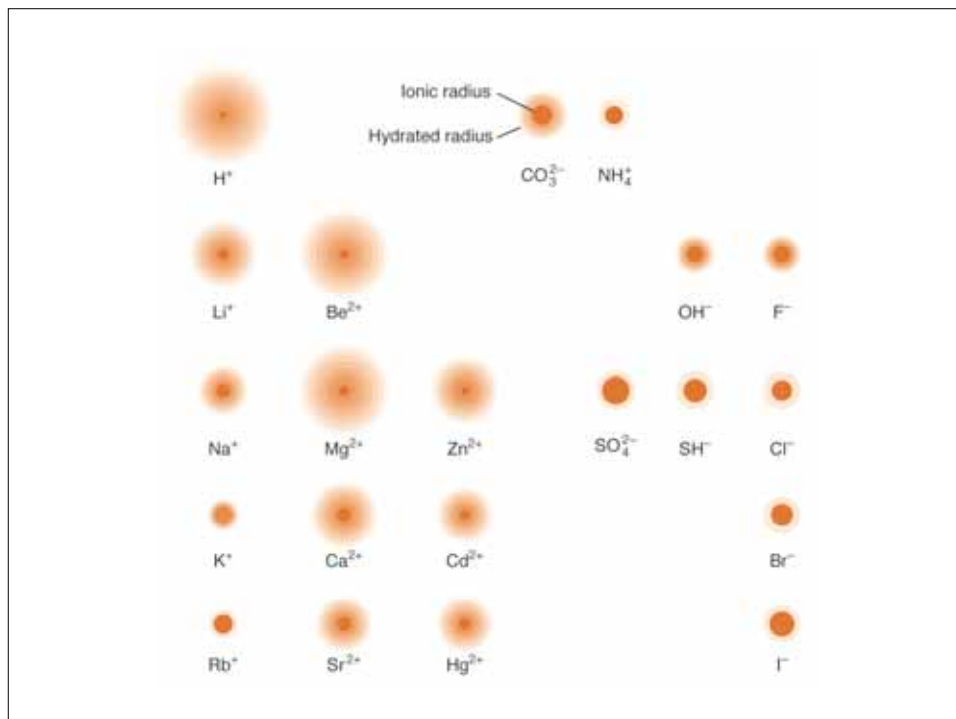
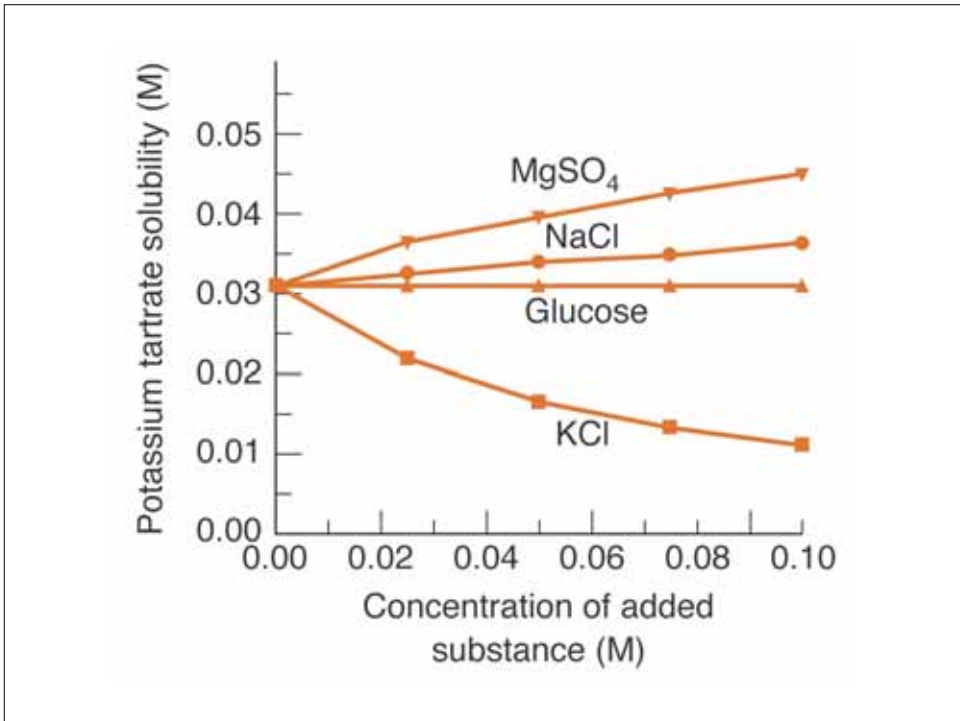
