Planck-Henderson Equation for the Diffusion Potential

The basic equation for diffusion potential is applicable only if the potential difference \( (d\psi) \) is considered over a very small distance \( (dx) \). However, the problem of obtaining an overall potential difference \( (\Delta\psi = \psi^0 - \psi^l) \) that develops from \( x = 0 \) to \( x = l \) was still there.

This was overcome by Planck-Henderson equation which can be obtained by recalling the basic equation for diffusion first i.e.

\[
-d\psi = \frac{1}{F} \sum \frac{t_i}{z_i} d\mu_i
\]  

(195)

Where \( t_i \) and \( z_i \) are the charge number of \( i \)th species whereas \( F \) represents the Faraday constant. Integrating equation (195), we get

\[
-\Delta\psi = \psi^0 - \psi^l = \frac{1}{F} \sum \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d\mu_i}{dx} dx
\]  

(196)

or

\[
-\Delta\psi = \frac{RT}{F} \sum \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d ln a_i}{dx} dx
\]  

(197)

or
At this stage, the things we need to evaluate the equation (198) are the concentration of all species in the interphase region, the variation of activity coefficient and transport number with concentration. For simplicity, the activity coefficients can be taken as unity and transport numbers as constant. In addition to these assumptions, the variation of concentration of \( i \)th species with distance is considered as linear i.e.

\[
c_i(x) = k_i x + c_i(0)
\]  (199)

For constant \( k_i \), differentiate above equation i.e.

\[
\frac{dc_i}{dx} = k_i = c_i(l) - c_i(0)
\]  (200)

Now using equation (199, 200) in equation (198), we get

\[
-\Delta \psi = \frac{RT}{F} \sum_i t_i \int_{x=0}^{x=l} \frac{dz_i c_i}{dx} dx
\]  (201)

or

\[
-\Delta \psi = \frac{RT}{F} \sum_i t_i \int_{x=0}^{x=l} \frac{k_i}{z_i c_i(0) + k_1 x} dx
\]  (202)

or

\[
-\Delta \psi = \frac{RT}{F} \sum_i t_i \int_{x=0}^{x=l} \frac{dz_i}{z_i} \ln \left( \frac{k_i x + c_i(0)}{k_1 x + c_i(0)} \right)
\]  (203)

or

\[
-\Delta \psi = \frac{RT}{F} \sum_i t_i \frac{c_i(l)}{c_i(0)} \ln \frac{c_i(l)}{c_i(0)}
\]  (204)

Which is the general form of the Planck-Henderson equation for diffusion potential. Using \( c_+ = c_- = c \) and \( z_+ = z_- = z \) for \( z \): \( z \) electrolyte, we have

\[
-\Delta \psi = \frac{RT}{zF} (t_+ - t_-) \ln \frac{c_i(l)}{c_i(0)}
\]  (205)

Furthermore, putting \( t_+ + t_- = 1 \), the equation (205) takes the form
\[-\Delta \psi = \frac{RT}{zF}(2t_+ - 1) \ln \frac{c_i(l)}{c_i(0)}\]  

(206)

Which is the another form of Planck-Henderson equation for simple systems.
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