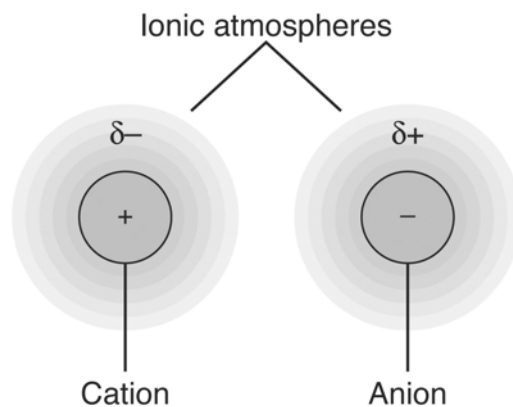


Chapter 8 Activity and the Systematic Treatment of Equilibria

- I. Ionic Strength and Activity
- II. Activity and Activity Coefficients
- III. Activity Calculations
- IV. Charge Balance and Mass Balance
- V. "The Method"
- VI. Examples
- VII. Spreadsheet Approach

I. Ionic Strength and Activity



I. Ionic Strength and Activity (cont.)

- *Ionic strength increases*
⇒ “activity” of the ions decreases
- Quantitative definition of ionic strength (μ)

Ex: Calculate the ionic strength for a solution that is 0.050 M in KNO_3 and 0.10 M in Na_2SO_4

II. Activity and Activity Coefficients

- *To account for ionic strength:*
 - concentration terms in equilibrium expressions are replaced by “activities” (A)
- *Extended Debye-Hückel Equation:*
 - used to calculate activity coefficients
 - can also use Table 8-1

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) ₄ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ 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) ₄ 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) ₃ NH ⁺ , (C ₃ H ₇) ₃ NH ₂ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , 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
⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH ₂ ⁺	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 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

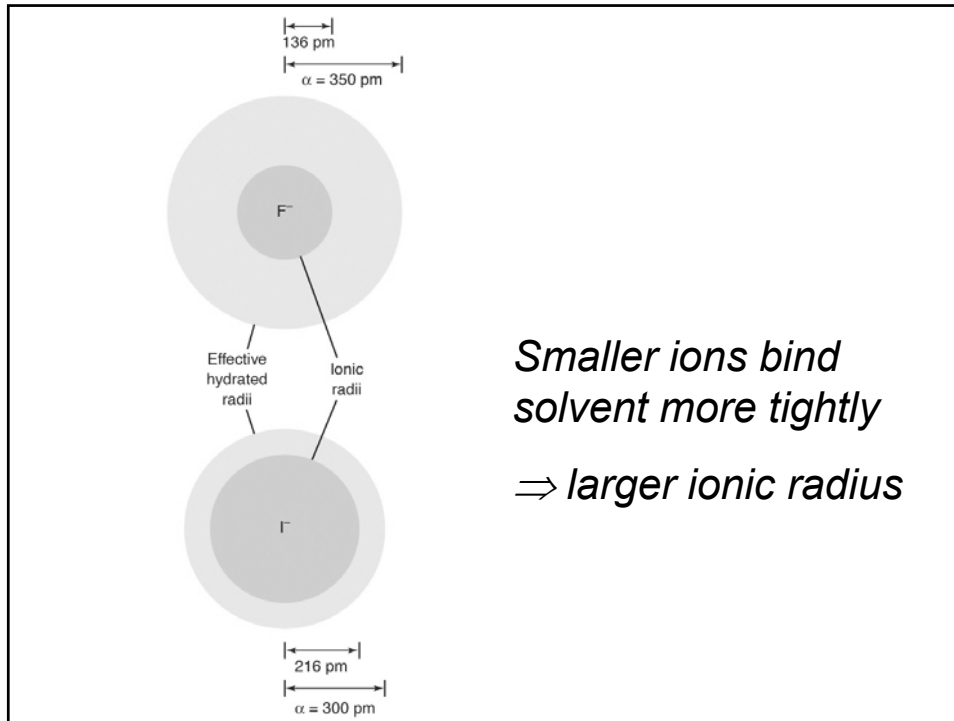
a. Lanthanides are elements 57-71 in the periodic table. SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, 59, 1675.

