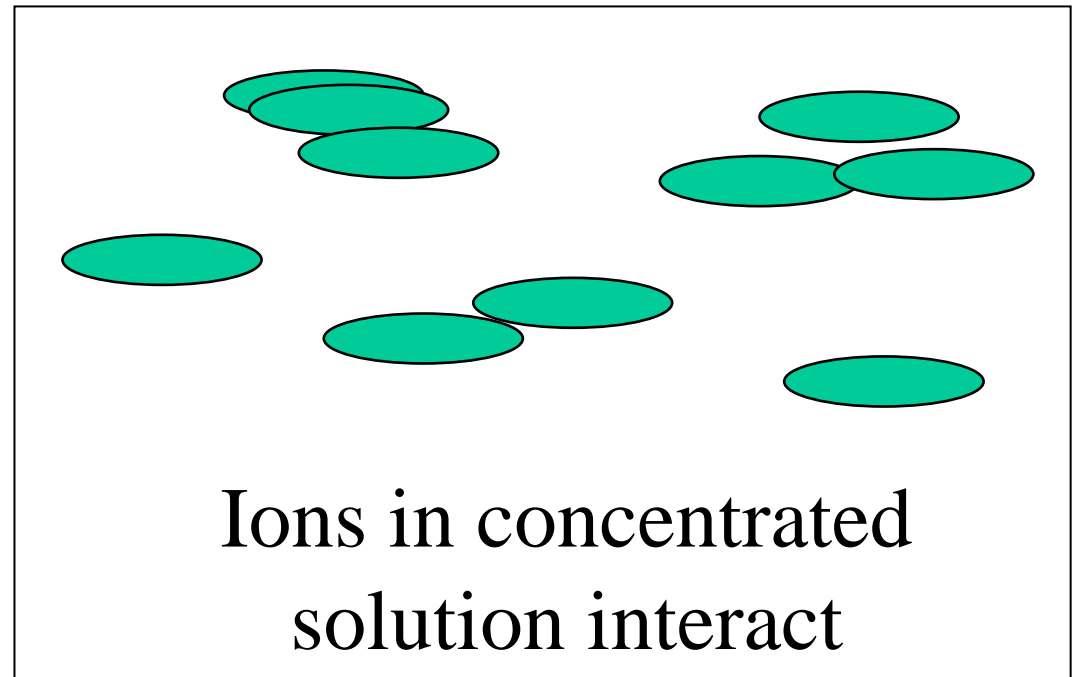
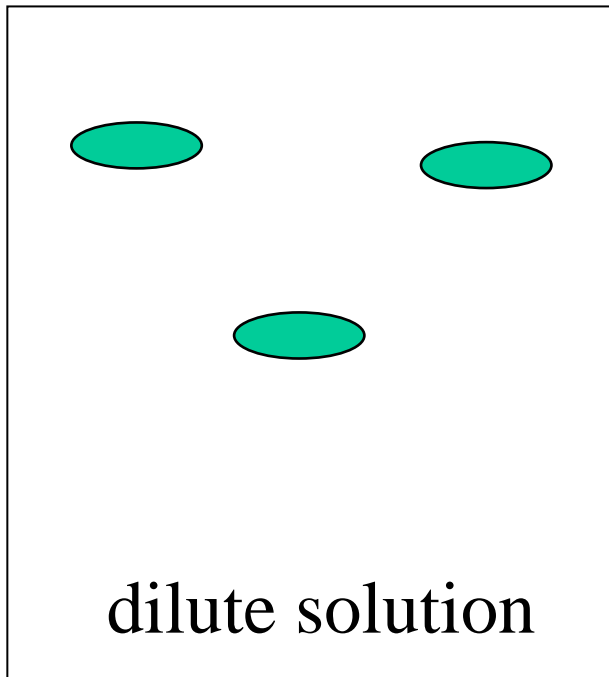


Chapter 8 - Activity

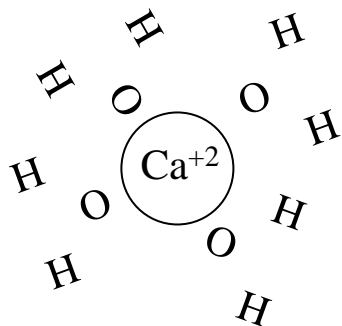


How do ionized species interact in solution?

