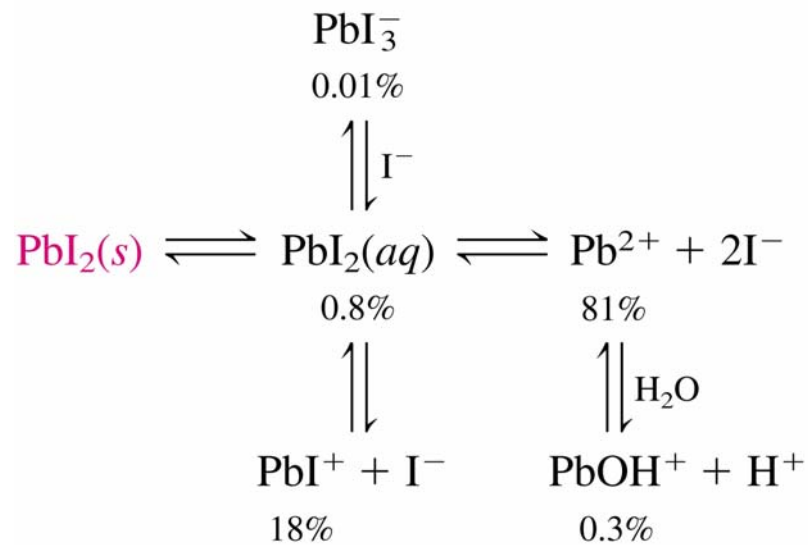


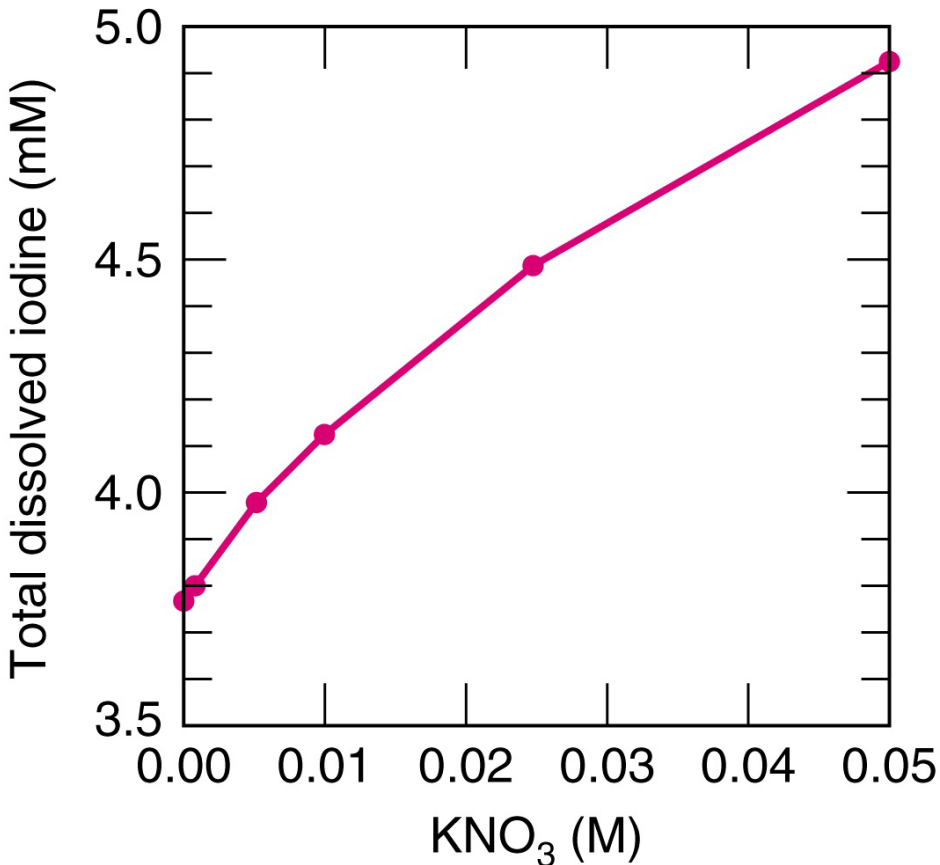
A More Detailed Look at Chemical Equilibria

- effect of ionic strength on solubility
- calculation of ionic strength
- activity coefficients
- effect of ionic strength and size/charge of ions on activity coefficients
- the real definition of pH---
- charge and mass balance in solutions-----simultaneous equilibria calculations!

