6.3: Free Energy of Ions in Solution

Returning to our continuum model of the solvation free energy, and apply this to solvating an ion. As discussed earlier, ΔG_{sol} will require forming a small cavity in water and turning on the interactions between the ion and water. We can calculate the energy for solvating an ion in a dielectric medium as the reversible work needed to charge the ion from a charge of 0 to its final value q within the dielectric medium:

$$w = \int_0^q \Phi_{\text{ion}} dq \tag{6.3.1}$$

As we grow the charge, it will induce a response from the dielectric medium (a polarization) that scales with electrostatic potential: $\Phi = q/4\pi\varepsilon r$. We take the ion to occupy a spherical cavity with radius a. Although we can place a point charge at the center of the sphere, it is more easily solved assuming that the charge q is uniformly distributed over the surface of the sphere. Then the electrostatic potential at the surface of the sphere is $q/4\pi\varepsilon a$ and the resulting work is

$$w = \frac{q^2}{8\pi\varepsilon b}$$

In a similar manner, we can calculate the energy it takes to transfer an ion from one medium with ε_1 to another with ε_2. We first discharge the ion in medium 1, transfer, and recharge the ion in medium 2. The resulting work, the Born transfer energy, is

$$\Delta w = \frac{q^2}{8\pi a}\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right)$$

If you choose to distribute the charge uniformly through the spherical cavity, the prefactor $q^2/8\pi a$ becomes $3q^2/20\pi a$