

# Activities of hydrogen ion from pH measurements

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**Goals:** pH measurements are presented for a series of HCl solutions of increasing concentration. The data are analyzed to determine the activities and activity coefficients of the hydrogen-ion. The results are compared to theoretical predictions from the extended Debye-Huckel equation.

**Prerequisites:** A knowledge of activities, activity coefficients and the Debye-Huckel equation for mean activity coefficients.

**Resources you will need:** The calculations and graphing associated with this exercise can be carried out within any quantitative analysis software.

## Background:

Students of chemistry are well acquainted with the relationship between solution  $pH$  and hydrogen-ion concentration;

$$pH = -\log[H^+]. \quad (1)$$

However, this expression is only accurate in the dilute limit. The exact relationship depends on the activity of the hydrogen ion;

$$pH = -\log a_{H^+}. \quad (2)$$

Consequently, activities for hydrogen-ion in a given solution can be determined through simple  $pH$  measurements, and the activity coefficient ( $\gamma$ ) can be evaluated using the relationship

$$a = \gamma C, \quad (3)$$

where  $C$  is concentration. Activities can be defined in terms of molar concentrations ( $M$ ) or molal concentrations ( $m$ ). Activities calculated through the use of equation (2) will be 'molar-based', which in turn yields a molar-based activity coefficient. This distinction is made clear here by rewriting equation (3) as

$$a_M = \gamma_M [H^+]. \quad (4)$$

The corresponding expression for a 'molality-based' activity is given by

$$a_m = \gamma_m m_{H^+}, \quad (5)$$

where the two types of activity coefficients are related by the expression

$$\gamma_M = \frac{\gamma_m [H^+] D}{m_{H^+}}. \quad (6)$$

and  $D$  is the solution density. For moderately dilute aqueous solutions at ambient conditions, the density of the solution is equal to that of pure water ( $D = 1 \text{ g/mL}$ ), meaning the molar and molal concentration are essentially equal (within experimental error). Consequently, the molar and molal activity coefficients are equal to one another.

In electrolytic solutions, a convention has been adopted whereby one assumes that the non-ideality of the solution is shared by the cation and anion. This is accomplished by defining a mean-activity coefficient according to the expression

$$\gamma_{\pm} = (\gamma_{+}^{v_{+}} \gamma_{-}^{v_{-}})^{1/(v_{+}+v_{-})} \quad (7)$$

where  $v_{+}$  and  $v_{-}$  are the number of cations and anions, respectively, in one formula unit of the electrolyte.

A number of theoretical approaches are available for estimating mean activity coefficients. One expression that is valid up to moderate concentrations is an empirical modification of the Debye-Huckel limiting law (the 'extended' Debye Huckel equation) given by

$$\log \gamma_{\pm} = -A |z_{+} z_{-}| \left( \frac{I^{1/2}}{1 + BI^{1/2}} \right), \quad (8)$$

where  $A$  is a constant that depends on properties of the solvent (0.5085 for water at 25°C),  $z_{+}$  and  $z_{-}$  are the ionic charges,  $I$  is the ionic strength, and  $B$  is an empirical constant. Activity coefficients calculated using equation (8) are molal-based.

The exercise outlined below will involve using  $pH$  data to experimentally determine activity coefficients for hydrogen-ion and subsequently using this data to test the validity of 'extended' Debye Huckel law.

### Experimental Data:

The following table gives experimentally determined  $pH$  values for a series of HCl solutions of increasing concentration at 25 °C.

| <u>Molar Concentration of HCl</u> | <u>Experimentally Determined pH</u> |
|-----------------------------------|-------------------------------------|
| 0.00050                           | 3.31                                |
| 0.0100                            | 2.04                                |
| 0.100                             | 1.10                                |
| 0.40                              | 0.52                                |

Data based upon information contained in Christopher G. McCarty and Ed Vitz\*, *Journal of Chemical Education*, 83(5), 752 (2006) and G.N. Lewis, M. Randall, K. Pitzer, D.F. Brewer, *Thermodynamics* (McGraw-Hill: New York, 1961; pp. 233-34).

### Exercise:

- For each solution, calculate the  $pH$  that would exist if equation (1) is assumed to be accurate (i.e. if molar concentrations can be used instead of activities). Then calculate the  $pH$  error ( $\Delta pH$ ) by subtracting your answer from the real experimental  $pH$  values in the above table. Estimate the concentration above which the error in using equation (1) becomes greater than 5 percent.
- Calculate the molarity-based activity of  $H^{+}$  for each solution from the  $pH$  value. Also calculate the molar-based activity coefficient of  $H^{+}$  for each solution. Since each of the solutions are relatively dilute, the activity coefficients that you obtain can be assumed to represent molal-based activity coefficients.
- You will now use the data from step (2) to test the validity of the extended Debye-Huckel limiting law. First calculate the ionic strength for each solution and in each case determine a value for the empirical constant  $B$  in equation (8). How well does equation (8) describe the data (i.e. do you obtain a relatively constant value for  $B$  or does it vary over the range of the data)? Is there any data point that you should consider throwing out? Pick a representative ('average') value of  $B$  and then plot the mean-activity coefficients given by equation (8) with your experimental activity coefficients. Does the extended Debye-Huckel equation fit the data well?

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

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