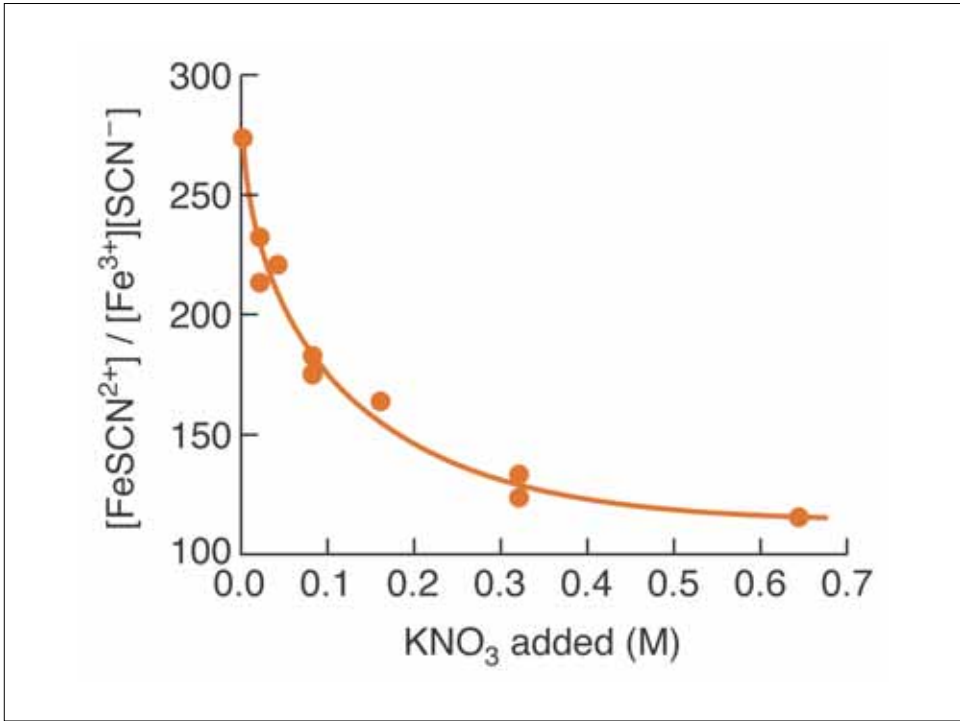
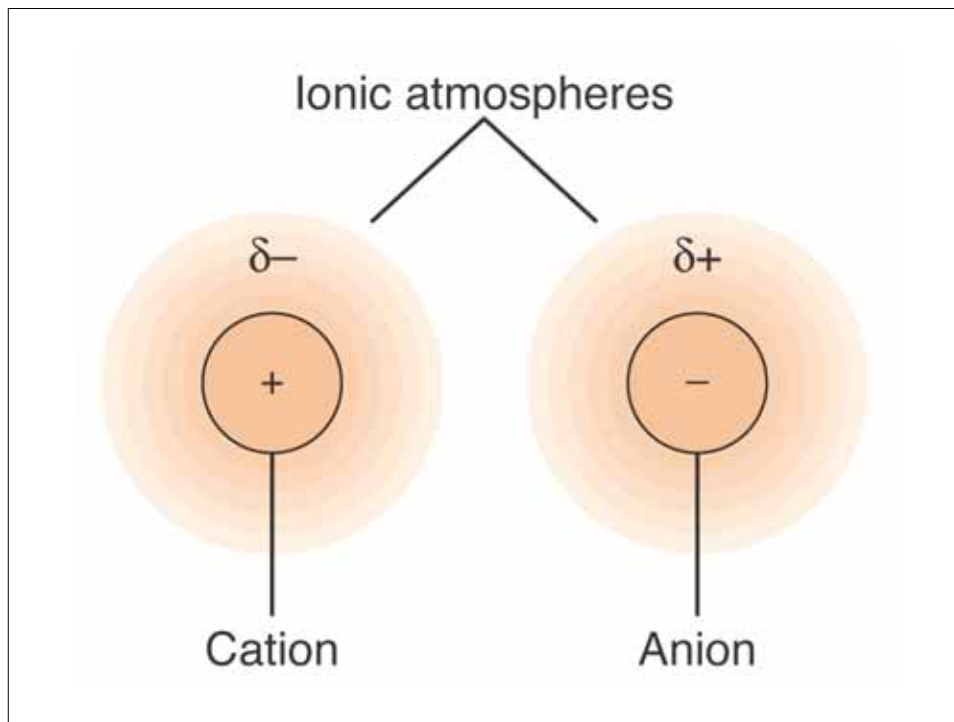


