Example 05.15 Henry Constant for CO_2 from Phase Equilibrium Data

problem: Determine the Henry constant for carbon dioxide (1) in water with the help of phase equilibrium data at 50°C.

general constants and definitions:

$cm := 0.01m \qquad R_{gas} := 8.31433 \frac{J}{K \cdot mol}$

$bar := 10^5 Pa \qquad kPa := 1000Pa$

input data

$n_{comp} := 2 \qquad i := 1 .. n_{comp} \qquad j := 1 .. n_{comp}$

Experimental data (partial pressure and liquid mole fraction of CO_2):

$$T := (50 + 273.15)K \qquad x_1 := \begin{pmatrix} 0.342 \\ 0.683 \\ 1.354 \\ 2.02 \\ 2.66 \\ 3.3 \\ 3.93 \\ 4.55 \\ 5.15 \\ 5.75 \end{pmatrix} \cdot 10^{-3} \qquad p_1 := \begin{pmatrix} 101.33 \\ 202.65 \\ 405.3 \\ 607.95 \\ 810.6 \\ 1013.3 \\ 1216 \\ 1419 \\ 1621 \\ 1824 \end{pmatrix} kPa$$

$n_{data} := rows(x_1) \qquad n_{data} = 10 \qquad k := 1 .. n_{data}$

Pure component vapor pressure of water at 50°C: $Ps_2 := 12.33kPa$

Virial coefficients: $B := \begin{pmatrix} -102 & -198 \\ -198 & -812 \end{pmatrix} \frac{cm^3}{mol}$

Solution

Henry coefficients can be determined by the following equation:

$$H_{12} = \lim_{x_1 \to 0} \frac{f_1}{x_1}$$

where the fugacity of the gas f_1 is often replaced by its partial pressure p_1 at low pressures. In this example, the Virial equation will be used to calculate the real vapor phase behavior. The result will be compared to that of the simplified approach.

In the experimental data, only the partial pressure of CO_2 is reported. As the mole fraction of water is nearly unity and the properties of the liquid mixture are not affected significantly by the small amount of dissolved CO_2, the partial pressure of water can be assumed to be equal to the pure component vapor pressure. At high pressures, it will be affected by the Poynting factor. In this case the relative change in total pressure is very small due to the low vapor pressure of the solvent, so that this effect can be neglected.

$$P := p_1 + Ps_2 \qquad P_1 = 113.66\,\text{kPa}$$

Using the partial and total pressure, the composition of the vapor phase, the Virial coefficient of the vapor and the fugacity coefficient of CO_2 can be calculated for all data points:

$$y_{k,1} := \frac{p1_k}{P_k} \qquad y_{k,2} := 1. - y_{k,1} \qquad y_{3,1} = 0.9705$$

$$BV_k := \sum_i \sum_j B_{i,j} \cdot y_{k,i} \cdot y_{k,j} \qquad BV_3 = -108.12\,\frac{\text{cm}^3}{\text{mol}}$$

$$\text{lnphi}1_k := \left[2 \cdot \left[\sum_j \left(y_{k,j} \cdot B_{1,j}\right)\right] - BV_k\right] \cdot \frac{P_k}{R_{gas} \cdot T}$$

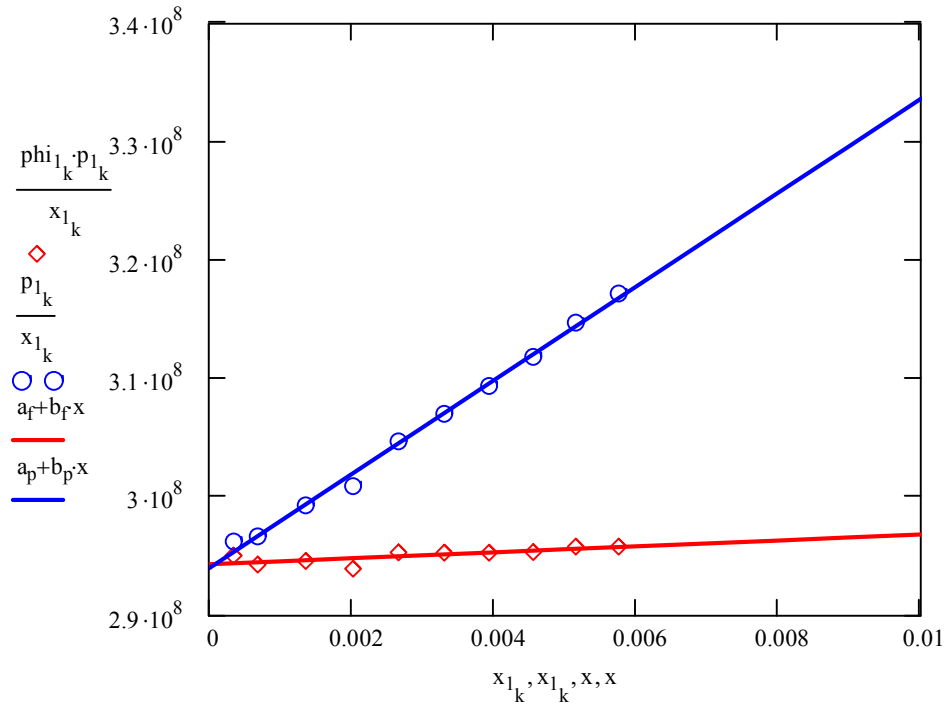
$$\text{phi}1_k := \exp\left(\text{lnphi}1_k\right) \qquad \text{phi}1_3 = 0.9843$$

Now the ratio of the fugacity to the liquid mole fraction for CO_2 can be regressed (linear equation) and plotted against the liquid mole fraction of CO_2. Extrapolation to a mole fraction of zero yields the correct value of the Henry constant:

$$Hf_k := \frac{\text{phi}1_k \cdot p1_k}{x1_k} \qquad a_f := \text{intercept}(x_1, H_f) \qquad b_f := \text{slope}(x_1, H_f)$$

$$Hp_k := \frac{p1_k}{x1_k} \qquad a_p := \text{intercept}(x_1, H_p) \qquad b_p := \text{slope}(x_1, H_p)$$

$x := 0, 0.001 .. 0.01$



Both approaches give a nearly identical value of the Henry coefficient (equal to the intercept from the linear regression):

$a_f = 2944\,\text{bar}$ $\qquad a_p = 2940\,\text{bar}$

Nevertheless, only the correct form of the Henry's Law using the fugacity and not the partial pressure of the gas gives the approximately correct description of the gas solubility at higher pressures.