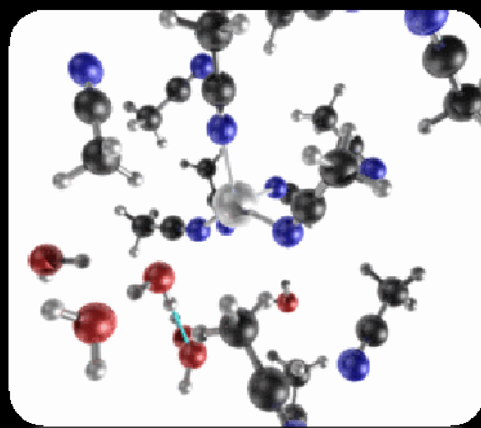


ACTIVITY OF IONS IN SOLUTION

Which flask will be more acidic?

pH = -log [H^+] = 1

Flask 2
0.1 M HCl and 0.1 M $Ca(NO_3)_2$ (aq)

Solubility of Salts

- PbI_2 (s) ⇌ Pb^{2+} (aq) + 2 I^- (aq)
- $K_{sp} = 7.9 \times 10^{-9}$
- But what if we try to dissolve the lead iodide in $Pb(NO_3)_2$ (aq) solution ? [Common Ion Effect]

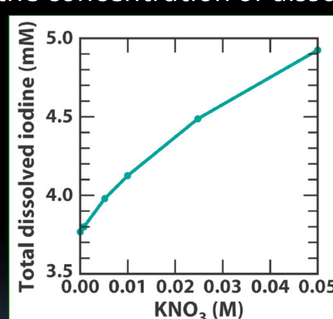
– Solubility Decreases.

- NOW! Let's Dissolve the lead iodide in KNO3(aq)

– THE SOLUBILITY INCREASES!

To further complicate the story…

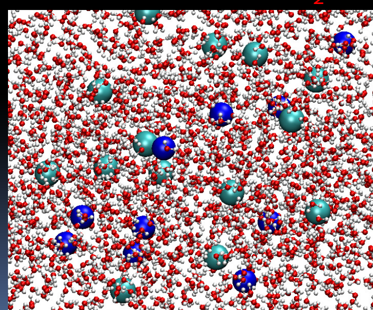
- When an inert salt (KNO_3) is added to the saturated solution of PbI_2 the concentration of dissolved I^- increases.

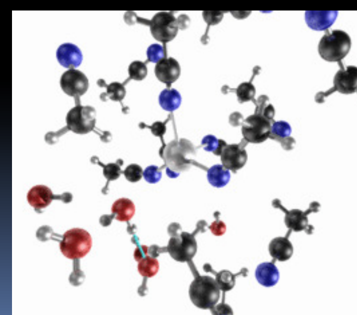


• Why does adding an inert salt to a low solubility salt increase solubility?

It's all about activity!

- Activity – "effective concentration"
- Until now we have assumed that activity is equal to concentration.
- Ion-ion and ion-H_2O interactions





..and activity is a result of ionic strength

- In solution the cation Pb2+ (ion with a + charge)

is surrounded by all ions (K+, Pb2+, NO3-, I-).

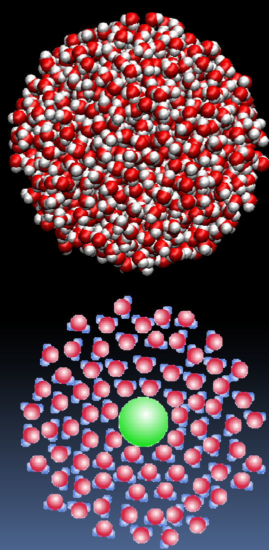
- More anions (ions with a - charge) will surround

Pb2+ then cations

In solution the anion I- is surrounded by all ions (K+, Pb2+, NO3-, I-).

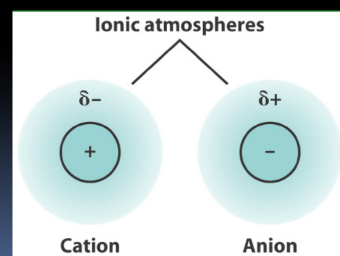
- More cations will surround I- then anions.