Table 8-1

Activity coefficients for aqueous solutions at 25°C

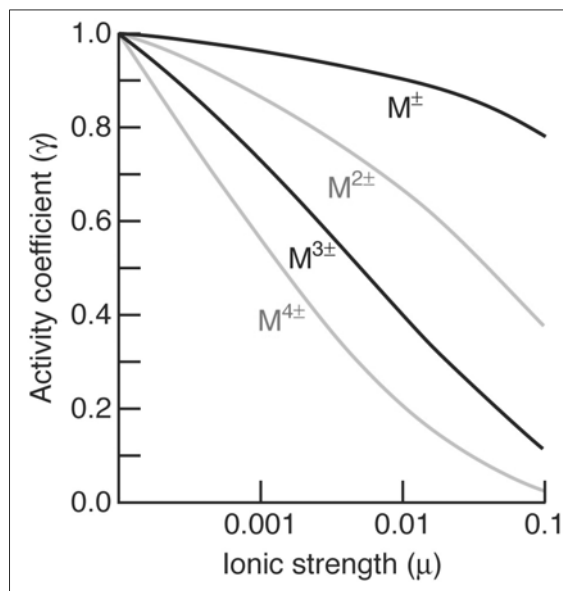
Ion	Ion size (α , pm)	Ionic strength (μ , M)				
		0.001	0.005	0.01	0.05	0.1
CHARGE = ± 2						
Mg ²⁺ , Be ²⁺	800	0.872	0.755	0.69	0.52	0.45
CH ₃ (CH ₂ CH ₂ CO ₂) ₂ , (CH ₂ CH ₂ CH ₂ CO ₂) ₂	700	0.872	0.755	0.685	0.50	0.425
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , C ₆ H ₄ (CO ₂) ₂ , H ₂ C(CH ₂ CO ₂) ₂ , (CH ₂ 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 , (ClOHCOC 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⁻ , Hcitrate ²⁻	450	0.867	0.742	0.665	0.455	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ 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						
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) ₃ 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⁺	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.



Plot γ vs μ :

- As $\mu \uparrow$, $\gamma \downarrow$
- As $\mu \downarrow$, $\gamma \rightarrow 1$
- As $z \uparrow$, $\gamma \downarrow$
- As $\alpha \downarrow$, $\gamma \downarrow$
- Activity corrections become more important as μ and z increase, and as α decreases



III. Activity Calculations

Ex: Find the relative error introduced by neglecting activities in calculating the solubility of $\text{Ba}(\text{IO}_3)_2$ ($K_{\text{sp}} = 1.57 \times 10^{-9}$) in a 0.0330 M solution of $\text{Mg}(\text{IO}_3)_2$.

Ex: Calculate the pH of pure water.

Ex: Calculate the pH of 0.10 M KCl.

IV. Charge Balance and Mass Balance

A. *Charge Balance*

A solution can have no net charge



The sum of the positive charges in a solution must equal the sum of the negative charges.

IV. Charge Balance and Mass Balance (cont.)

B. Mass Balance

The sum of the amounts of all forms of a particular atom or (or group of atoms) in a solution must equal the amount of that atom (or group of atoms) delivered to the solution.

V. “The Method”

Ex: Find $[\text{Ag}^+]$, $[\text{CN}^-]$, and $[\text{HCN}]$ in a saturated solution of AgCN .

Steps:

