5.8: Ionic Activity

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a r^{-7} dependence, and for practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law, which has a r^{-2} dependence. Consequently, the behavior of an electrolyte solution deviates considerably from that an ideal solution. Indeed, this is why we utilize the activity of the individual components and not the concentration to calculate deviations from ideal behavior. In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, $\gamma_\pm$, and could explain how the behavior of ions in solution contribute to this constant.

> 📌 **Assumptions of Debye-Hückel Theory**
>
> The Debye-Hückel theory is based on three assumptions of how ions act in solution:
>
> 1. Electrolytes completely dissociate into ions in solution.
> 2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
> 3. Each ion is surrounded by ions of the opposite charge, on average.

Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient $\gamma_\pm$:

$$\log \gamma_\pm = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} \mid z_+ z_- \mid \sqrt{I} \tag{5.8.1}$$

where

- ε is the dielectric constant,
- z_+ and z_- are the charges of the cation and anion, respectively, and
- I is the ionic strength of the solution.

The Equation 5.8.1 is known as the **Debye-Hückel Limiting Law**. The ionic strength is calculated by the following relation:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \tag{5.8.2}$$

where m_i and z_i are the molality and the charge of the ith ion in the electrolyte. Since most of the electrolyte solutions we study are aqueous ($\varepsilon = 78.54$) and have a temperature of 298 K, the Limiting Law in Equation 5.8.1 reduces to
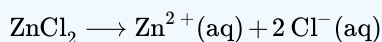
$$\log \gamma_\pm = -0.509 \mid z_+ z_- \mid \sqrt{I} \tag{5.8.3}$$

> ✔ **Example 5.8.1**
>
> Calculate ionic strength, mean ionic activity coefficient $\gamma_\pm$, and the mean ionic molality $m_\pm$ for a 0.02 *molal* aqueous solution of zinc chloride, $ZnCl_2$.
>
> **Solution**
>
> Zinc chloride will dissolve as
>
> $$ZnCl_2 \longrightarrow Zn^{2+}(aq) + 2\,Cl^-(aq)$$
>
> The concentrations of the zinc and chloride ions will then be 0.02 and 0.04 molal, respectively. First calculate the mean ionic molality. The mean ionic molality is defined as the average molality of the two ions (see Electrolyte Solutions):
>
> $$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{\frac{1}{\nu}}$$
>
> where ν is the stoichiometric coefficient of the ions, and the total of the coefficients in the exponent. In our case, the mean ionic molality is

$$m_{\pm} = \left(m_{Zn}^{\nu(Zn)} m_{Cl}^{\nu(Cl)}\right)^{\frac{1}{\nu(Zn)+\nu(Cl)}}$$

$$= [(0.02)^1 (0.04)^2]^{\frac{1}{3}}$$

$$= [(0.02)(0.0016)]^{\frac{1}{3}}$$

$$= 3.17 \times 10^{-2}$$

To calculate the mean ionic activity coefficient, we first need the ionic strength of the solution from Equation 5.8.2:

$$I = \frac{1}{2}[(0.02)(+2)^2 + (0.04)(-1)^2]$$

$$= \frac{1}{2}(0.08 + 0.04) = 0.06$$

Now we can use Equation 5.8.3 to calculate the activity coefficient:

$$\log \gamma_{\pm} = -0.509 \mid (+2)(-1) \mid \sqrt{0.06}$$

$$= (-0.509)(2)(0.245)$$

$$= -0.250$$

$$\gamma_{\pm} = 10^{-0.25}$$

$$= 0.1627$$

? Exercise 5.8.1

Determine the mean ionic activity coefficient and mean activity of a 0.004 molal of $Ba(HCO_3)_2$?

Apr 11, 2020, 9:58 PM

https://socratic.org/questions/560b11bf581e2a331df2c7fd

Answer

$$\gamma_{\pm} = 10^{-0.10188} \approx 0.7909$$

$$a_{\pm} = 0.7909 \times 0.2785\, m = 0.2203\, m$$

Figure 5.8.1: Example activity coefficients. https://www.youtube.com/watch?v=MZCNooIEzQQ

The kinetic salt effect is the effect of salts preset in solution on the rate of a reaction.

Kinetic Salt Effect

In biological systems, salts influence how well proteins and DNA function. Salts are formed by ionic bonds, between a metal and an electromagnetic atom(s). Some examples of salts include NaCl, KCl, and Na_2SO_4. Salt molecules are able to disassociate, forming cations and anions. An increase in the charge (- or +) of a transition state or an activated complex results in an increase in solvation (creating more order in the system), and causes a decrease in the change of entropy (ΔS). In contrast, a decrease in the charge of the transition state causes an increase in ΔS.

$$I^- + C^+ \rightleftharpoons E^o \rightarrow Product \tag{5.8.4}$$

The kinetic salt effect describes the way salts stabilize reactants. For example, in the above reaction, each reactant has a charge. The negatively-charged reactant is stabilized by the positive charges from the salt, and the positively-charged reactant is stabilized by the negative charges from the salt. As a result, the rate at which the reactants come together decreases, thus decreasing the rate at which E forms. Because a charged intermediate is also stabilized in the solution, the half life of the intermediate at equilibrium increases, shifting the reaction toward product formation. Because the rate of the product formation is higher due to increased amounts of the intermediate present on the solution, first order kinetics is used to derive the rate constant equation:

$$\log K_{TS} = \log K_{TS^o} + 2 Z_A Z_B \sqrt{I} \tag{5.8.5}$$

where

- Z is the charge on the cation and ion from the salt. $Z_A Z_B$ is a product value.
- I is the ionic strength. I is also dependent on the solubility of the salt in the reaction mixture. Ionic strength is directly proportional to the solubility of the salt. Changing the ionic strength manipulates the solvation of the reactants and intermediates, thus changing ΔS, and affecting the reaction rate.
- $\log K_{TS^o}$ is the rate constant without the salt in the reaction mixture.
- A is also a constant for the solvent the solution is in. The A value for water is 0.509 at 298 K.

The relationship between $Z_A Z_B$, I, and the rate of the reaction is presented in tabular form below:

$Z_A Z_B$	Rate of Reaction
+	Increases (salt present in the reaction mixture)
-	Decreases (the ionic strength increases)

Note: I=0 at very dilute salt concentrations or if the salt is inert.

References

1. Atkins, P.W. Physical Chemistry. 5th Ed. New York: WH Freeman, 1994.
2. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

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