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# Vapour-liquid equilibria on the carbon dioxide-aqueous solutions systems from 293 to 393 K: experiments and modeling

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## Industrial context

Oxy-fuel combustion capture consisting in using pure oxygen rather than air during the combustion step of a power plant is one of the promising approaches for CCS

Air Liquide is involved in the oxy-fuel combustion both for supplying pure oxygen and for separating and purifying $CO_2$ of impurities ($SO_x$, $NO_x$, $O_2$) in $CO_2$ compression and purification unit ($CO_2$ CPU)

Calculation of thermodynamics properties of phase equilibria is the heart of CAPE tools used for design and optimization of processes

## Objectives

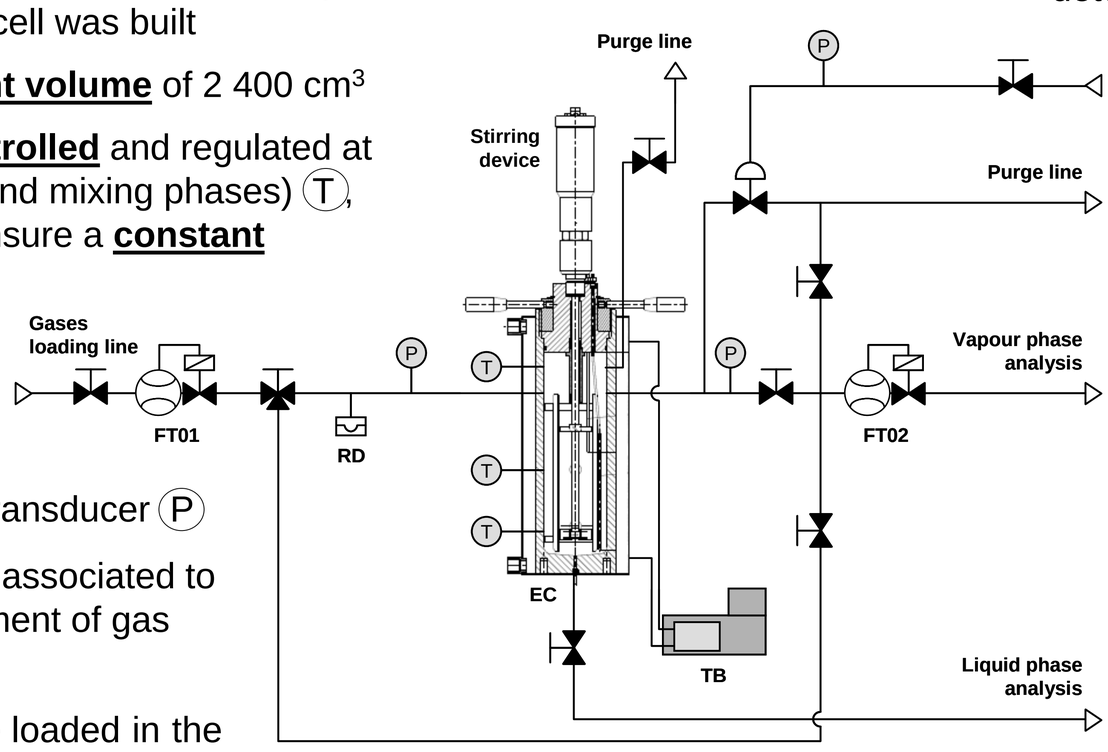
The general purpose of this work is the **characterization** of the behaviour of raw **$CO_2$ containing $SO_x$, $NO_x$ and $O_2$ with aqueous solutions** (water and water / NaOH) under pressure at thermodynamic equilibrium

In this study the $CO_2$ / water system is investigated to validate the experimental apparatus

New experimental data are obtained for the $CO_2$ / NaOH / water

## Experimental setup

- An **experimental apparatus** based on a Hastelloy **well stirred batch** equilibrium cell was built
- The cell has a **large constant volume** of 2 400 $cm^3$
- **Temperature** is **strictly controlled** and regulated at three locations (vapour, liquid and mixing phases) (T), the cell is double jacketed to ensure a **constant temperature**
- Pressure is measured by a transducer (P)
- The mass flow meter (FT01) associated to gas meter allows the measurement of gas volume loaded in the reactor
- The mass of aqueous phase loaded in the cell is weighted by an analytical balance




Composition of the aqueous phase is determined by two methods:

- Synthetic method based on **$CO_2$ balance**: *P* and *T* at the equilibrium and the volume of the gaseous phase allow the calculation of $CO_2$ mole number in the vapour phase

  Relative uncertainties of the method (GUM): 8 to 17%

- Analytical method: sampling of the liquid phase followed by **ion chromatography** gives the amount of $CO_2$ in the aqueous phase.