Important point: presence of other “inert” ions in solution influence the equilibria of other ions with their respective species!



total concentration of dissolved iodine species (iodide (I⁻) + PbI⁺) increases as we add “inert” KNO₃ to the solution---Why?



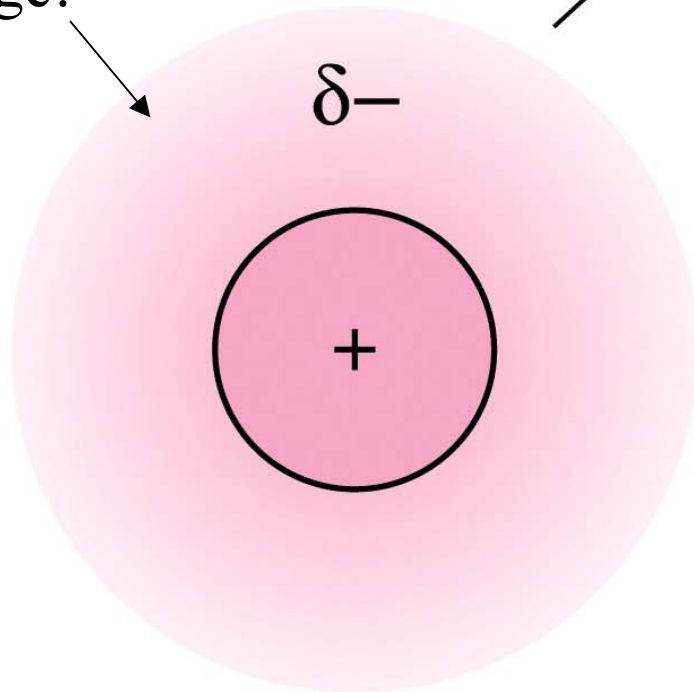
higher concentration of inert ions in the solution “shields” the ions in the equilibrium with counter-cations and counter-anions in their “ionic atmosphere” and decreases, in this case, the tendency for Pb⁺² + 2 I⁻ to come together to form crystals of PbI_{2(s)}

Presence of KNO₃ decreases attraction of Pb⁺² and I⁻

This is a general phenomena---as you add salt to solutions-- you increase solubility of insoluble salts--and decrease formation constants of ionic-complexes (e.g., [Fe(III)-SCN]⁺²)

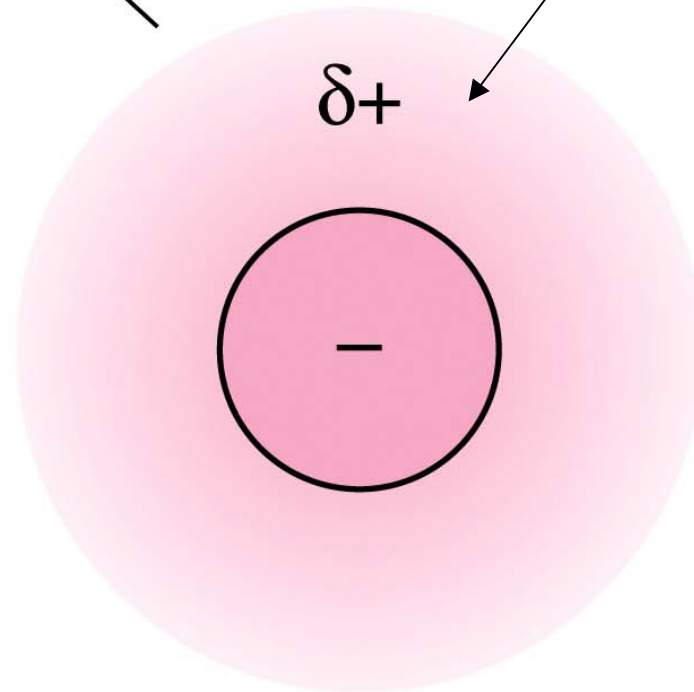
Ionic atmospheres

counter anions in
area--shield positive
charge!