Chapter 8

Ionic Strength and Activity







Ionic Strength

$$\mu = \frac{1}{2}(c_1z_1^2 + c_2z_2^2 + \dots)$$

What is the ionic strength of a 0.1 M H_2SO_4 ?

What about 0.05 M Na_3PO_4 ?

Activity coefficient and the Extended Debye-Hückel equation

$$A = \gamma C$$

$$\log r = - \frac{0.51z^2\sqrt{\mu}}{1 + \frac{\alpha\sqrt{\mu}}{305}}$$

From the Extended Debye-Hückel equation, we lay out some general trends:

- 1) As μ increases, γ decreases.
- 2) As the charge of the ion increases, γ decreases
- 3) The smaller the hydrated radius of the ion, the more important activity effects becomes.

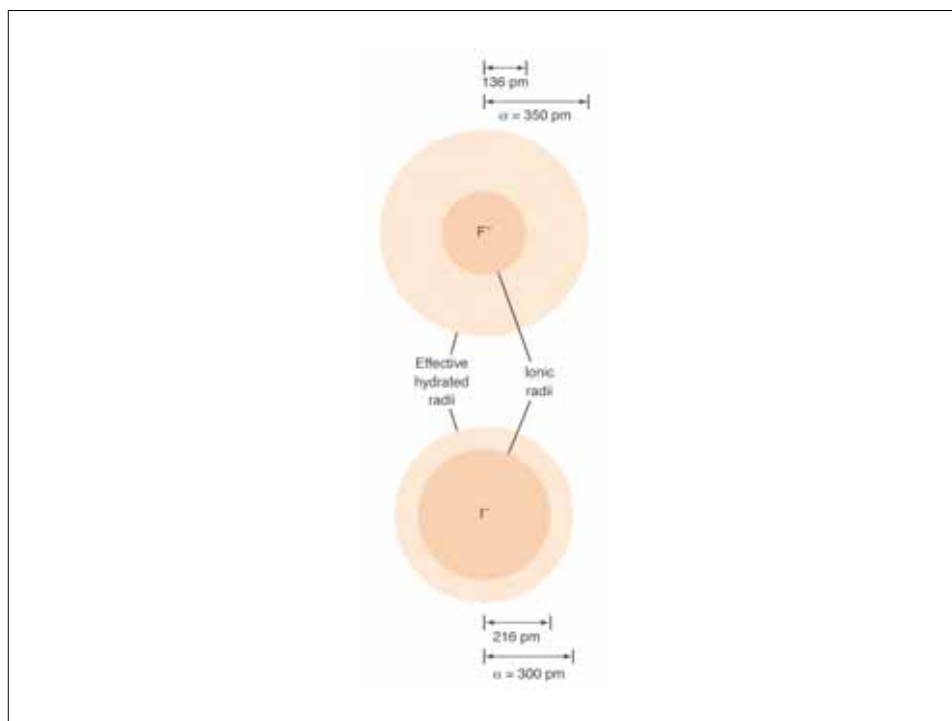


Table 8-1

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 ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₂ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₂ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₂ NH ⁺ , CH ₃ OC ₂ 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 ₃ H ₇) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₂ NH ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₂ ⁻ , HCO ₂ ⁻ , H ₂ PO ₄ ⁻ , HSO ₄ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ 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
¹⁴ H ₂ NCH ₂ CO ₂ H, (CH ₃) ₂ NH ⁺ , CH ₃ CH ₂ NH ₂ ⁺	400	0.964	0.927	0.901	0.815	0.77
OH ⁻ , F ⁻ , SCN ⁻ , OCN ⁻ , HS ⁻ , ClO ₂ ⁻ , ClO ₂ ⁻ , BrO ₃ ⁻ , IO ₂ ⁻ , MnO ₂ ⁻ , HCO ₂ ⁻ , H ₂ citrate ⁻ , CH ₃ NH ₂ ⁺ , (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