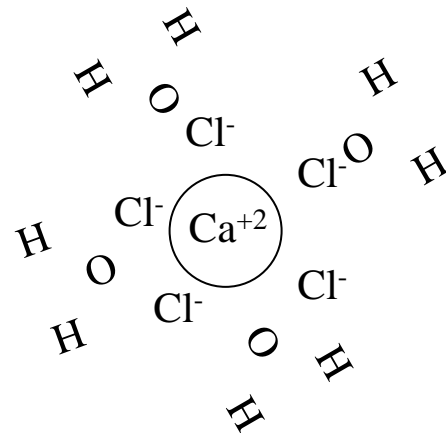
- The charge on the ions attracts or repels other ionic species as well as polar species.
- The more dense the charge, the stronger the attraction.
- The more diffuse the charge, the weaker the attraction.
- The ion attracts polar water molecules and becomes surrounded or hydrated; thus, ions have a hydration sphere.
- If there are other ions in solution, these ions perturb the hydration sphere. For example, if Ca^{+2} present in distilled water, it is surrounded by H_2O molecules to form its hydration sphere.

For example:

If Ca^{+2} present in distilled water, it is surrounded by H_2O molecules to form its hydration sphere.



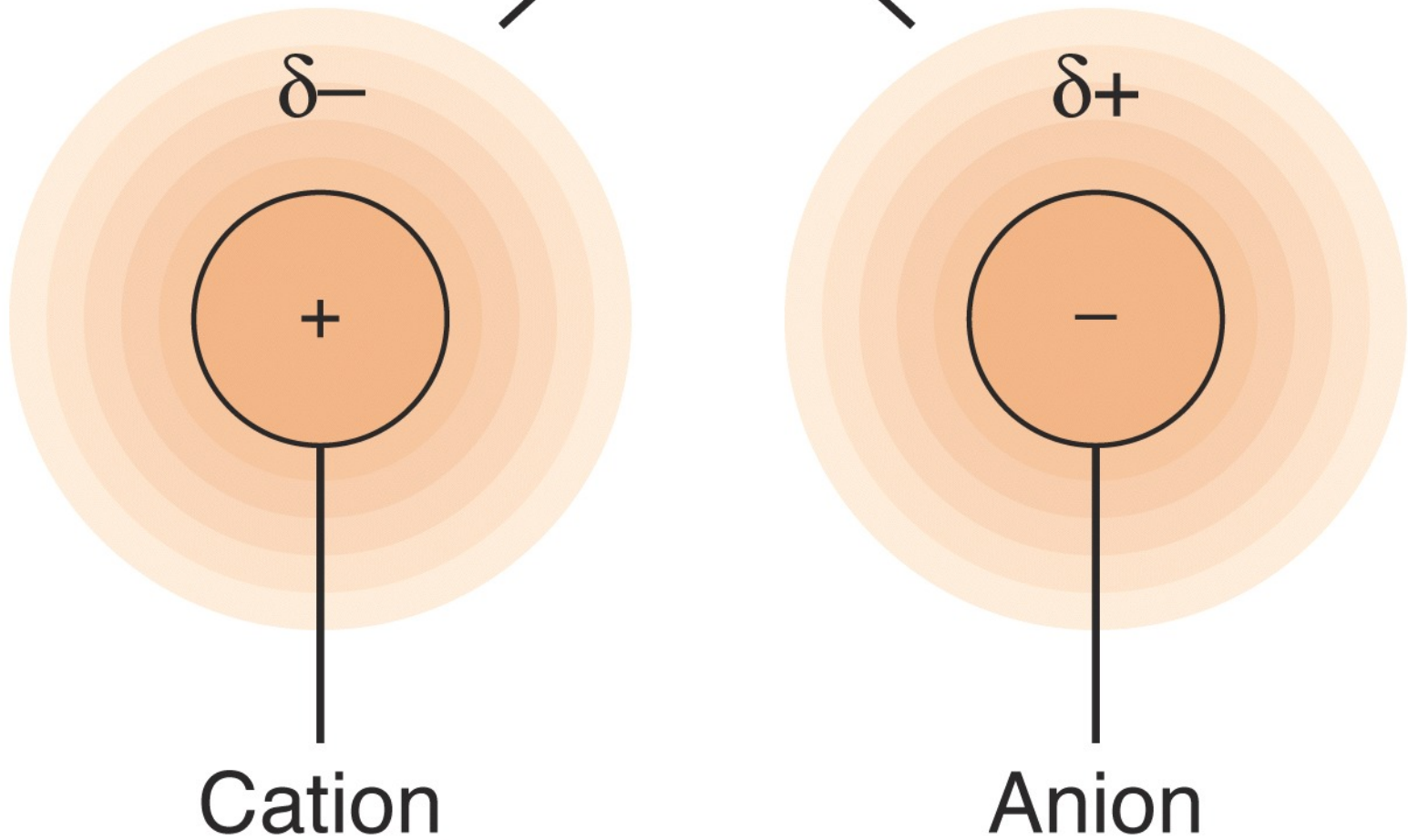
If Ca^{+2} is present in water with Cl^- present also, the Cl^- has a stronger negative attraction than the dipolar negative aspect of H_2O . The Cl^- will gain closer access to the Ca^{+2} ion, and perturb the hydration sphere.



