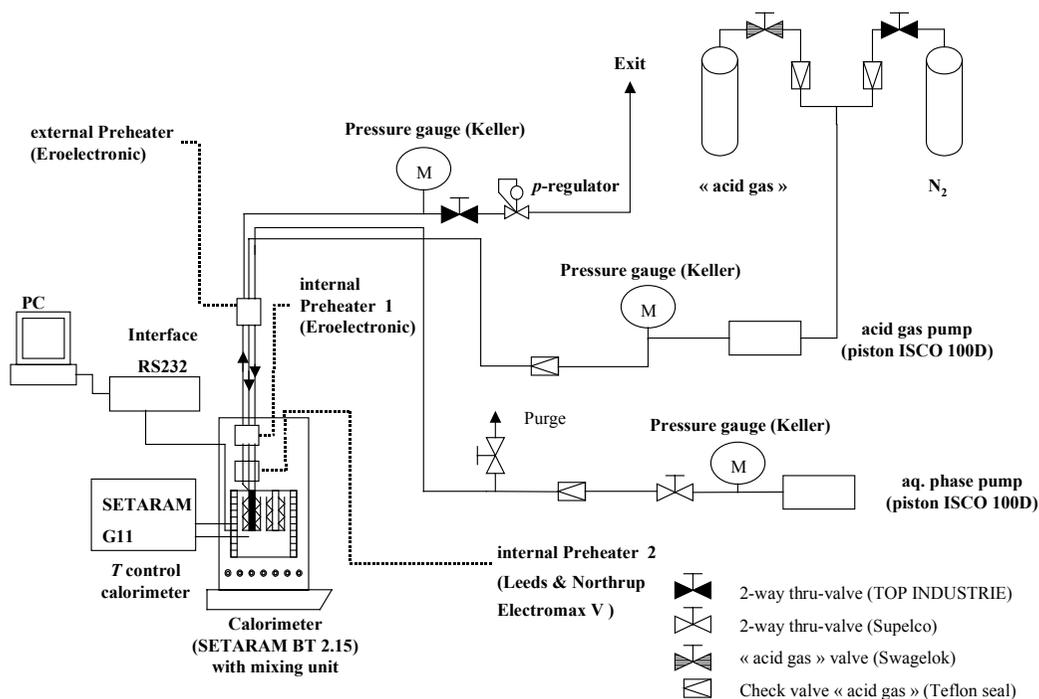


Fig. 1. Scheme of the experimental arrangement: calorimeter, mixing unit, flow system, temperature and pressure controls.

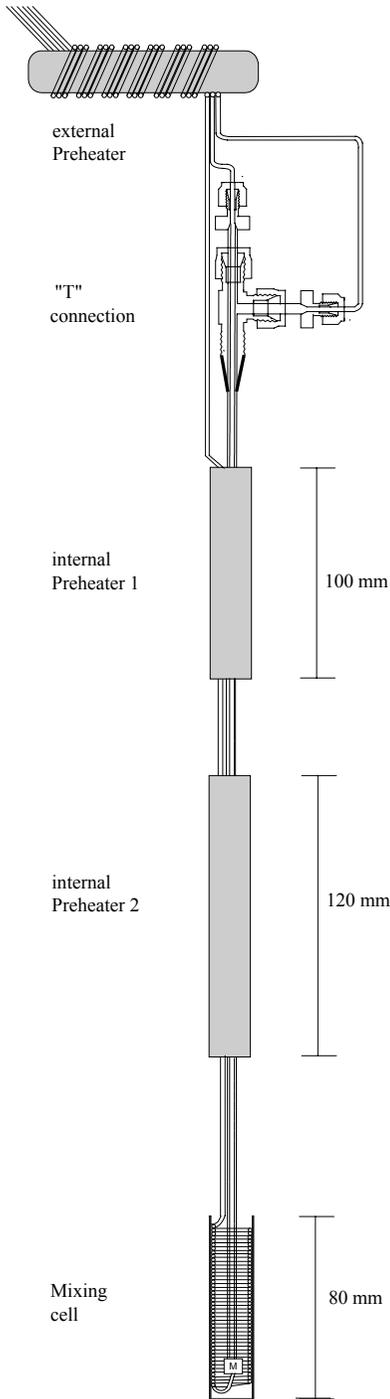


Fig. 2. Mixing unit constructed at LTSP.

