

Table 23.1 The Debye length $1/\kappa$ describes the range of the potential, given here for various concentrations c of aqueous monovalent salt solutions at 25 °C.

c (mol L ⁻¹)	$1/\kappa$ Å
0.5	4.30
0.2	6.80
0.1	9.62
0.05	13.6
0.02	21.5
0.01	30.4
0.005	43.0
0.002	68.0
0.001	96.2

Now you have all the terms necessary to formulate the **Poisson-Boltzmann equation**. Substitute $n_+(x)$ and $n_-(x)$ from Equations (23.1) and (23.2) into Equation (23.3) for ρ and then into Equation (21.30):

$$\nabla^2\psi = \frac{ze n_\infty}{D\epsilon_0} (e^{ze\psi/kT} - e^{-ze\psi/kT}), \quad (23.4)$$

Equation (23.4) can be expressed more compactly in terms of the hyperbolic sine function, $\sinh(x) = (e^x - e^{-x})/2$:

$$\nabla^2\psi = \frac{2ze n_\infty}{D\epsilon_0} \sinh(ze\psi/kT). \quad (23.5)$$

The Poisson-Boltzmann equation (23.5) is a nonlinear second-order differential equation from which you can compute ψ if you know the charge density on P and the bulk salt concentration, n_∞ . This equation can be solved numerically by a computer. However, a linear approximation, which is easy to solve without a computer, applies when the electrostatic potential is small. For small potentials, $ze\psi/kT \ll 1$, you can use the approximation $\sinh(x) \approx [(1+x) - (1-x)]/2 = x$ (which is the first term of the Taylor series expansion for the two exponentials in $\sinh(x)$ (see Appendix C, Equation (C.1)). Then Equation (23.5) becomes

$$\nabla^2\psi = \frac{2ze n_\infty}{D\epsilon_0} (ze\psi/kT) = \kappa^2\psi, \quad (23.6)$$

where κ^2 is defined by

$$\kappa^2 = \frac{2z^2 e^2 n_\infty}{D\epsilon_0 kT}. \quad (23.7)$$

Equation (23.6) is called either the **linearized Poisson-Boltzmann** or the **Debye-Hückel equation**. $1/\kappa$ is called the **Debye length**. The Debye length is a screening, or shielding, distance. A charge that is closer to P than $1/\kappa$ 'sees' the charged plane and interacts with it. A charge that is further than $1/\kappa$ from P is shielded from it by the intervening salt solution, which weakens its attraction or repulsion for the plane. Table 23.1 shows that increasing the concentration of the salt decreases the Debye length. Example 23.1 shows how the Debye length is computed.

EXAMPLE 23.1 Computing Debye lengths. For a monovalent salt, $z = 1$, with concentration 0.1 mol L^{-1} , show that the Debye length is 9.62 Å if $D = 78.54$ (see Table 23.1).

Multiply the numerator and denominator on the right-hand side of Equation (23.7) by Avogadro's number \mathcal{N} to get

$$\kappa^2 = \frac{2(ze)^2 n_\infty \mathcal{N}}{D\epsilon_0 RT}.$$

From the units given in the box on page 370, $e^2 \mathcal{N}/(4\pi\epsilon_0) = 1.386 \times 10^{-4} \text{ J m mol}^{-1}$, so

$$\kappa^2 = 2(4\pi) (1.386 \times 10^{-4} \text{ J m mol}^{-1}) (0.1 \text{ mol L}^{-1}) (10^3 \text{ L m}^{-3})$$

$$\begin{aligned} & \times \frac{(6.022 \times 10^{23} \text{ molecule mol}^{-1})}{[(78.54)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(298 \text{ K})]} \\ & = 0.01078 \times 10^{20} \text{ m}^{-2} \Rightarrow \frac{1}{\kappa} = 9.62 \times 10^{-10} \text{ m} = 9.62 \text{ \AA}. \end{aligned}$$

Equation (23.4) may also be used for *asymmetrical* electrolyte solutions, in which the valency z_- of the anion is not the same as the valency z_+ of the cation. If ionic species i has valency z_i and molar concentration m_i , replace $n_\infty z^2$ in Equation (23.7) with the quantity $I = (1/2) \sum_i m_i z_i^2$, which is the **ionic strength** of the solution.

The Poisson-Boltzmann model is used to compute the electrostatic potential ψ if you know the charge on a surface and the concentration of salt in the solution. In Example 23.2, we compute $\psi(x)$ in the direction normal to a charged plane in a salt solution.

EXAMPLE 23.2 The potential near a uniformly charged plane in a salt solution. Because ψ depends only on x in this case, you need to solve the Poisson-Boltzmann Equation (23.6) in only one dimension to find the potential at a distance x from a plane having surface charge density σ :

$$\frac{d^2 \psi}{dx^2} = \kappa^2 \psi. \quad (23.8)$$

You can verify that the function

$$\psi(x) = A_1 e^{\kappa x} + A_2 e^{-\kappa x} \quad (23.9)$$

satisfies Equation (23.8) for any constants A_1 and A_2 by substituting Equation (23.9) into Equation (23.8) and carrying out the two differentiations indicated.

To solve Equation (23.8), we need two boundary conditions. We follow the same conventions that we used in solving the Poisson equation. First, the electrostatic potential is defined to be zero $\psi(\infty) = 0$ as $x \rightarrow \infty$; this gives $A_1 = 0$. Second, we require that at $x = 0$, $\psi = \psi_0$, where ψ_0 is the potential at the surface. This gives $A_2 = \psi_0$, so the electrostatic potential is

$$\psi(x) = \psi_0 e^{-\kappa x}. \quad (23.10)$$

Equation (23.10) predicts that the electrostatic potential in salt solutions approaches zero *exponentially* as a function of distance from the charged plane. In contrast, Equation (21.12) shows that in the absence of salt, the electrostatic potential varies *linearly* with distance from a charged plane.

To complete Equation (23.10), compute the surface potential ψ_0 from the given surface charge σ , the number of charges per unit area. This can be done in different ways. The surface charge on the plane must be compensated by the net charge (of opposite sign) in the solution, so

$$\sigma = - \int_0^\infty \rho(x) dx = D\epsilon_0 \int_0^\infty \frac{d^2 \psi}{dx^2} dx \quad (23.11)$$