So what does that mean?

- An ion in which the hydration sphere has been changed now has an ionic environment in place of the hydration sphere.
- A cation will build up anions around it, and an anion will build up cations around it.
- The ionic environment decreases the attraction of the ion's ability to attract any additional ions of the opposite charge.
- This ionic environment, in a sense, weakens the attractive force compared to the attractive force of the same ion that only has a hydration sphere (in water only).

Ionic atmospheres



Addition of “inert” ionic species to solution.

- By adding ions that do not react with the analyte ions in solution except to get close to them and form an ionic environment (termed inert ions), these inert ions can increase the solubility of ionic compounds.

For example:



In water only, the Ba^{+2} and SO_4^{-2} are more attracted to each other, than to the water molecules, so they form BaSO_4 again. If other ions are added (like KNO_3), the K^+ decreases the SO_4^{-2} attraction for other cations (like Ba^{+2}). Likewise, the NO_3^- decreases the Ba^{+2} attraction for other anions (like SO_4^{-2}).

Significance

- K_{sp} for $BaSO_4$
in water: 1×10^{-10}
in 0.01 M KNO_3 : 2.9×10^{-10}
- Solubility is altered because K^+ and NO_3^- act to shield Ba^{2+} and SO_4^{2-} from each other in solution so they don't recombine.
- Analogy: big class vs. small class

Account for this effect using activity coefficient:

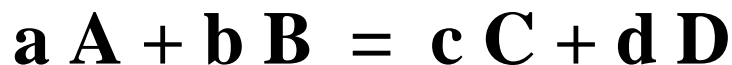
$$a_A = \gamma_A [A]$$

where: a_A is activity of A

γ_A is the activity coefficient

$[A]$ is molarity (moles/L)

RECALL --



$$\mathbf{K = [C]^c [D]^d / [A]^a [B]^b}$$

BUT REALLY....

$$\mathbf{K = \mathcal{A}_c^c \mathcal{A}_d^d / \mathcal{A}_a^a \mathcal{A}_b^b}$$

or

$$\mathbf{K = [C]^c \gamma_c^c [D]^d \gamma_d^d / [A]^a \gamma_a^a [B]^b \gamma_b^b}$$

How do we determine the activity (\mathcal{A})?

$$\mathcal{A} = [\mathbf{X}]^x \gamma_{\mathbf{X}}^x$$

We know $[\mathbf{X}]$ is the molar concentration (moles/L).

$\gamma_{\mathbf{X}}$ is the activity coefficient for species \mathbf{X} .

It is dependent on:

- the ionic strength of the solution (μ)
- the charge of the ion (z)
- the ionic size (α).

Ionic Strength

$$\mu = 0.5 \sum c_i z_i^2$$

where:

c_i is molarity of i th ion

z_i is charge on i th ion

Note: effect of square is to remove sign of charge so + and - don't cancel out!

