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ANALYTICAL CHALLENGE

Solution to Ostwald's dilution law challenge

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The winner of the Ostwald's dilution law challenge (published in volume 406 issue 12) is:

Claus Hansen, Department of Pharmacy, University of Copenhagen, Sweden

The award entitles the winner to select a Springer book of his choice up to a value of €100.

Our Congratulations!

Solution

The Ostwald's dilution law challenge [1] sought to rectify the erroneous conclusion that one might obtain from the popular expression of Ostwald's dilution law,

$$K_1 = \frac{C \cdot \alpha^2}{1-\alpha} \tag{1}$$

One should take into account that Eq. (1) was obtained under the assumption that the equality $[H^+] = [L^-]$ is valid. However, unlike the concentration of L^- ions, the hydrogen-ion concentration is not zero at infinite dilutions. Rather,

$$\lim_{C \to 0} [H^+] = \sqrt{K_w} \tag{2}$$

In other words, infinitely diluted aqueous-acid solution is equivalent to pure water.

Combining the amount balance

$$[HL] + [L^-] = C \tag{3}$$

with the definitions of the dissociation constant (K_a) and degree of dissociation (α),

$$K_a = \frac{[H^+][L^-]}{[HL]} \tag{4}$$

$$\alpha = \frac{[L^-]}{C} \tag{5}$$

yields:

$$\alpha = \frac{1}{1 + [H^+]/K_a} \tag{6}$$

From here, using (2), we obtain

$$\alpha_0 = \lim_{C \to 0} \alpha = \frac{1}{1 + \sqrt{K_w}/K_a} = \frac{1}{1 + 10^{pK_a - \frac{1}{2}pK_w}} \tag{7}$$

Putting pK_w=14 and pK_a=4.75 into (7), we obtain α_0= 0.994 for acetic acid. Thus, under infinite dilution, 0.6 % of acetic acid remains undissociated. For cyanic acid, HCN, with pK_a=9.2, we obtain α_0=0.00627, i.e., 99.4 % of HCN remains undissociated, under infinite dilution. These results contradict the simple inferences resulting from Eq. (1).

This column provides a detailed treatment of the problem associated with Ostwald's dilution law. In conclusion, it is suggested that the word "dilution" should be omitted from the name of this law. Ostwald's law, in the authors' opinion, has some applications for testing acid–base equilibria in aqueous and non-aqueous media. In particular, one can refer to the papers [2, 3] devoted to formulation of $pK_a = pK_a(x_B)$ relationships for some binary-solvent systems, where x_B is the amount fraction of co-solvent (B) in a mixture of solvents (A + B).

This article is the solution to the Analytical Challenge to be found at http://dx.doi.org/10.1007/s00216-014-7700-4

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