Activity

In our earlier discussion of equilibrium constant expressions, we defined K for an equilibrium as follows:

If aA + bB = cC + dD, then

$$\frac{(a_C)^c(a_D)^d}{(a_A)^a(a_B)^b} = K$$

where K is the equilibrium constant, and a_X is the *activity* of X and described by the activity coefficient γ_X and [X]:

$$a_X = \gamma_X[X]$$

We said that typically we setup experimental parameters such that γ_X is very close to one, close enough to say that activity and concentration are equal.

How can we get away with this? More importantly, **<u>when</u>** can we get away with this? Lets look at γ_X.

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Activity Coefficients

We typically calculate γ using the extended Debye-Hückel equation, which relates activity coefficients to the ability of ions in solution to interact with one another.

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

z = charge of the ion

α = effective diameter "hydrated" of the ion in picometers

NOTE: This is an empirical parameter!

μ = ionic strength of the solution

How do each of these terms affect the activity of an ion?

Parameter	Small Extreme	Large Extreme	γ @ small extreme	γ @ large extreme
z				
μ				
α				

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Activity Coefficients

How do each of these terms affect the activity of an ion?

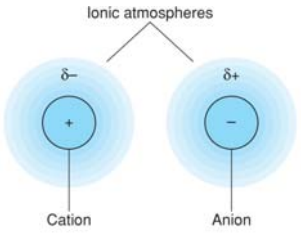
Ionic Strength:

Ionic strength describes the total concentration of ions in solution

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

where c is concentration and z is charge of each ion

Increasing the overall ionic strength provides individual ions a larger number of counterions to interact with, increasing the overall charge in the *ionic atmosphere* nearest the ion.



Question: What does this mean in terms of solubility and dissociation?

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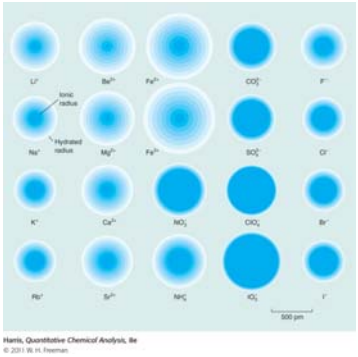
Activity Coefficients

Hydrated Radius (diameter):

Because of their high charge density, ions with small ionic radii and large charge tend to more strongly bind to solvent molecules.

Ion-dipole interactions



The result of this binding is a larger hydrated radius, causing diminished interaction with other ions.

Ionic Charge:

Multiply charged ions are generally more likely to interact with other ions than singly charged.

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Pulling it All Together

Let's revisit the Debye-Hückel equation:

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

- We'd like to use concentrations instead of activities in equilibrium constant expressions, what restriction does that put on γ?
- How do we accomplish this experimentally?

In situations where γ is not close to unity (1), we have to account for activities in our calculations.

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Pulling it All Together

TABLE 7-1 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		*Activity coefficient (γ)*				
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
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_2NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_2CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	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
Charge = ±2		*Activity coefficient (γ)*				
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(H_2CH_2CH_2CO_2^-)_2$	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-}, $S_2O_3^{2-}$, $S_2O_5^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3		*Activity coefficient (γ)*				
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-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4		*Activity coefficient (γ)*				
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.

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Pulling it All Together

Example: Using activities, find the concentration of OH^- in a solution of 0.075M $NaClO_4$ saturated with $Mn(OH)_2$. (from Table 7-1, α is 350 pm for OH^- and 600 pm for Mn^{2+})

$$Mn(OH)_2 = Mn^{2+} + 2OH^- \qquad K_{sp}=1.6 \times 10^{-13}$$

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