Example: Calculate the ionic strength of 0.010 M Na_2SO_4^- .

$$\begin{aligned}\mu &= 0.5 \sum c_i z_i^2 \\ &= 0.5 ([\text{Na}^+](+1)^2 + [\text{SO}_4^{-2}](-2)^2) \\ &= 0.5 ((0.02)(1) + (0.01)(4)) \\ &= 0.030 \text{ M}\end{aligned}$$

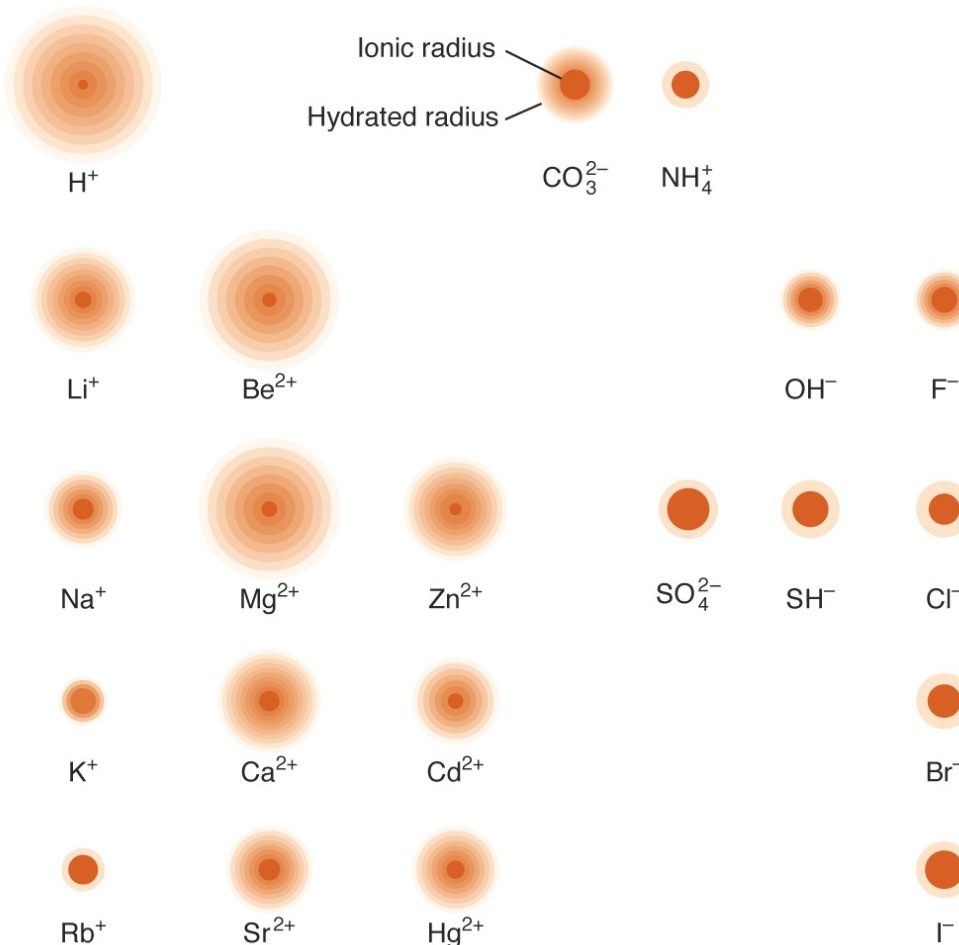
Ionic Size

Overall charge on ion is more diffuse if:

1. Larger the radius
2. The lower the charge

So...

More diffuse the overall charge, the less it will affect the activity



Ionic sizes are tabulated on page 154 of Harris

Debye-Hückel Equation:

In 1923, P. Debye and E. Hückel used the ionic atmosphere model to derive a theoretical expression that permits the calculation of activity coefficients of ions from their charge and their average size.

