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ANALYTICAL CHALLENGE

Ostwald's dilution law challenge

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We would like to invite you to participate in the Analytical Challenge, a series of puzzles to entertain and challenge our readers. This special feature of "Analytical and Bioanalytical Chemistry" has established itself as a truly unique quiz series, with a new scientific puzzle published every other month. Readers can access the complete collection of published problems with their solutions on the ABC homepage at http://www.springer.com/abc. *Test your knowledge and tease your wits in diverse areas of analytical and bioanalytical chemistry by viewing this collection.*

In the present challenge, 'dilution' is the topic. And please note that there is a prize to be won (a Springer book of your choice up to a value of €100). Please read on…

Meet the challenge

Ostwald's dilution law has become a staple of physical and general chemistry. It refers to the formula introduced in 1888 [1] by the Latvian-born chemist Friedrich Wilhelm Ostwald (1853–1932), one of the founders of physical chemistry and the 1909 Nobel Laureate for Chemistry [2]. Ostwald's dilution law refers, in particular, to the relation between the dissociation constant, K_a, and the degree of ionization, α, of a weak monoprotic acid, HL [3]. On the basis of reaction

$$HL = H^+ + L^- \quad (1)$$

we formulate the expression for dissociation constant K_a of HL

$$K_a = \frac{[H^+][L^-]}{[HL]} \quad (2)$$

In this solution, we can establish the equations for concentration balance

$$[HL] + [L^-] = C \quad (3)$$

and charge balance [4, 5]

$$[H^+]-[OH^-]-[L^-] = 0 \quad (4)$$

The degree of dissociation (ionization) of HL is defined by formula

$$\alpha = \frac{[L^-]}{C} \quad (5)$$

Applying Eqs. (3) and (4) in (2), we obtain

$$K_a = \frac{[H^+]([H^+]-[OH^-])}{C-[H^+]+[OH^-]} \quad (6)$$

On the basis of (4) and (5), at $[H^+] >> [OH^-]$, one can write

$$[H^+] = [L^-] = \alpha \cdot C \quad (7)$$

and from (2) or (6) we have the well-known formula

$$K_a = \frac{C \cdot \alpha^2}{1-\alpha} \quad (8)$$

expressing the Ostwald's dilution law. The use of the word *dilution* suggests that the law is particularly valid for diluted solutions. This challenge seeks to find if this is indeed the case.

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The challenge

The limiting value for α at extremely diluted solutions can be obtained by transforming Eq. (8) into quadratic equation

$$C \cdot \alpha^2 + K_a \cdot \alpha - K_a = 0 \tag{9}$$

From here we obtain

$$\alpha = \frac{K_a}{2C}\left(\sqrt{1 + 4 \cdot C/K_a} - 1\right) \tag{10}$$

Applying the approximation $\sqrt{1 + 4C/K_a} \approx 1 + 2C/K_a$, valid for extremely diluted solutions with $4C << K_a$, we have

$$\alpha(C \to 0) = \lim_{C \to 0} \frac{K_a}{2C}\left(\sqrt{1 + 4 \cdot C/K_a} - 1\right) \approx \frac{K_a}{2C} \cdot \frac{2C}{K_a} = 1 \tag{11}$$

The above equation suggests that all weak acids dissociate completely at infinite dilution, irrespective of the K_a value. This statement, however, is invalid. Consider, for example, cyanic acid, HCN with pK_a=9.2. In large dilutions, the pH of HCN solutions will be near that of pure water, and HCN will be almost completely *undissociated*.

Can you find the proper expression for calculating the degree of dissociation?

Calculate the degree of dissociation of acetic acid under infinite dilution.

References

1. Ostwald WF (1888) Z Phys Chem 2:36–37
2. Servos JW (1990) Physical chemistry from Ostwald to Pauling. The making of a science in America. Princeton University Press, Princeton
3. Stock JT (1997) J Chem Educ 74(7):865–867
4. Asuero AG, Michałowski T (2011) Crit Rev Anal Chem 41:151–187
5. Michałowski T, Asuero AG (2012) Crit Rev Anal Chem 42:220–244

We invite our readers to participate in the Analytical Challenge by solving the puzzle above. Please send the correct solution to abc-challenge@springer.com *by June 1, 2014. Make sure you enter "*Ostwald's dilution law challenge*" in the subject line of your e-mail. The winner will be notified by e-mail and his/her name will be published on the "Analytical and Bioanalytical Chemistry" website at* http://www.springer.com/abc *and in the journal (volume 406/issue 22) where the readers will find the solution and a short explanation.*

The next Analytical Challenge will be published in 406/17, July 2014. If you have enjoyed solving this Analytical Challenge you are invited to try the previous puzzles on the ABC homepage.