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

Table 8-1

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 ₃ (CH ₂ CH ₂ CO ₂) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂) ₂	700	0.872	0.755	0.685	0.50	0.425
Cu ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂) ₂	600	0.870	0.749	0.675	0.485	0.405
H ₂ C(CH ₂ CO ₂) ₂ , (CH ₂ CH ₂ CO ₂) ₂	500	0.868	0.744	0.67	0.465	0.38
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₃ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂) ₂ , (CH ₂ CO ₂) ₂ , (CHOHCO ₂) ₂	450	0.867	0.742	0.665	0.455	0.37
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⁻ , Citrate ²⁻	400	0.867	0.740	0.660	0.445	0.355
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₈ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻						
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 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						
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	1100	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. Kuffland, *J. Am. Chem. Soc.* 1937, 59, 1675.

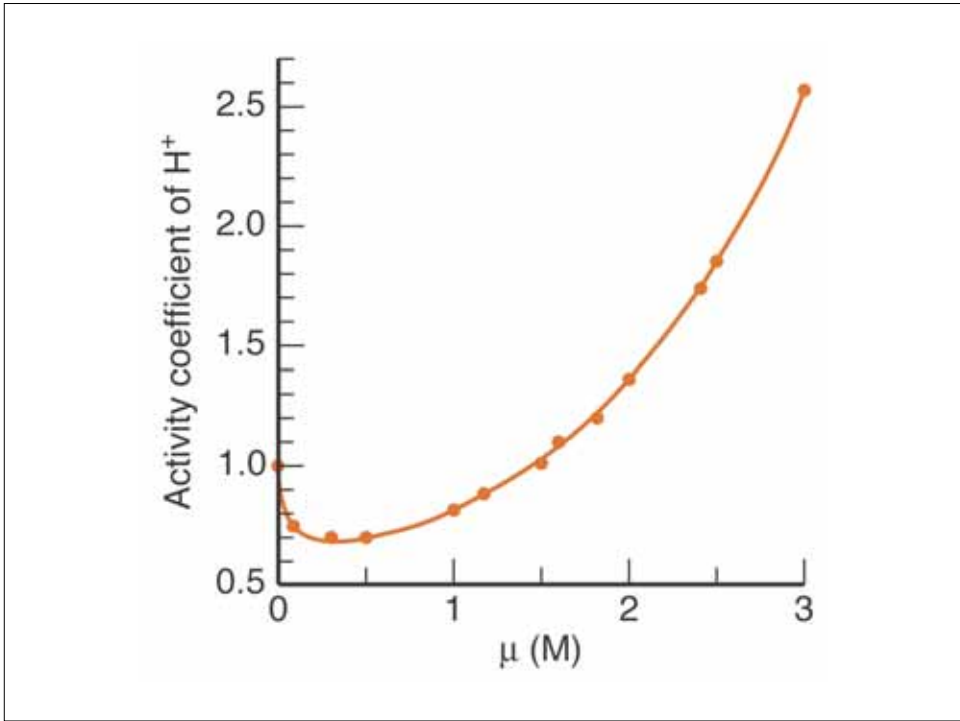
The use of activity coefficients for calculations related to precipitation and pH of water in the presence of a strong, inert electrolyte

1. Solubility problem:

Calculate the solubility of AgCl (a) in the absence of any other salts and (b) in the presence of 0.1 M KNO₃. (K_{sp} of AgCl = 1.0×10^{-10})

2. pH of water containing a salt

Calculate the pH of water containing 0.01 M K₃PO₄.



	A	B	C
1	Spreadsheet for LIF iterative solubility computation		
2			
3	Size (pm) of Li+ =	Ionic strength	x = [Li+] = [F-]
4	600	0.00000	0.04123
5	Size (pm) of F- =		
6	350		
7	Ksp =		
8	0.0017		
9	Activity coeff (Li+) =		
10	1.000		
11	Activity coeff (F-) =		
12	1.000		
13			
14	Formulas used:		
15	A10 = 10 [^] (-0.51)*Sqrt(B4)/(1+(A4*Sqrt(B4)/305))		
16	A12 = 10 [^] (-0.51)*Sqrt(B4)/(1+(A6*Sqrt(B4)/305))		
17	C4 = Sqrt(A8/(A10*A12))		