

# Lab 1 - Experimental determination of Henry's constant for CO<sub>2</sub>

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## Introduction

The CO<sub>2</sub> content in the atmosphere has been increasing out of proportion since the beginning of the industrial age. This increase has not only successively trapped the incoming solar radiation, heating the planet, but also increased the acidity in our aquatic systems. The increase in acidity is directly related to the increased partial pressure of CO<sub>2</sub> in the atmosphere; the higher the partial pressure, the more CO<sub>2</sub> is dissolved. Different gases dissolve at different rates depending on the temperature, the different molecular structures of the gases, and the different solvents used. This rate of dissolution, or capacity of solubility, can be determined as a constant when fixing the aforementioned parameters. This constant is called Henry's solubility constant.

The aim of this lab is to determine Henry's solubility constant  $K_H$  for CO<sub>2</sub> in water at 20°C, and to make light of the relationship between the partial pressure of CO<sub>2</sub> in the atmosphere and the pH-value in aquatic systems.

## Materials, method and theory

### Materials

The materials and chemicals used in this lab are as follows:

- pH-meter
- Magnetic stirrer and magnet
- 250 ml beaker
- Plastic hose
- Metal clamp
- Stand
- Deionized water
- Scale
- NaCl
- N<sub>2</sub> gas with 0.1%, 0.3%, 1%, 5% CO<sub>2</sub> content
- Buffer solutions with pH values 4 and 7

## Method

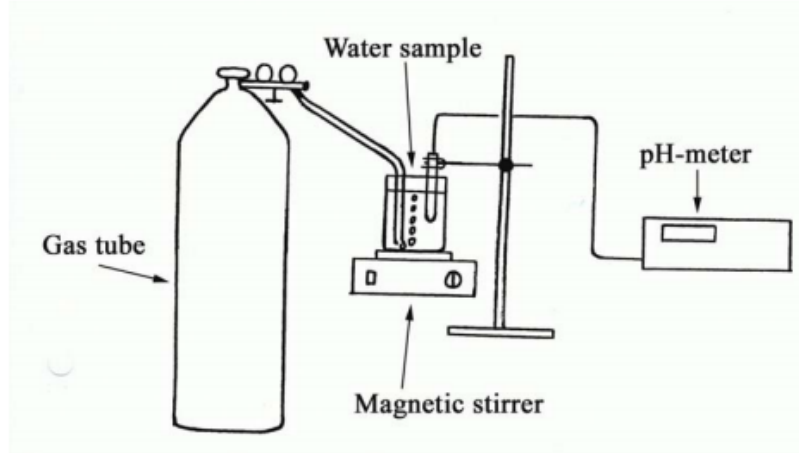


Figure 1: Experimental set-up of the materials ([Warfvinge, 2018](#))

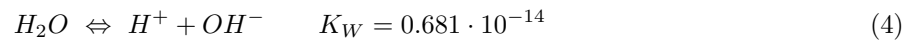
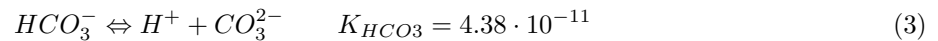
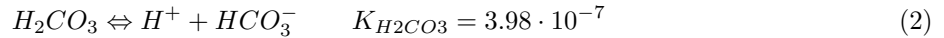
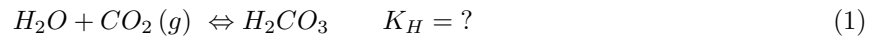
The lab was set up with four stations, each station containing one of the gas tubes with a specific concentration of  $CO_2$ . The following method was then carried out at each of the stations.

First, the pH-meter was calibrated using the buffer solutions with pH-values 4 and 7. The beaker was then filled with 2/3 of deionized water. 0.1 g of NaCl was measured using the scale and then added to the beaker. The materials were then set up according to Fig. 1, with the plastic hose attached to the gas tube with the metal clamp and then put in the beaker. A steady flow of  $N_2/CO_2$ -gas was then bubbled through the solution in the beaker while the magnetic stirrer was put on vigorous stirring. The pH was then measured after waiting approximately 5 minutes for chemical equilibrium to be achieved.

## Theory of equations

### Deriving a function of $pH$ dependent on $P_{CO_2}$

Below is the complete carbonate system, consisting of 7 components and 4 reactions. Each reaction has a corresponding equilibrium constant  $K_x$ , whose value at 20° C ([Warfvinge](#)) is also shown below. The solubility constant  $K_H$  is to be determined in this lab:



Reaction 2 is the only reaction contributing to a notable concentration of  $[H^+]$ , this is made apparent by the low values of  $K_{HCO_3}$  and  $K_W$ . This makes it so that for  $pH$ -values under 6 the contribution of  $[H^+]$  from reaction 3 and 4 can be neglected. This leaves us with reaction 1 and 2 as the only reactions contributing species to the carbonate system.

