❖ 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.

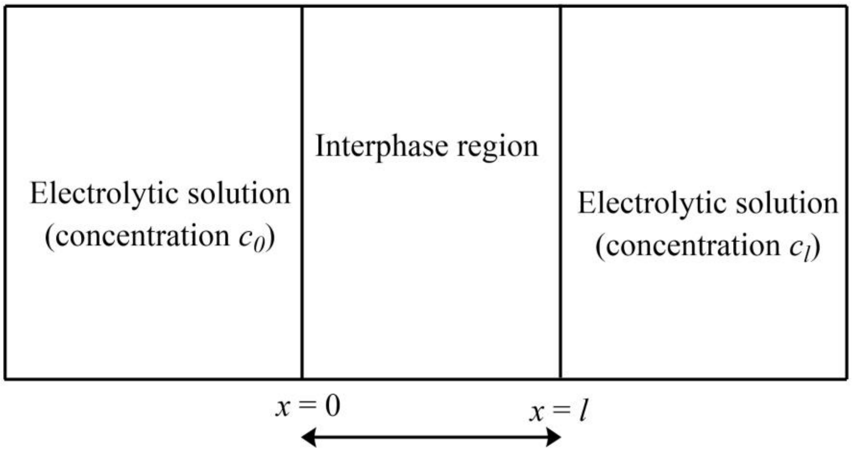

Figure 12. The overall potential difference across the complete interphase domain between electrolytes with concentration c_0 and c_l.

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

$$-d\psi = \frac{1}{F}\sum \frac{t_i}{z_i} d\mu_i \tag{195}$$

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

$$-\Delta\psi = \psi^0 - \psi^l = \frac{1}{F}\sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d\mu_i}{dx} dx \tag{196}$$

or

$$-\Delta\psi = \frac{RT}{F}\sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d \ln a_i}{dx} dx \tag{197}$$

or

$$-\Delta\psi = \frac{RT}{F}\sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i}\frac{1}{f_i c_i}\frac{d\,(f_i c_i)}{dx}dx \tag{198}$$

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 ith species with distance is considered as linear i.e.

$$c_i(x) = k_i x + c_i(0) \tag{199}$$

For constant k_i, differentiate above equation i.e.

$$\frac{dc_i}{dx} = k_i = \frac{c_i(l) - c_i(0)}{l} \tag{200}$$

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

$$-\Delta\psi = \frac{RT}{F}\sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i}\frac{k_1}{c_i(0) + k_1 x}dx \tag{201}$$

or

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

or

$$-\Delta\psi = \frac{RT}{F}\sum_i \frac{t_i}{z_i}\{\ln[k_1 x + c_i(0)]\}_{x=0}^{x=l} \tag{203}$$

or

$$-\Delta\psi = \frac{RT}{F}\sum_i \frac{t_i}{z_i}\ln\frac{c_i(l)}{c_i(0)} \tag{204}$$

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

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

Furthermore, putting $t_+ + t_- = 1$, the equation (205) takes the form

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$$-\Delta\psi = \frac{RT}{zF}(2t_+ - 1)\ln\frac{c_i(l)}{c_i(0)} \tag{206}$$

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

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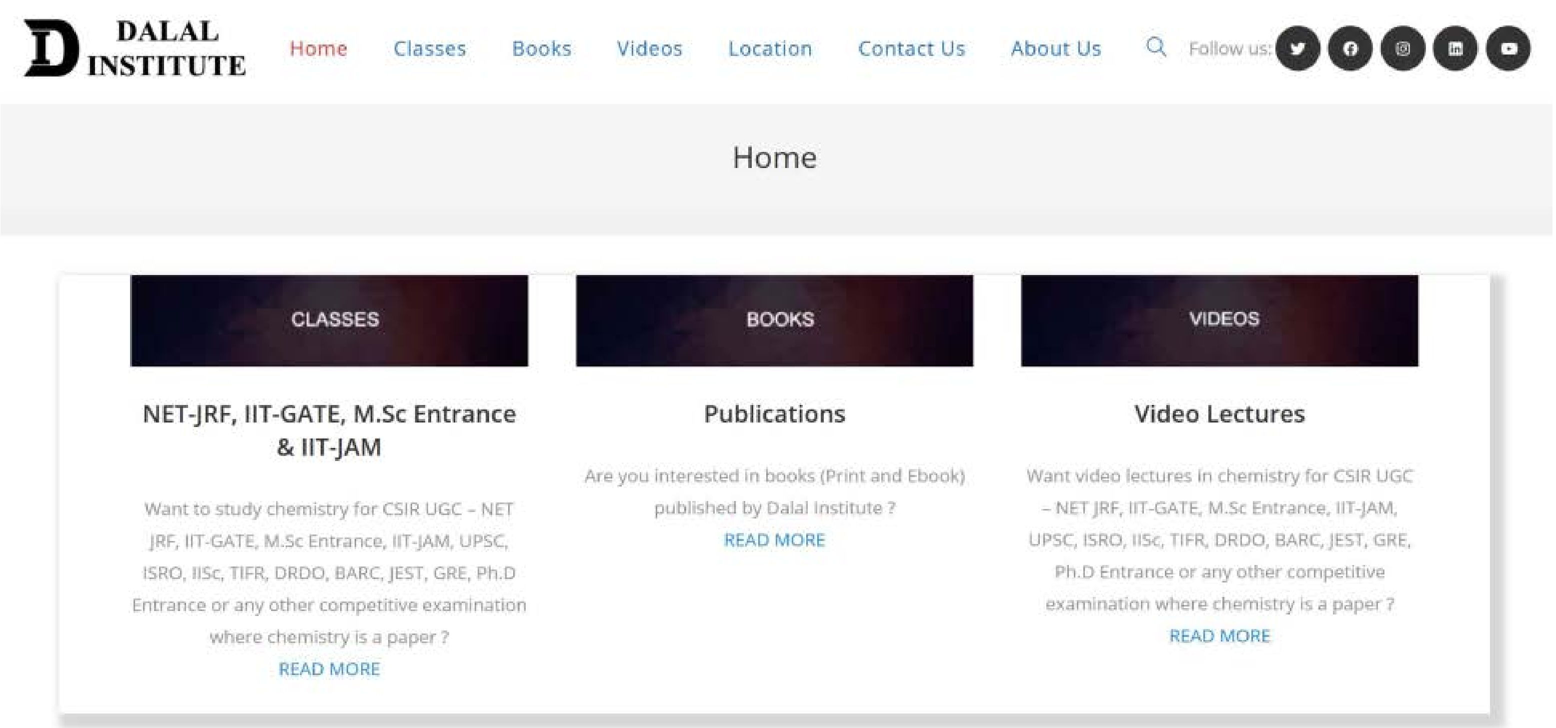