  Relative uncertainties of the method (GUM): 4%

  This last method was chosen in this work for $CO_2$ solubility determination

## Modeling approach

**Simulis® Thermodynamics** is a thermophysical calculation server that generates pure component and mixture properties (thermodynamic, transport, compressibility …) and fluid phase equilibria (vapour-liquid, liquid-liquid and vapour-liquid-liquid)

The **Sour Water model** of Simulis® Thermodynamics, based on the model proposed by Edwards et al., is used for modeling aspects

**Thermodynamic profile: Sour Water**

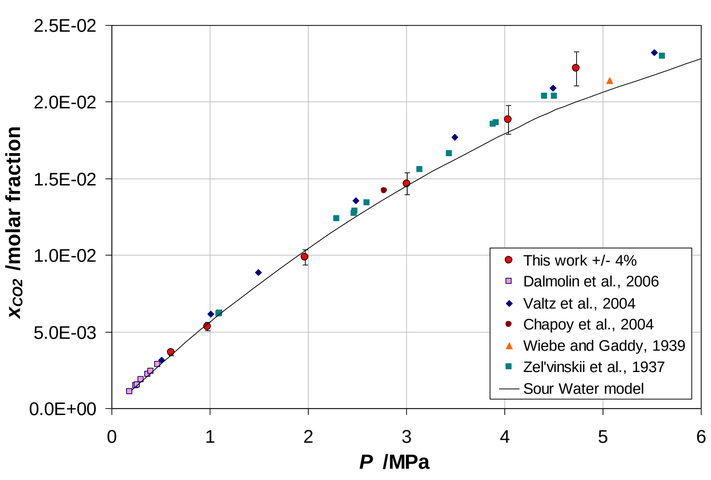
*Equation of state for gaseous phase: Peng-Robinson*
*Activity coefficient model: Edwards (Pitzer)*
*Liquid molar volume: Rackett modified by Gunn-Yamada*
*Liquid fugacity: Henry's law with Poynting correction*
*Enthalpy reference: ideal gas, 298.15 K, 1 atm*

**Validity range**

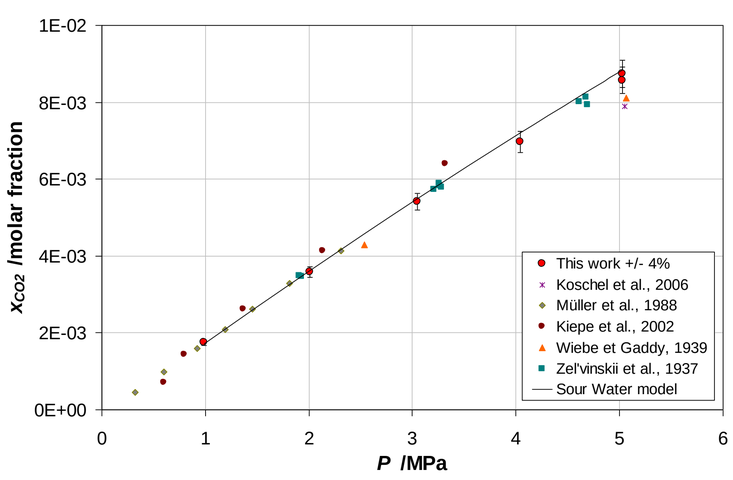
*T = 273 to 473 K*
*P = 0.1 to 5 MPa*
*Molality = 0 to 10 mol/kg of water*

## $CO_2$ solubility measurements

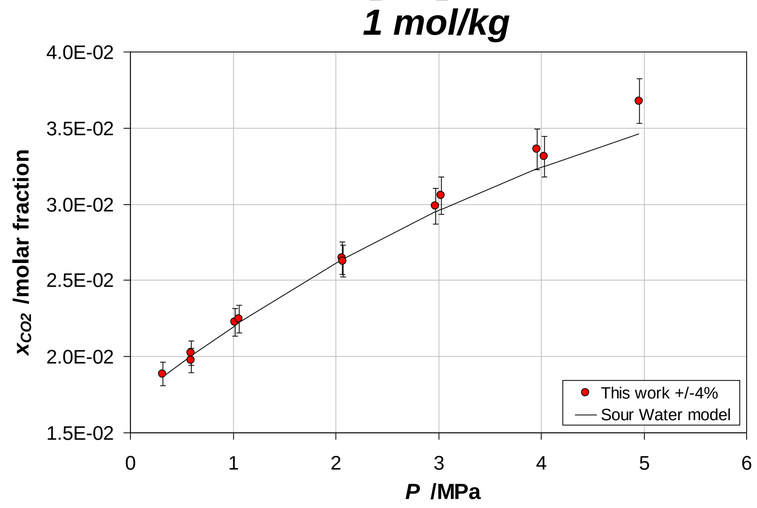
***298.15 K – $CO_2$ / $H_2O$ system***




***373.15 K – $CO_2$ / $H_2O$ system***




***293.15 K – $CO_2$ / $H_2O$ / NaOH system 1 mol/kg***




- Results obtained are in **good agreement** with literature data for the $CO_2$ / water system
- Sour Water model is **well adapted** to describe the behaviour of $CO_2$ / water system under pressure in the whole temperature range
- Data obtained for the $CO_2$ / NaOH / water ternary system are **slightly higher** than Sour Water model for high pressure

## Perspectives

- **Experimental perspectives: measurement of co-solubility ($CO_2$ / $O_2$, $CO_2$ / $NO_x$, $CO_2$ / $SO_2$) in aqueous solutions**
- **Modeling perspectives: enhance the Sour Water model with data provided by this work**

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