Cation

counter cations
in area shield
negative charge



Anion

ionic strength---I or μ ---a measure of the total ion concentration in solution----but ions with more charge are counted more due to stronger electrostatic interactions with other ions! (I.e., can influence the increase “ionic atmosphere” greater than singly charged ions!)

$$\mu = \frac{1}{2} \sum_i c_i z_i^2$$

where c_i is conc. of i^{th} species
and z_i is the charge on i^{th} species

What is ionic strength of 0.01 M NaCl solution?

$$\mu = 1/2 ([\text{Na}^+]z_{\text{Na}}^2 + [\text{Cl}^-]z_{\text{Cl}}^2) = 1/2 (0.01 (1)^2 + 0.01(-1)^2) = 0.01 \text{ M}$$

What is ionic strength of 0.01 M Na₂SO₄ solution?

$$\mu = 1/2([\text{Na}^+]z_{\text{Na}}^2 + [\text{SO}_4^{-2}]z_{\text{SO}_4}^2) = 1/2(0.02 (1)^2 + 0.01 (-2)^2) = 0.03 \text{ M}$$

if you have several salts--need to sum all ions present using formula!

note: $[\text{Na}^+] = 2 \times [\text{Na}_2\text{SO}_4]$

Once you know ionic strength of a solution--you can calculate the **Activity Coefficients** (γ_i) of ions in that solution!!

activity = $a_i = \gamma_i[i]$; so activity is simply the concentration of the species times the activity coefficient!

For all chemical equilibria--strictly speaking---we should write in terms of activity units--not concentration of species!

for $A + B \rightleftharpoons C + D$; $K_{\text{eq}} = \frac{[C]\gamma_C [D]\gamma_D}{[A]\gamma_A [B]\gamma_B}$

for solubility products: $K_{\text{sp(AB)}} = [A]\gamma_A [B]\gamma_B$; if AB_2 --- $K_{\text{sp}} = [A]\gamma_A [B]^2\gamma_B^2$

So if solubility increases with ionic strength---meaning that concentrations increase---then activity coefficients decrease as you increase ionic strength!!

Extended Debye-Huckel equation is used to estimate the effect of ionic strength on the activity coefficient of a given ionic species:

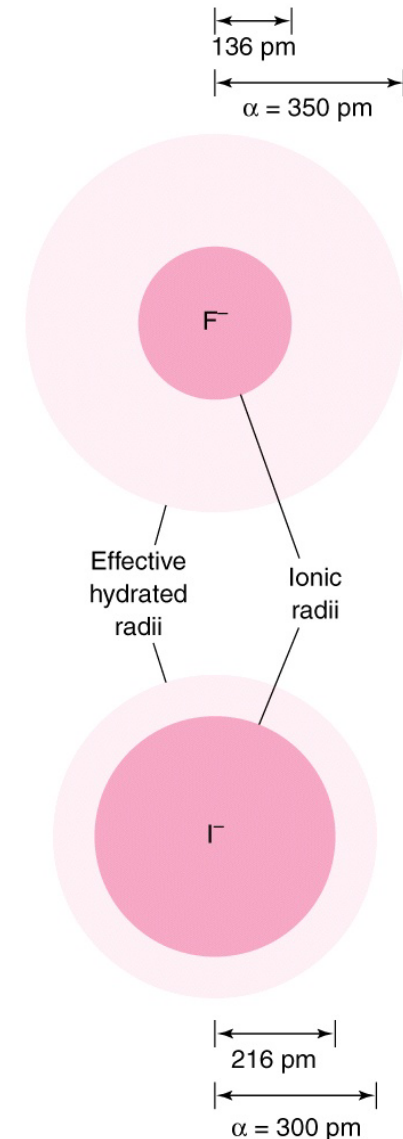
$$\log \gamma_i = \frac{-0.51 z_i^2 \sqrt{\mu}}{1 + \left(\alpha \frac{\sqrt{\mu}}{305} \right)}$$

where α = size of hydrated ion in pm (picometers)

Debye-Huckel equation valid from $\mu = 0 \rightarrow 0.1$ M; beyond, not very accurate at predicting activity coefficient!

General trends--

1. as μ increases, γ_i decreases!-- $\gamma_i \rightarrow 1$ when $\mu \rightarrow 0$
2. increase charge on ion, z_i , more effect of μ on activity coeff. (decrease)
3. the smaller the hydrated radius--more effect of μ on activity coeff. (decrease)



Activity coefficient for hydrogen ion---when $\mu = 0.025 \text{ M}$

using Debye-Huckel--- $\log \gamma_{\text{H}^+} = -0.054$; $\gamma_{\text{H}^+} = 0.88$

Therefore, if you had 0.025 M solution of HCl, what is a_{H^+} ?

$$a_{\text{H}^+} = \gamma_{\text{H}^+} [\text{H}^+] = 0.88 (0.025 \text{ M}) = 0.022 \text{ M}$$

