

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, **when** 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.

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

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:

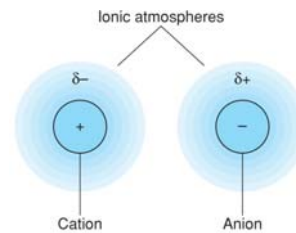
Ionic strength describes the total concentration of ions in solution

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

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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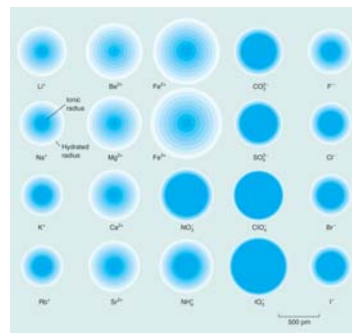
Activity Coefficients

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:

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

- 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 (a, pm)	Ionic strength (μ , M)				
		0.001	0.005	0.01	0.05	0.1
Charge = ±1		<i>Activity coefficient (γ)</i>				
H ⁺	900	0.967	0.933	0.914	0.86	0.83
(C ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₆ H ₅) ₃ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₂ C ₆ H ₃ O ⁻ , (C ₆ H ₅) ₂ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻	700	0.965	0.930	0.909	0.845	0.81
Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₂ N ⁺ , (C ₆ H ₅) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
C ₆ CHCO ₂ ⁻ , C ₆ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₂ H ₅) ₃ NH ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CaCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₂ ⁻ , H ₂ PO ₄ ⁻ , HSO ₄ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₆ (NO ₂) ₂ ²⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₃ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻	450	0.964	0.928	0.902	0.82	0.775
*H ₂ NCH ₂ CO ₂ H, (CH ₃) ₂ NH ⁺ , CH ₃ CH ₂ NH ₃ ⁺	400	0.964	0.927	0.901	0.815	0.77
OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₂ ⁻ , ClO ₂ ⁻ , BrO ₂ ⁻ , IO ₂ ⁻ , MnO ₄ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH 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		<i>Activity coefficient (γ)</i>				
Mg ²⁺ , Be ²⁺	800	0.872	0.755	0.69	0.52	0.45
CH ₃ (CH ₂ CH ₂ CO ₂) ₂ , (CH ₃ CH ₂ CH ₂ CO ₂) ₂	700	0.872	0.755	0.685	0.50	0.425
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sr ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂) ₂ , H ₂ C(CH ₃ CO ₂) ₂ , (CH ₃ CH ₂ CO ₂) ₂	600	0.870	0.749	0.675	0.485	0.405
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂) ₂ , (CH ₂ CO 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) ₃ Cl ²⁺ , Fe(CN) ₅ NO ²⁺ , C ₂ O ₄ ²⁻ , H ₂ citrate ²⁻	450	0.867	0.742	0.665	0.455	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₈ ²⁻ , S ₂ O ₈ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3		<i>Activity coefficient (γ)</i>				
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) ₅ H ₂ O ³⁺	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4		<i>Activity coefficient (γ)</i>				
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. Kolthoff, 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 $\text{Mn}(\text{OH})_2$. (from Table 7-1, α is 350 pm for OH^- and 600 pm for Mn^{2+})