Ion Atmosphere



- These interactions result in ion atmospheres -

(regions of net charge around a particular ion)



Ion Atmosphere's Influence on Solubility

- The ionic atmosphere decreases the attraction between ions in solution.
- Attraction is decreased by decreasing the overall net attractions of the ions.
- The higher the concentration of ions in solution, the higher the charge in the ionic atmosphere…
- As ionic strength increases in a solution, ion dissociation increases.

Ionic Strength

- Ionic Strength (μ) - a measure of the total concentration of ions in solution.
- As the number of ions in solution increases, so does the ionic strength of the solution.
- ionic strength = one half the sum of the concentration of each ion multiplied by the charge of the ion squared

$$\mu = \frac{1}{2}\left(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \ldots\right) = \frac{1}{2}\sum_i c_i z_i^2$$

Calculate Ionic Strength

- What is the ionic strength of…
- 0.010 M Na_2SO_4 **2:1 = 3M**
- 0.50 M $NaNO_3$ **1:1 =1 M**
- **What is the ionic strength of Lake Superior?**

The Lake contains : HCO_3^-, SO_4^{2-}, Cl^-, NO_3, Ca^{2+}, Mg^{2+}, Na^+, K^+ Fe^{2+}, SiO_2

$I = 1/2\ \Sigma m_i z_i^2$

$I = 0.5[(HCO_3^-)\cdot 1^2 + (SO_4^{2-})\cdot 2^2 + (Cl^-)\cdot 1^2 + (NO_3^-)\cdot 1^2 + (Ca^{2+})\cdot 2^2 + (Mg^{2+})\cdot 2^2 + (Na^+)\cdot 1^2 + (K\text{-})\cdot 1^2 + (Fe^{2+})\cdot 2^2 + (SiO_2)\cdot 0^2]$

Substituting values for Lake Superior

$I = 0.5(0.00082\cdot 1^2 + 0.00005\cdot 2^2 + 0.00004\cdot 1^2 + 0.000008\cdot 1^2 + 0.00035\cdot 2^2 + 0.00015\cdot 2^2 + 0.00013\cdot 1^2 + 0.00001\cdot 1^2 + 0.000006\cdot 2^2 + 0.00007\cdot 0^2)$

$I = 0.0016$ — ***How does this value compare with other natural waters?***

Water	Typical Ionic Strength
Rivers and lakes	0.001 - 0.005
Potable groundwater	0.001 - 0.02
Seawater	0.7
Oil field brines	>5

Equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

Chemical Equilibrium was previously written as

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

This equation is too simplistic and does not account for the effect of ionic strength on the chemical reaction.

- To account for the ionic strength we use activities (A) instead of concentrations…

$$K = \frac{A_C^c A_D^d}{A_A^a A_B^b}$$

Concentration can be related to activity using the activity coefficient γ, where

$$A = \gamma [C]$$

Until now we have assumed that activity, *A*, is equal to concentration, *C*, by setting γ = 1 when dealing with dilute aqueous solutions…

The Real Chemical Equilibrium Equation…

$$K = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b}$$

Where γ represents the activity coefficient that accounts for ionic strength

γ is calculated using the extended Debye-Hückel equation…

charge

$$\log \gamma = \frac{-0.51 z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$$

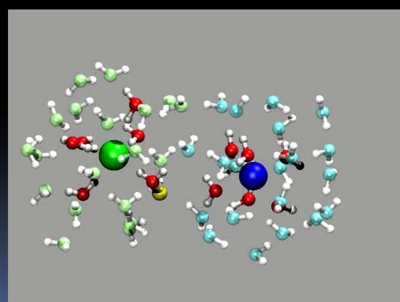
Ionic strength

Activity Coefficient

Hydrated diameter

Effective Hydrated Diameter

- the ion size (α) is the effective hydrated diameter of the ion and it's tightly bound covering of water molecules – electrostatic interactions.



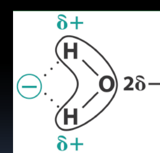


TABLE 12-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75

a. Lanthanides are elements 57–71 in the periodic table.
SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937,** *59,* 1675.

TABLE 12-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±2						
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO^-_2)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, Hcitrate^{2-}	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3						
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3-}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
citrate^{3-}	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4						
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.
SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937,** *59,* 1675.