ACTA CHEMICA SCANDINAVICA 1 (1947) 388—391

The Number Average of Diffusion Constants

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The diffusion curve of a normally diffusing substance with diffusion constant D_i and concentration c_i is obtained from the equation

$$y_i = \frac{c_i}{2\sqrt{\pi D_i t}} \cdot e^{-\frac{x^2}{4 D_i t}} = \psi(c_i, D_i) \qquad (1)$$

where x is the distance from the original, sharp boundary, y_i is the concentration gradient $\frac{dc_i}{dx}$ and t is the time. If several substances with different diffusion constants diffuse with a common original boundary we get a sum of diffusion curves:

$$y = \sum_i \psi\,(c_i, D_i) \qquad (2)$$

It has been shown [1, 2], that the formula

$$D_m = \frac{1}{2t} \cdot \frac{m_2}{m_0} \qquad (3)$$

gives a weight average of the diffusion constants:

$$D_m = \frac{\Sigma\, c_i D_i}{\Sigma\, c_i} \qquad (4)$$

Here, m_2 is the second moment of the curve, defined by the integral

$$m_2 = \int_{-\infty}^{+\infty} x^2\, y\, dx \qquad (5)$$

and m_0 is the "zero'th" moment, which is equal to the area A between the curve and the x-axis. This area is proportional to the concentration:

$$m_0 = A = \int_{-\infty}^{+\infty} y \, dx = k \, c = k \int dc \tag{6}$$

The same average (equation (4)) is obtained by using Boltzmann's equation

$$D = \frac{1}{2\,ty} \cdot \int_{x}^{\infty} x \; y \; dx \tag{7}$$

and forming the quotient $\frac{\int D \, dc}{\int dc}$, the integrations extended over the whole curve.

The formula

$$D_A = \frac{A^2}{4\pi t \, H^2} \tag{8}$$

where H is the maximum ordinate, gives the average

$$D_A = \left(\frac{\Sigma \, c_i}{\Sigma \, \frac{c_i}{\sqrt{D_i}}} \right)^2 \tag{9}$$

On differentiating (1) we get

$$\frac{dy_i}{dx} = - \frac{x \; y_i}{2 \; D_i \; t} \tag{10}$$

By summation of (10) for a constant x we get

$$\frac{\Sigma \, dy_i}{dx} = \frac{dy}{dx} = - \frac{x}{2t} \cdot \Sigma \, \frac{y_i}{D_i} \tag{11}$$

If D_i is a constant ($= D$) for all the components in the mixture this equation gives

$$D = -\frac{x\ \Sigma\ y_i}{2t} \cdot \frac{dx}{dy} = -\frac{x \cdot y \cdot dx}{2t \cdot dy} \tag{12}$$

If D_i varies and the formula (12) is applied at the point x, we get the average

$$D_x = \frac{\Sigma\ y_i \cdot dx}{\Sigma \frac{y_i}{D_i} \cdot dx}$$

or, as $y_i\ dx = k\ dc_i$

$$D_x = \frac{\Sigma\ dc_i}{\Sigma \frac{dc_i}{D_i}} \tag{13}$$

The number average is defined as

$$D_n = \frac{\Sigma\ c_i}{\Sigma \frac{c_i}{D_i}} = \frac{\int dc}{\int \frac{dc}{D}} \tag{14}$$

and thus D_x is a number average at the point x. As D_i is independent of x, we can perform an integration over the whole curve and get

$$k \cdot \int \frac{dc}{D} = \int \Sigma \frac{y_i}{D_i}\ dx = \int \frac{\Sigma\ y_i\ dx}{D_x} = \int \frac{y\ dx}{D_x} \tag{15}$$

This equation can be used for calculating a number average D_n of the diffusion constants.

It is also possible to get a formula for the direct calculation of D_n from the curve. The introduction of D_x from equation (12) into (14) and (15) gives

$$D_n = \frac{\int y\ dx}{\int \frac{y\ dx}{D_x}} = -\frac{\int y \cdot dx}{2t \int \frac{y\ dx \frac{dy}{dx}}{x\ y}} = -\frac{1}{2\ t} \cdot \frac{\int y \cdot dx}{\int \frac{\frac{dy}{dx} \cdot dx}{x}} \tag{16}$$

In a still simpler form this can be written

$$D_n = -\frac{1}{2t} \cdot \frac{A}{\int \frac{dy}{x}} \tag{17}$$

where the integration should be extended over the whole curve. The equations (16) and (17) thus make it possible to calculate the number average D_n. Jullander[3] and, later, Singer[4] have shown that D_n should be especially valuable for the calculation of the weight average of molecular weights by using Svedberg's formula. As no method for the calculation of D_n has been available, the formulas derived here should fill a gap and give further possibilities of characterizing the polydispersity of a substance.

SUMMARY

The formula

$$D_n = -\frac{1}{2t} \cdot \frac{A}{\int \frac{dy}{x}}$$

gives the number average, $\frac{\int dc}{\int \frac{dc}{D}}$, of the diffusion constants of a mixture. Here x is the distance from the original, sharp boundary, y is the concentration gradient, and t is the time. A is the area $\int y dx$, and the integrations shall be extended over the whole curve.

The formula derived gives new possibilities of characterizing the polydispersity of a substance.

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Received April 16, 1947.