A “T” connection in the upper part is used for supplying the fluids in two concentric stainless steel

tubes of 1.6 and 3.2 mm o.d. A gas and an aqueous phase get in contact at the bottom of the cell in a mixing point M where enter two concentric tubes and exits a stainless steel tube of 1.6 mm o.d. The quantitative mixing occurs in this 2.8 m long coiled tube in good thermal contact with the inner wall of the confinement cylinder.

The preheaters are counter current heat exchangers consisting of metallic cylinders with the tubing wound on its outer surface (external preheater) or tightly fitted in grooves inside the preheater. They are thermoregulated with the help of heating cartridges and a platinum resistance thermometer connected to a P.I.D controller. The temperatures of the external and first internal preheaters are maintained constant to 0.1 K by means of the Eroelectronic LFS regulators. The second internal preheater is regulated by a Electromax V model from Leeds &Northrup, and controls the temperature with stability to 0.01 K.

2.3. Operation procedure The enthalpy of solution and solubility are determined simultaneously from the analysis of the measured heat as a function of the amount of gas introduced in an aqueous phase. In Fig. 3 the heat of solution per one mole of solvent is plotted versus loading α . This graph makes it possible to distinguish the sections before and after saturation. First, the gas is totally absorbed by the solution and therefore the heat per mole of water increases constantly with α . Second, the heat per mole of water stays constant because the solution is saturated and addition of gas does not produce any heat effect. The limit of solubility is determined from the intersection of the straight lines fitting the data in these two sections and the enthalpy of solution per one mole of solute corresponds to the slope of the section where an increasing trend is observed.

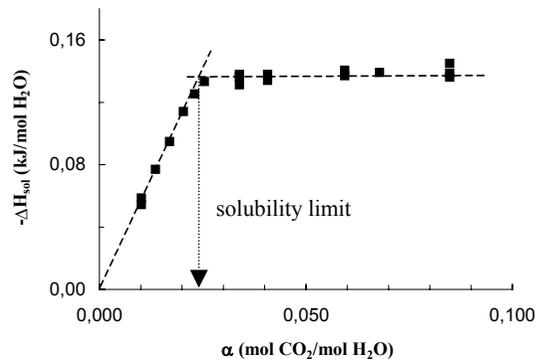


Fig. 3. Determination of the solubility limit from the concentration dependence of ΔH_{sol} .

Before measuring the dissolution heat effect, a base line signal from thermopiles is recorded with a solvent flowing through the calorimeter only. The baseline signal (S_{BL}) is generally close to zero ($\pm 10 \mu V$), with a stability of $\pm 1 \mu V$ and is recorded during at least 20 min before the introduction of a solute. The heat effect due to dissolution corresponds typically to the thermopile signal (S_M) between 100 and 600 μV , measured during 30 minutes. The enthalpy of solution ΔH_{sol} is calculated as:

$$\Delta H_{sol} = \frac{(S_M - S_{BL})}{K \dot{n}_x} \quad (1)$$

where K denotes the calibration constant of the calorimeter and \dot{n}_x the molar flow of solute or solvent. The calibration constant converting the thermopile voltage to the heat can be determined from the Joule effect using a calibration heater or chemically with the help of a reference system. The latter method was adopted in this study with ethanol + water system used for calibration with the data from Ott *et al.* [3]. It was found that the calibration constant is independent of the total flow rate and of the measured signal (heat flow).

3. Results and Discussion

3.1. System CO₂+ H₂O

3.1.1. Solubility As an example, the solubility of carbon dioxide in water in terms of molality is reported at a temperature of 323 K in a pressure range between 5 and 20 MPa. The experimental data obtained are compared with literature data in Fig. 4.