From a general equilibrium reaction



The equilibrium constant can be determined through

$$K_x = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6)$$

By moving around the nominator and denominator in equation 6, the concentrations of each component at equilibrium can be expressed as

$$[C]^c = K_x \cdot \frac{[A]^a [B]^b}{[D]^d} \quad (7)$$

We can thus express our concentrations of  $[H_2CO_3]$  and  $[HCO_3^-]$  as

$$[H_2CO_3] = K_H P_{CO_2} \quad (8)$$

$$[HCO_3^-] = K_{H_2CO_3} \cdot \frac{[H_2CO_3]}{[H^+]} \quad (9)$$

where  $P_{CO_2}$  is the partial pressure of  $CO_2$  in  $[atm]$ .

We can now combine equation 8 and 9 so we get a new expression for  $[HCO_3^-]$ :

$$[HCO_3^-] = K_{H_2CO_3} \cdot \frac{K_H P_{CO_2}}{[H^+]} \quad (10)$$

The number of cations in a solution is always equal to the number of anions, this is known as the charge balance. For our solution it can be expressed as

$$[H^+] + [Na^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [Cl^-] \quad (11)$$

The concentrations  $[CO_3^{2-}]$  and  $[OH^-]$  are only prevalent for high  $pH$ -values and can be neglected due to adding an acid into the aquatic system, lowering the  $pH$ -value. The concentrations  $[Na^+]$  and  $[Cl^-]$  are exactly the same due to the stoichiometry of  $NaCl$ , so both of these concentrations can be subtracted. We then can utilize this to create an expression for  $[H^+]$ :

$$[H^+] = [HCO_3^-] \quad (12)$$

Inserting equation 10 into 12 gives

$$[H^+] = \sqrt{K_{H_2CO_3} \cdot K_H \cdot PCO_2} \quad (13)$$

The value of  $pH$  is given by

$$pH = -\log([H^+]) \quad (14)$$

Insertion equation 13 into 14 gives a linear function of  $pH$  that depends on  $PCO_2$ :

$$pH(PCO_2) = -\frac{1}{2} \log(K_{H_2CO_3} \cdot K_H \cdot PCO_2) \quad (15)$$

By applying laws of logarithms, function 15 can be rearranged into a slope-intersect form  $y = kx + m$  as such

$$pH(CO_2) = -\frac{1}{2} \log(PCO_2) - \frac{1}{2} \log(K_H \cdot K_{H_2CO_3}) \quad (16)$$

$$y = pH(CO_2) \quad (17)$$

$$k = -\frac{1}{2} \quad (18)$$

$$x = \log(PCO_2) \quad (19)$$

$$m = -\frac{1}{2} \log(K_H \cdot K_{H_2CO_3}) \quad (20)$$

When  $m$  has been derived through the least square method,  $K_H$  can be determined:

$$K_H = \frac{10^{-2m}}{K_{H_2CO_3}} \quad (21)$$

### Statistical derivation of the solubility constant $K_H$ with the least square method

The statistical derivation of  $K_H$  is done with the linear regression function in Google Sheets to find the intercept of the  $y$ -axis for a set of  $x$  and  $y$  data. Doing this, Google Sheets utilizes the least square method. It is used to find an estimate of the “true” measurement when there is a number of different data measuring the same quantity. The estimation is then validated through the use of the statistical measure  $R^2$ . It is a measure of how close the regressed line fits the measured data, and the closer it is to 1, the more accurate the estimation.

The intercept of the  $y$ -axis will occur when  $y = m$ , and since  $K_{H_2CO_3}$  is known,  $K_H$  can be determined using equation 20. #

## Results

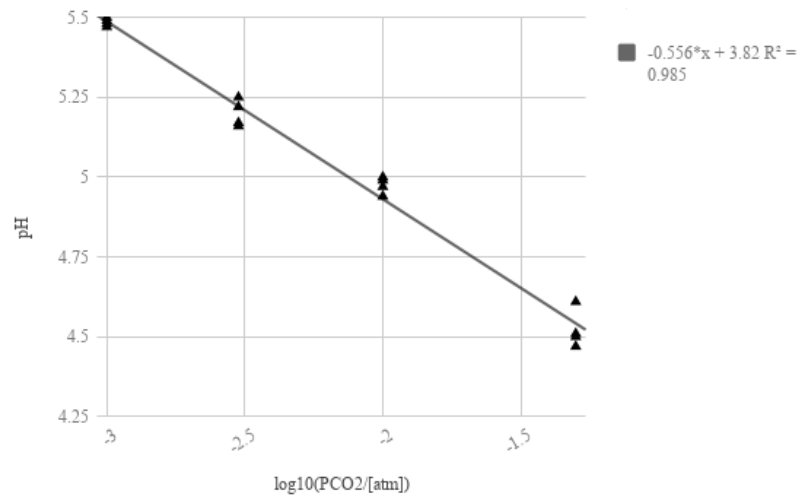


Figure 2: Linearized model of the pH-value as a function of partial pressure of  $\text{CO}_2$