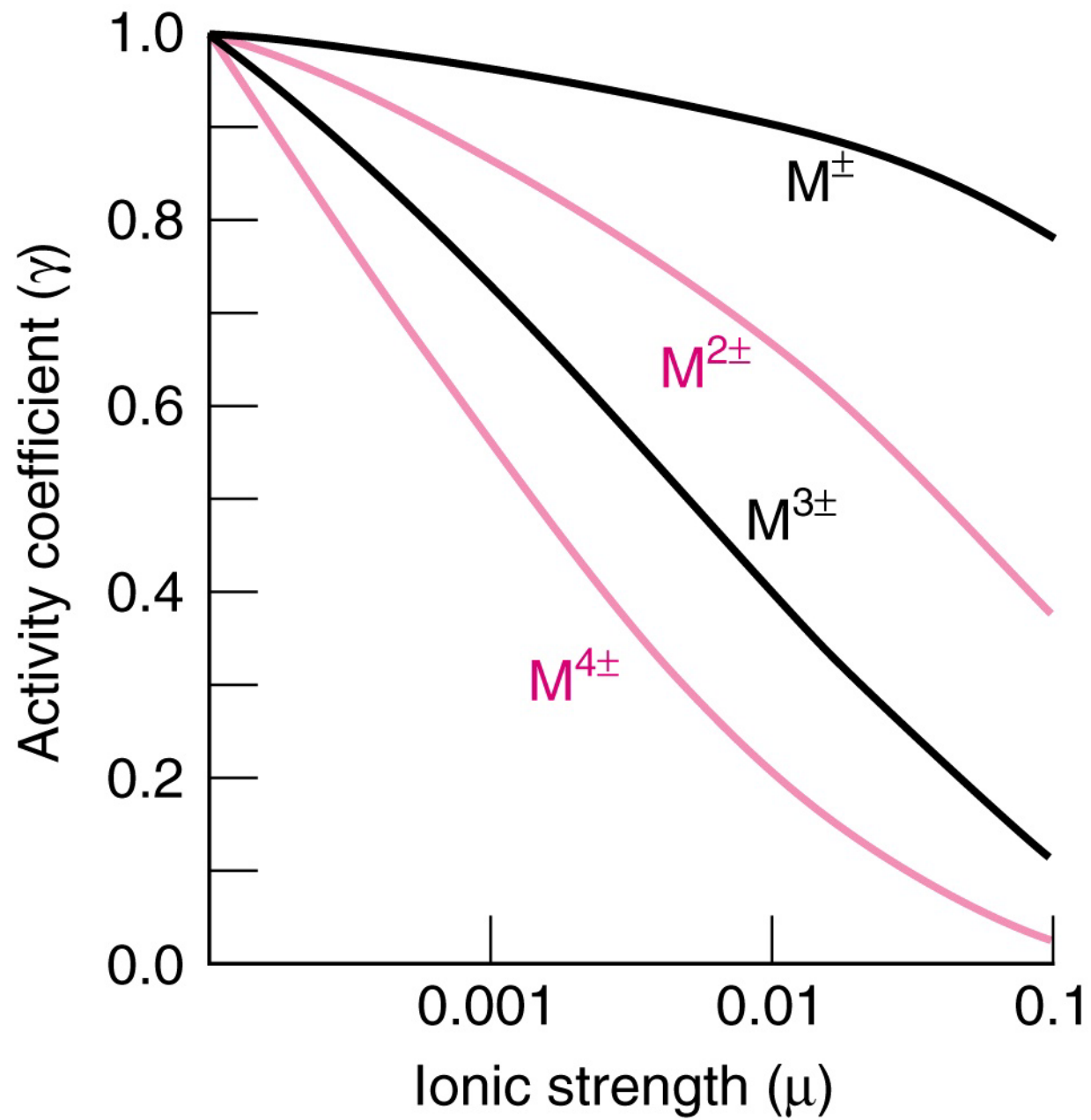
Real Definition of pH: $-\log a_{\text{H}^+} = -\log (\gamma_{\text{H}^+} [\text{H}^+])$