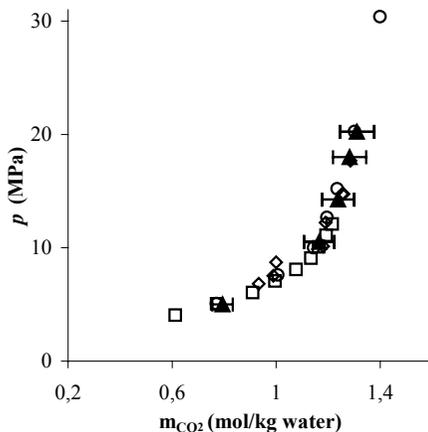


Fig. 4. Solubility of CO₂ in H₂O at 323 K ▲ our data points with error bars of 5%; ○ Wiebe and Gaddy [4], ◇ Briones *et al.* [5], □ Bamberger *et al.* [6].

The relative error of the solubility determination is estimated to be below 5%. Our results are compared with the experimental data from three representative literature sources [4-6]. It can be observed that the solubility of CO₂ increases sharply with pressure near below 10 MPa and much slower at higher pressures. The comparison of our values and the literature data shows an agreement within the expected experimental uncertainty.

3.1.2. Enthalpy of solution The measured values of the enthalpy of solution of carbon dioxide in water ΔH_{sol} at temperature of 323 K range between -13.1 and -4.7 kJ/mol CO₂ in the pressure range from 5 to 20 MPa. The expected accuracy is 6%. From our experimental results we calculated the enthalpy of hydration ΔH_{hyd} at standard pressure ($p_0 = 0.1$ MPa), which corresponds to the difference between the enthalpy of solute in the state of infinite dilution and in the state of ideal gas. Since the saturation concentration of CO₂ in water is relatively low the relation between the two properties can be approximated by the following equation:

$$\Delta H_{hyd}(p_0) = \Delta H_{res}^*(p_0 \rightarrow p) + \Delta H_{sol}(p) - \Delta H_{res}^\infty(p_0 \rightarrow p) \quad (2)$$

where ΔH_{res}^* and ΔH_{res}^∞ are the residual enthalpies of pure solute and solute in the state of infinite dilution, respectively. The term ΔH_{res}^* is strongly increasing with pressure, changing from -2.0 to -10.0 kJ/mol and was calculated from an equation of state using a ALLPROPS software [7], the term ΔH_{res}^∞ is much less important (0.1 to 0.5 kJ/mol) and was estimated from the correlation proposed by Sedlbauer *et al.* [8]. The values of ΔH_{hyd} obtained via equation (2) from ΔH_{sol} are 15.2 ± 0.1 kJ/mol CO₂ for all five pressures. The constancy of these values indicates good internal consistency of measurements at different pressures. Another comparison is possible using the temperature derivative of the Henry's law constants for aqueous CO₂ available in literature along the saturation line of water. At low pressures the enthalpy of hydration ΔH_{hyd} can be calculated as

$$\Delta H_{hyd} \cong -RT^2 \left(\frac{d \ln k_H}{dT} \right)_{sat} \quad (3)$$

The most representative value can be obtained from the temperature correlation of $k_H(T)$ recently published by Fernandez-Prini *et al.* [9] using the equation of Harvey [10]. The calculated enthalpy of hydration at temperature of 323 K relating to p_{sat} (not much different from $p_0 = 0.1$ MPa) is -15.2 kJ/mol CO_2 . This value is in excellent agreement with our result obtained from the calorimetric data via equation (2), which confirms validity of the thermal measurements.

