



**OLI Tips #61**

How pH is calculated in the Mole Fraction based concentration basis

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Overview..... 1

Definitions of Symbols and Superscripts..... 1

    Definitions of symbols:..... 1

    Superscripts..... 1

The Standard Aqueous Model ..... 2

pH definition..... 2

Converting to molality based activity coefficients ..... 2

Calculating the pH on the MSE H+ Basis ..... 3

Calculating pH in the hydronium ion basis..... 3

**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  $x_j \rightarrow 0$ )
- $\gamma_j^x$  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

**Superscripts**

$\infty$  – infinite dilution in water reference state

<sup>m</sup> – molality-based

<sup>x</sup> – mole-fraction-based

## The Standard Aqueous Model

In this simulation we have taken a sample at 25 °C, 1.0 Atmospheres, 55.508 moles of H<sub>2</sub>O 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)
$x_{H^+}$	=	$1.8 \times 10^{-6}$ (mole fraction of hydrogen ion)
$x_{H_2O}$	=	0.999998 (mole fraction of water – true basis)
$m_H$	=	0.0001 mole/Kg H <sub>2</sub> O

## pH definition

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

$$pH = -\text{Log}(a_{H^+})$$

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:  $pH = -\log(m_{H^+} \gamma_{H^+}^{m,\infty})$

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

We can define the activity of the hydrogen ions on the molality basis as:

$$\gamma_{H^+}^{m,\infty} = X_w \gamma_{H^+}^{x,\infty} \text{ This combines to: } pH = -\log(55.509 X_{H^+}^{x,\infty} \gamma_{H^+}^{x,\infty})$$

Evaluating the above values we obtain:

$$pH = -\log(55.509 * 1.8 \times 10^{-6} * 0.98848) = -(-4.005) = 4.005$$

## Converting to molality based activity coefficients

To calculate the pH on a molality basis we need to convert the activity coefficient. To do this we can use the following formula.

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

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:

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

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:

$$\begin{aligned} \text{pH} &= 4.005 \\ \gamma_{H^+}^x &= 0.988501 \text{ (activity coefficient for the hydrogen ion – Bromley Basis)} \\ x_{H^+} &= 1.8 \times 10^{-6} \text{ (mole fraction of hydrogen ion)} \\ x_{H_2O} &= 0.999998 \text{ (mole fraction of water – true basis)} \end{aligned}$$

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:

$$pH = -\text{Log}[(55.509)(0.98848)(1.8 \times 10^{-6})] = -(-4.005) = 4.005$$

### 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:

$$\begin{aligned} X_{H_3O^+} &= 1.8 \times 10^{-6} \\ X_{H_2O} &= 0.999996 \\ \gamma_{H_3O^+}^{x1} &= 0.988515 \\ \gamma_{H_2O}^x &= 1.0000 \\ \text{pH} &= 4.005 \end{aligned}$$

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:



Since the activities on both sides must be equal,

$$a_{H_3O^+} = a_{H^+} a_{H_2O}$$

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<sup>1</sup> These activity coefficients are on the MSE basis.

Or

$$a_{H^+} = \frac{a_{H_3O^+}}{a_{H_2O}}$$

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

$$a_{H^+}^m = a_{H^+}^x \frac{1000}{M_{H_2O}}$$

Where  $M_{H_2O}$  is the molecular weight of water (approximately equal to 18.1054 g/mole)

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

$$a_{H^+}^m = \frac{a_{H_3O^+}^x}{a_{H_2O}^x} \frac{1000}{M_{H_2O}}$$

So pH becomes

$$pH = -\log(a_{H^+}^m) = -\log\left(\frac{a_{H_3O^+}^x}{a_{H_2O}^x}\right) - \log\left(\frac{1000}{M_{H_2O}}\right)$$

Where

$$a_{H_3O^+}^x = \gamma_{H_3O^+}^x X_{H_3O^+} = (0.988515)(1.8 \times 10^{-6}) = 1.77933 \times 10^{-6}$$

And

$$a_{H_2O}^x = \gamma_{H_2O}^x X_{H_2O} = (1.000)(0.999996) = 0.999996$$

Thus pH becomes

$$pH = -\log(a_{H^+}^m) = -\log\left(\frac{1.77933 \times 10^{-6}}{0.999996}\right) - \log(55.509) = 4.005$$