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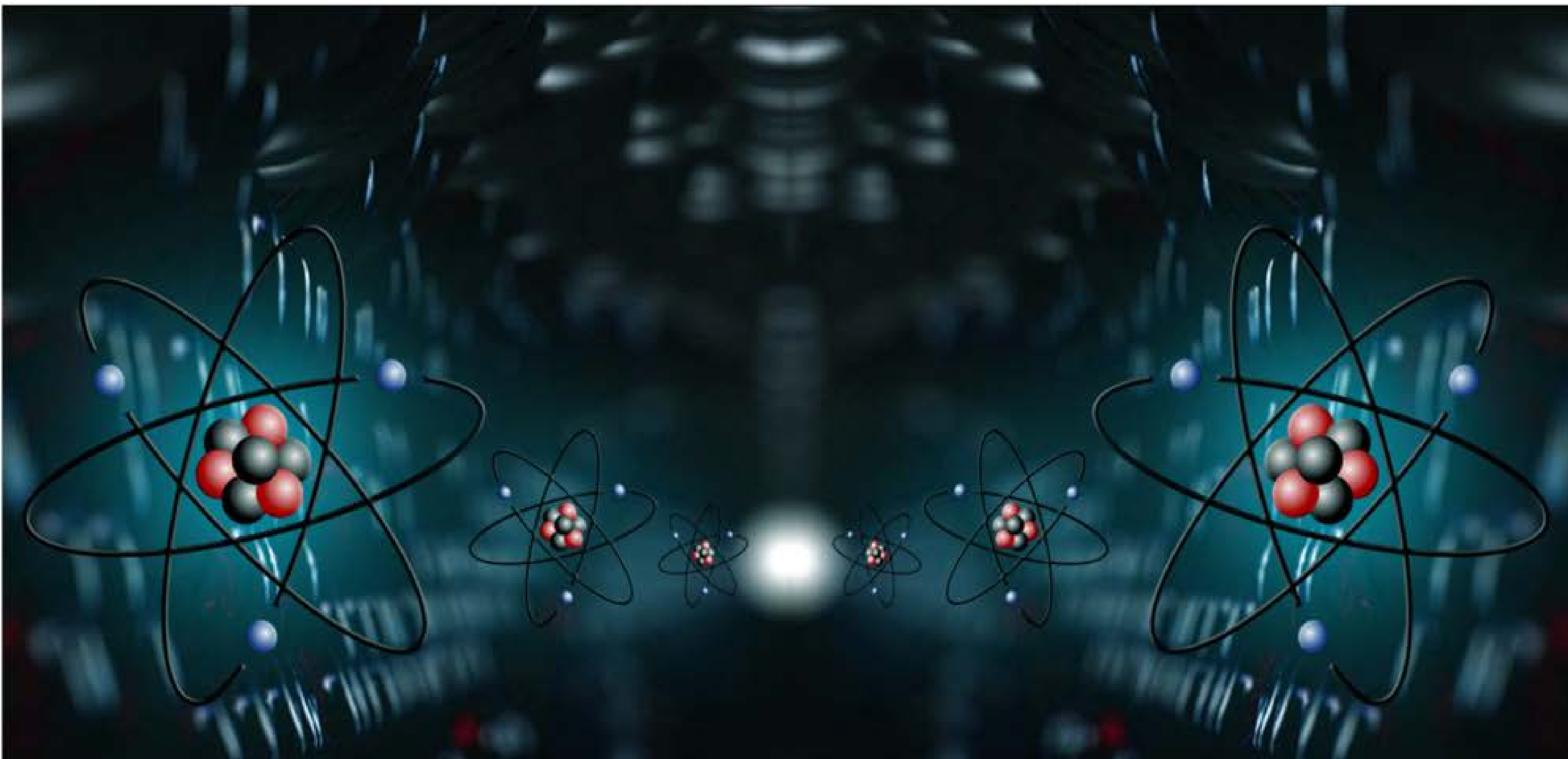

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