Figure 2 shows the linearized relationship between the  $pH$ -value and the partial pressure of  $\text{CO}_2$ . The linear regression gives an  $m = 3.82$  with a corresponding  $R^2$ -value of 0.985. The value of  $K_H$  is, through the use of equation 20, determined to  $5.76 \cdot 10^{-2} \text{ kmol} \cdot \text{L}^{-1} \text{atm}^{-1}$ .

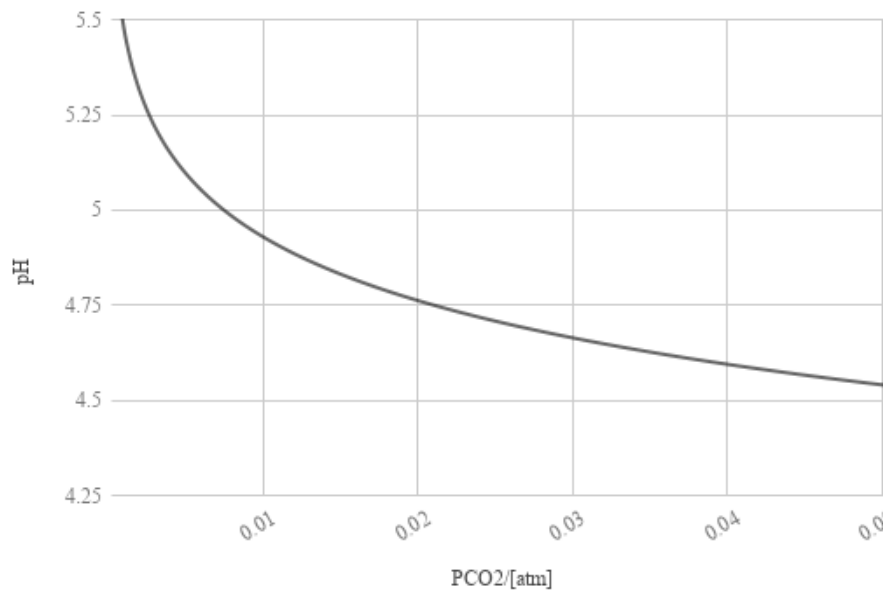


Figure 3: pH-value at chemical equilibrium between water and different partial pressures of  $\text{CO}_2$

Figure 3 shows the logarithmic relationship between pH-values at chemical equilibrium between water and  $CO_2$ .

Table 1: 4 sets of data of pH-values for different partial pressures of  $CO_2$

<b><math>PCO_2/[atm]</math></b>	0.001	0.003	0.01	0.05
<b>1</b>	pH 5.47	pH 5.22	pH 4.99	pH 4.61
<b>2</b>	pH 5.48	pH 5.25	pH 5.00	pH 4.51
<b>3</b>	pH 5.49	pH 5.16	pH 4.94	pH 4.50
<b>4</b>	pH 5.50	pH 5.17	pH 4.97	pH 4.47

Table 1 contains raw data from 4 sets of measuring pH against different partial pressures of  $CO_2$ .

## Discussion

The results can be regarded as certain as the  $R^2$  value is very close to one. There is a 44% deviation when compared to a previously recorded value of  $K_H$  at  $20^\circ C$ ,  $3.98 \cdot 10^{-2} \text{ kmol} \cdot m^{-3} \cdot atm^{-1}$  (Warfvinge, 2018). This deviation could be due to a lower temperature in the laboratory for than accounted for in the equilibrium constants used in the theory; the temperature in the laboratory was  $19^\circ C$  and the equilibrium constants account for a temperature of  $20^\circ C$ .

The main purpose of adding NaCl to the solution is to keep the activity factor of the solution constant. When the activity factor is constant the pH-measurement becomes more accurate. The measuring of the pH is also the biggest source of error in this lab, as the accuracy and the handling of the equipment plays into how accurate the given pH-values are. Adding NaCl to the solution also creates sites of nucleations where bubbles of  $CO_2$  can form from the carbonic acid, speeding up the process of reaching equilibrium.

This experiment is for determining Henrys constant in clean de-ionized water with a little bit of NaCl. There is limited use applying the experimental value given in this lab to real world situations as real aquatic systems are affected by many different abiotic and biotic factors changing Henrys constant in a dynamic way.

## References

Per Warfvinge. Applied Aquatic Chemistry.

Per Warfvinge. Applied Aquatic Chemistry, 2018.