3.2 System $\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}$

3.2.1. Solubility The results are reported for measurements with carbon dioxide in 1 and 3M NaCl solutions at four pressures between 5 and 20 MPa and temperature of 323 K. The experimental procedure did not change significantly compared to dissolution measurements with water and estimated uncertainty in the solubility determination is again 5%. The solubility of CO_2 in pure water is higher than in aqueous solutions of NaCl and decreases with increasing salinity, due to the so-called salting out effect. A considerable number of results from direct phase equilibrium measurements are available in literature. The papers of Drummond [11], Rumpf *et al.* [12] and Takenouchi and Kennedy [13] can be cited as examples. In Fig. 5 our solubility values of CO_2 in NaCl solutions are compared with the direct experimental data of Malinin and Savelyeva [14] and computed values obtained from the recent correlation of Duan and Sun [15]. This latter source can be considered as the most representative since it is based on a database of all available experimental values. The graph shows an agreement between the calorimetric measurements and the literature values within the expected experimental uncertainty. The salting out effect, the percentage decrease in solubility of a gas related to solubility in pure water, for a solution of 1 M increases with pressure first from 20 to 22% for $p < 10$ MPa and then decreases to 18% at 20 MPa. Malinin and Savelyeva [14] have found a salting out effect of 23% for a 1.01 M NaCl solution near 5 MPa. The salting out effect observed for an aqueous 3M NaCl solution increases again with pressure from 38 to 45% for $p < 10$ MPa and then decreases to 41% at 20 MPa. The similar uncrossing in the salting out effect with pressure was reported by Duan and Sun. [15] and the flat maximum near 10 MPa seems to be real. Their values of salting out effect above 10 MPa are near 19 and 44% at 1 and 3 M NaCl, respectively, which is close to our results.

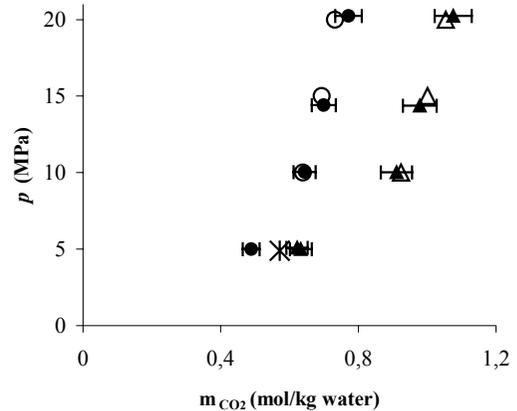


Fig. 5 Solubility of CO_2 in aqueous NaCl solutions at 323 K. \blacktriangle 1M, \bullet 3M - our data points with error bars of 5%; $*$ 1.012 M - Malinin and Savelyeva [14]; \triangle 1M, \circ 3M - calculated values by Duan and Sun [15].

3.2.2. Enthalpy of solution The enthalpic data obtained from the measurements allow determination of ΔH_{sol} which decreases with pressure from -13.2 to -4.2 kJ/mol CO_2 and from -11.4 to -3.4 kJ/mol for 1 and 3 M NaCl solution, respectively. It seems that the presence of salt attenuates somewhat the exothermal effect of gas dissolution. The enthalpy of hydration ΔH_{hyd} at pressure $p_0 = 0.1$ MPa was calculated again neglecting the presence of salts when evaluating term $\Delta H_{\text{res}}^\infty$. The values are between -14.6 and -15.5 kJ/mol CO_2 and between -13.5 and -14.0 kJ/mol CO_2 for 1 and 3 M NaCl solution, respectively. This suggests a similar experimental error like in the case of experiments with pure water. In addition, our values are also reasonably close to ΔH_{hyd} of Drummond [11] derived from the temperature correlation of the Henry's law constant (-14.2 and -13.3 kJ/mol CO_2 for 1 and 3 M NaCl solutions, respectively).

4. Conclusions

A calorimetric flow technique was adapted for the determination of the solubility and enthalpy of solution of acid gases in water and salt solutions using an analysis of the calorimetric signal. The results are in good agreement with the direct solubility measurements ($\pm 5\%$). The enthalpies of hydration at standard pressure of 0.1 MPa derived

from heats of solution at different pressures are internally consistent and compare well with the values obtained from the temperature dependence of the Henry's law constant. Our measurements show clearly an important salting out effect in NaCl solutions consistent with results from direct solubility measurements. Furthermore, this flow technique is particularly adapted for experiments with acid gases at high pressure; it permits working with a relatively small quantity of gas which is preferable for reasons of safety, particularly in case of H₂S. Therefore the method can be considered as an alternative to direct phase equilibrium measurements.

Acknowledgements

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