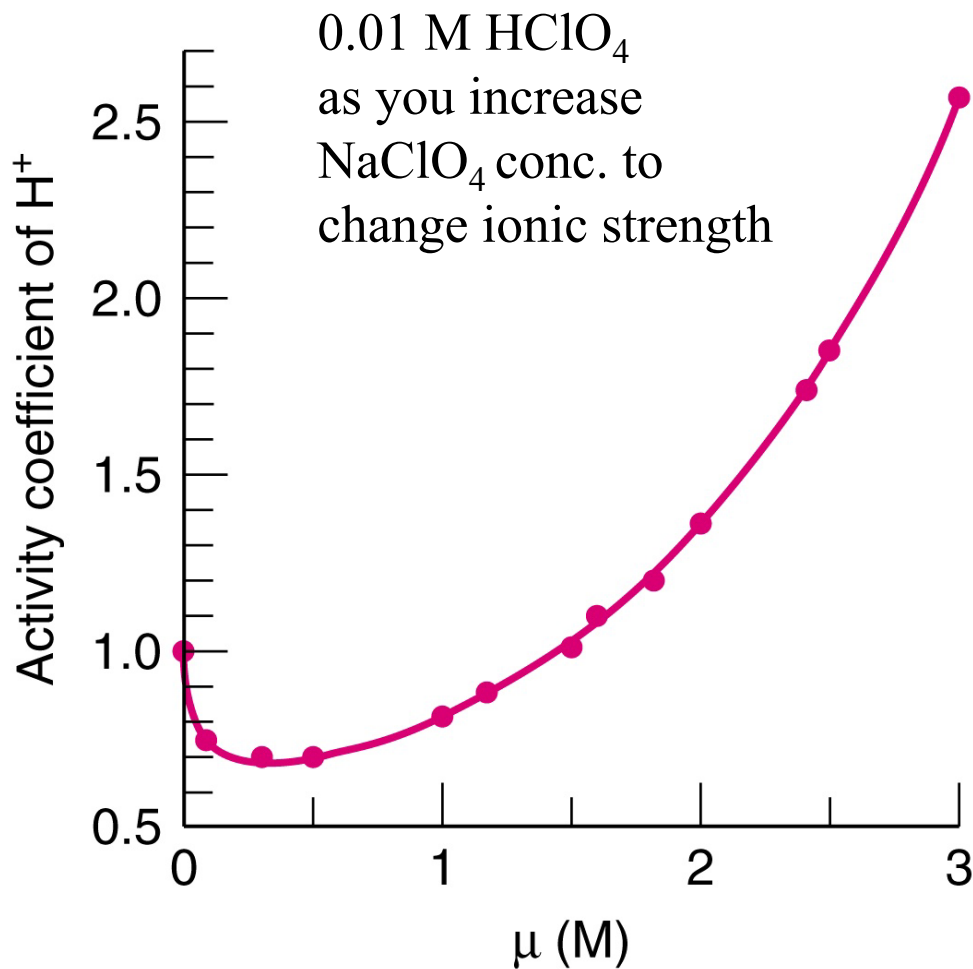
pH = 1.66 (when you take into account activity coefficient)

pH = 1.60 (without correction for activity coefficient)

What is pH of 0.025 M HCl in a solution that also contains 0.075 M NaCl?

must first calculate total ionic strength ($\mu = 0.1 \text{ M}$)--then need activity coefficient for H^+ at this ionic strength = 0.83 (from DB eqn (or from table); **pH = $-\log (0.83 (0.025 \text{ M})) = 1.68$**





Activity coefficients do not continue to decrease with increase in ionic strength--as you go beyond $\mu = 0.5$ M γ increases---solvent changes---solution has greater mole fraction of salt!!

Better estimate of solubility of given salt---back to PbI_2 ??

We previously determined that:

$$[\text{Pb}^{+2}] = 1.2_5 \times 10^{-3} \text{ in saturated solution---} (K_{\text{sp}} = x(2x)^2) = 7.9 \times 10^{-9}$$

$$\text{and } [\text{I}^-] = 2.5 \times 10^{-3} \text{ M}$$

But we did not take into account activity--to do that we write:

$$7.9 \times 10^{-9} = [\text{Pb}^{+2}] \gamma_{\text{Pb}} [\text{I}^-]^2 \gamma_{\text{I}}^2 = x (0.781) (2x)^2 (0.937)^2$$

activity coeff

for Pb^{+2} --based on

ionic strength of 0.0037_5

calculated for above saturated soln.

activity coeff
of I^-

$$x = 1.4_2 \times 10^{-3} \text{ M} = [\text{Pb}^{+2}] ; 2x = [\text{I}^-] = 2.8_4 \times 10^{-3} \text{ M}$$

more soluble than initially predicted without activity coefficients!