Value Through Technology

OLI Tips #61
How pH is calculated in the Mole Fraction based concentration basis
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Overview

The new mole fraction based concentration basis available in the OLI software (ESP version 7.0 or Analyzers 2.0 or later) report activity coefficients on a different basis than in the older software. Hand calculations of such values such as pH can be confusing. This document will take you through two examples of how pH is calculated.

Further confusion is that the reported activity coefficient is different depending on the basis selected. We will examine each basis in turn.

Definitions of Symbols and Superscripts

Definitions of symbols:

$\gamma_j^{m,\infty}$ activity coefficient of species j on the basis of molality and infinite dilution reference state (unsymmetrical) ($\gamma_j^{m,\infty} \rightarrow 1$ as $m_j \rightarrow 0$)

$\gamma_j^{x,\infty}$ activity coefficient of species j on the basis of mole fraction and infinite dilution reference state (unsymmetrical) ($\gamma_j^{x,\infty} \rightarrow 1$ as $x_j \rightarrow 0$)

γ_j^{x} activity coefficient of species j on the basis of mole fraction and fused salt reference state (symmetrical) ($\gamma_j^{x} \rightarrow 1$ as $x_j \rightarrow 1$)

X_w The mole fraction of water

X_{H+} The mole fraction of the hydrogen ion

a_{H+} activity of the hydrogen ion.

Mw Molecular weight of water, 18.0154 g/mole

Superscripts

$^{\infty}$ – infinite dilution in water reference state
^{m} – molality-based
^{x} – mole-fraction-based

The Standard Aqueous Model

In this simulation we have taken a sample at 25 ^{o}C, 1.0 Atmospheres, 55.508 moles of H_2O and 0.0001 moles of HCl. The standard Bromley-Zematis activity model was selected. The program reports the following information:

pH	=	4.005
$\gamma_H^{x,\infty}$	=	0.98848 (activity coefficient for the hydrogen ion – Bromley Basis)
x_H	=	1.8 x 10^{-6} (mole fraction of hydrogen ion)
x_{H2O}	=	0.999998 (mole fraction of water – true basis)
m_H	=	0.0001 mole/Kg H2O

pH definition

The definition of pH in the OLI software is the following:

$$pH = -Log\left(a_{H+}\right)$$

Where a_{H+} is the activity of the hydrogen ion and a_{H+} is $a_{H+} = m_{H+}\gamma_{H+}^{m,\infty}$

In the traditional molality based calculation, this expands to: $pH = -\log\left(m_{H+}\gamma_{H+}^{m,\infty}\right)$

We also know that the activity on the molality basis can be represented on the mole fraction basis as:

$$a_{H+}^{m} = a_{H+}^{x} * \left(\frac{1000}{Mw}\right)$$

This changes the pH equation to $pH = -log(55.509X_{H+}^{x}\gamma_{H+}^{x,\infty})$

Evaluating the above values we obtain:

$$pH = -\log(55.509 * 1.8x10^{-6} * 0.98848) = -(-4.005) = 4.005$$

Converting to molality based activity coefficients

To calculate the pH on a molality basis we need to convert the activity coefficient.

The molality concentration unit can be converted easily to the mole fraction basis via this equation: $m_{H+} = 55.509\frac{x_{H+}}{x_w}$

This allows us to define the molal based activity coefficient by expanding both sides of the activity relationship:

$$a_{H+}^{m} = a_{H+}^{x} * \left(\frac{1000}{Mw}\right)$$

$$\gamma_{H+}^{m,\infty} * 55.509 * \frac{X_{H+}}{Xw} = \gamma_{H+}^{x,\infty} * X_{H+} * 55.509$$

This solves to:

$$\gamma_{H+}^{m,\infty} = X_w \gamma_{H+}^{X,\infty}$$

Evaluating this equation using the simulation values we obtain:

$$\gamma_{H+}^{m,\infty} = (0.999998)(0.98848) = 0.98848$$

The definition of pH on the molality basis is:

$$pH = -Log\left(a_{H+}\right) = -Log(\gamma_{H+}^{m} m_{H+}) = -\log\left[(0.98848)(0.0001)\right] = -(-4.005) = 4.005$$

So you can see that the pH of the solution is the same regardless of the basis.

Calculating the pH on the MSE H+ Basis

The simulation is very similar to previous simulation. Here are the results:

pH = 4.005
γ_H^x = 0.988501(activity coefficient for the hydrogen ion – Bromley Basis)
x_H = 1.8×10^{-6} (mole fraction of hydrogen ion)
x_{H2O} = 0.999998 (mole fraction of water – true basis)

Since the definition of pH is the following: $pH = -log(55.509 X_{H+}^{x,\infty} \gamma_{H+}^{x,\infty})$

We now enter this value in for pH and obtain:

$$pH = -Log\left[(55.509)(0.98848)\left(1.8x10^{-6}\right)\right] = -(-4.005) = 4.005$$

Calculating pH in the hydronium ion basis

In the hydronium ion basis, there is no hydrogen ion. This makes a direct conversion difficult. Some additional conversions are required. We are using the same compositions as before.

The solution results are:

X_{H3O+} = 1.8×10^{-6}

X_{H2O} = 0.999996
γ_{H3O+}^{x}[1] = 0.988515
γ_{H2O}^{x} = 1.0000
pH = 4.005

Our major concern here is that we need to have an effective concentration of the hydrogen ion which does not exist in this framework. We know that the following definition is true:

$H_3O^+ = H^+ + H_2O$

Since the activities on both sides must be equal,

$a_{H3O+} = a_{H+}a_{H2O}$

Or

$$a_{H+} = \frac{a_{H3O+}}{a_{H2O}}$$

We also know that to convert the mole fraction basis to the molality basis we can use this conversion:

$$a_{H+}^{m} = a_{h+}^{x} \frac{1000}{M_{H2O}}$$

Where M_{H2O} is the molecular weight of water (approximately equal to 18.1054 g/mole)

Thus the activity of they hydrogen ion on a molality basis is:

$$a_{H+}^{m} = \frac{a_{H3O+}^{x}}{a_{H2O}^{x}} \frac{1000}{M_{H2O}}$$

So pH becomes

$$pH = -\log(a_{H+}^{m}) = -\log\left(\frac{a_{H3O+}^{x}}{a_{H2O}^{x}}\right) - \log\left(\frac{1000}{M_{H2O}}\right)$$

Where

$$a_{H3O+}^{x} = \gamma_{H3O+}^{x} X_{H3O+} = (0.988515)(1.8x10^{-6}) = 1.77933x10^{-6}$$

And

[1] These activity coefficients are on the MSE basis.

$$a^{x}_{H2O} = \gamma^{x}_{H2O} X_{H2O} = (1.000)(0.999996) = 0.999996$$

Thus pH becomes

$$pH = -\log(a^{m}_{H+}) = -\log\left(\frac{1.77933x10^{-6}}{0.999996}\right) - \log(55.509) = 4.005$$