This is called Debye-Hückel Equation:

$$-\log \gamma_i = \frac{AZ_i^2 \mu^{1/2}}{1 + Ba_i \mu^{1/2}} \quad \mu < 0.1 \text{ M}$$

$$\mu = \frac{1}{2} \sum_i C_i Z_i^2 \cong 2.5 \times 10^{-5} (\text{TDS})$$

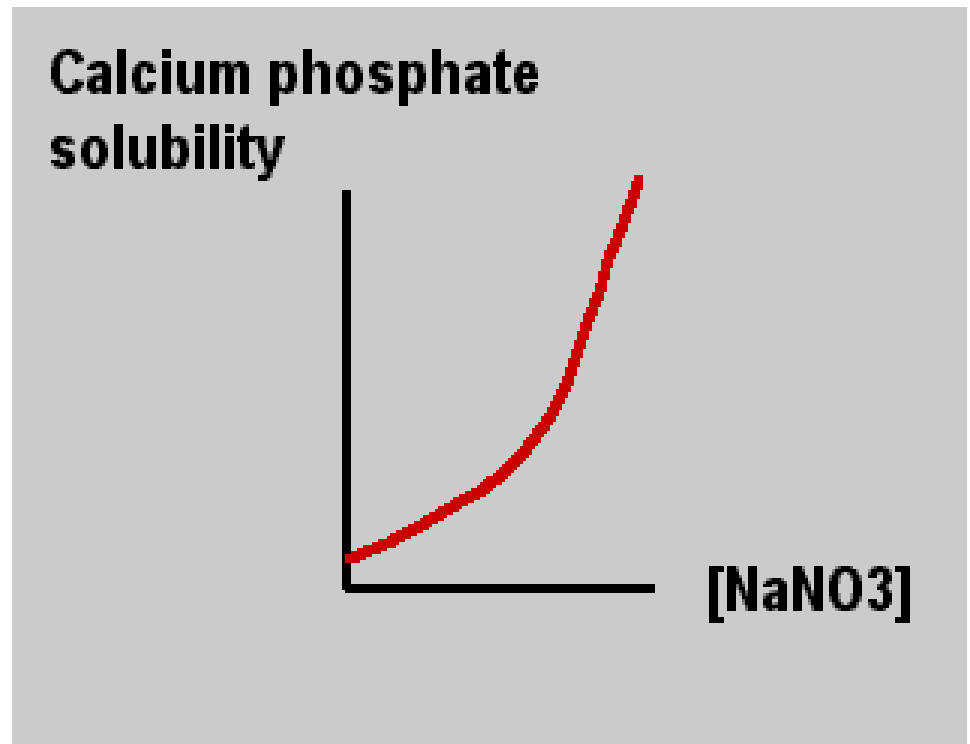
- $A = 0.5$ and $B = 0.326 \times 10^8$ for water (15°C)
- $a_i = 4 \times 10^{-8}$ for monovalent ions
- Z = ionic charge
- μ = ionic strength
- C = molar concentration
- TDS = total dissolved solids, mg/l

Points concerning the Debye-Hückel Equation

- The constants A and B are applicable to aqueous solutions at 25°C.
- The equation works fairly well for $\mu \leq 0.1\text{M}$.
- α is the effective hydrated radius of the ion and its tightly bound sheath of water molecules.
- As ionic strength increases, the activity coefficient decreases. For all ions, γ approaches unity as μ approaches zero.
- As the charge of the ion increases, the departure of its activity coefficient from unity increases. Activity corrections are much more important for an ion with a charge of ± 3 than for one with a charge of ± 1 .
- The smaller the hydrated radius of the ion, the more important activity effects become.

Does γ really matter?

- The solubility of $\text{Ca}_3(\text{PO}_4)_2$ (s) is measured in pure water and in aqueous solutions of NaNO_3
- The behavior on the right is found



Points concerning Activity (\mathcal{A}):

- Concentration of ions (ionic strength, μ) is important.
- Charge on ions (z) is important.
- Size of ions (α) is important.
- Molar concentrations are an approximation for activity of solution species.
- “Activity” (\mathcal{A}) should be used for exact work.
- The activity coefficient (γ_x) of a species is a measure of the effectiveness with which that species influences an equilibrium.
- In very dilute solutions (μ is small), this effectiveness becomes constant and the activity coefficient is unity. The activity and molar conc. of the species is equal.