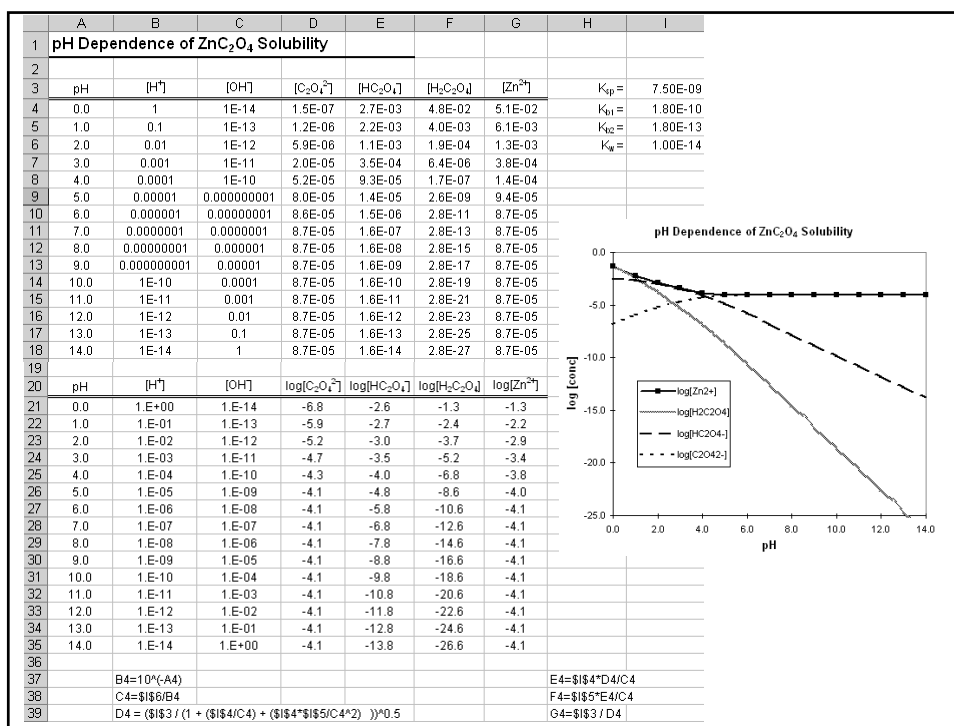
1. Write all pertinent reactions.
2. Write the charge balance expression.
3. Write the mass balance expression.
4. Write the equilibrium expression for each reaction.
5. Count the equations and the unknowns.
6. Solve for the unknowns.

V. “The Method” (cont.)

Ex: Calculate the solubility of ZnC_2O_4 in a solution held at a pH of 3.00.

VI. Spreadsheet Approach

[Link to spreadsheet](#)



	A	B	C	D	E	F	G	H	I	J	K
1	Solved rigorously:										
2											
3				pH	[H ⁺]	[OH ⁻]	[C ₂ O ₄ ²⁻]	[HC ₂ O ₄ ⁻]	[H ₂ C ₂ O ₄]	[Zn ²⁺]	charge balance
4	K _{sp} =	7.50E-09		0.0	1	1E-14	1.5E-07	2.7E-03	4.8E-02	5.1E-02	1.1E+00
5	K _{b1} =	1.80E-10		14.0	1E-14	1	8.7E-05	1.6E-14	2.8E-27	8.7E-05	-1.0E+00
6	K _{b2} =	1.80E-13		7.0	1E-07	1E-07	8.7E-05	1.6E-07	2.8E-13	8.7E-05	1.6E-07
7	K _w =	1.00E-14		8.0	1E-08	1E-06	8.7E-05	1.6E-08	2.8E-15	8.7E-05	-9.7E-07
8				7.5	3.2E-08	3.2E-07	8.7E-05	4.9E-08	2.8E-14	8.7E-05	-2.4E-07
9				7.3	5E-08	2E-07	8.7E-05	7.8E-08	7.0E-14	8.7E-05	-7.1E-08
10				7.2	6.3E-08	1.6E-07	8.7E-05	9.8E-08	1.1E-13	8.7E-05	2.9E-09
11				7.25	5.6E-08	1.8E-07	8.7E-05	8.8E-08	8.9E-14	8.7E-05	-3.4E-08
12				7.23	5.9E-08	1.7E-07	8.7E-05	9.2E-08	9.7E-14	8.7E-05	-1.9E-08
13				7.22	6E-08	1.7E-07	8.7E-05	9.4E-08	1.0E-13	8.7E-05	-1.2E-08
14				7.21	6.2E-08	1.6E-07	8.7E-05	9.6E-08	1.1E-13	8.7E-05	-4.5E-09
15				7.205	6.2E-08	1.6E-07	8.7E-05	9.7E-08	1.1E-13	8.7E-05	-7.7E-10
16				7.204	6.3E-08	1.6E-07	8.7E-05	9.7E-08	1.1E-13	8.7E-05	-3.8E-11
17				7.203	6.3E-08	1.6E-07	8.7E-05	9.8E-08	1.1E-13	8.7E-05	7.0E-10
18											
19											
20					E4 =	10^(-D4)					
21					F4 =	\$B\$7 / E4					
22					G4 =	(\$B\$4 / (1 + (\$B\$5/F4) + (\$B\$5 * \$B\$6/F4^2))) ^ 0.5					
23					H4 =	\$B\$5 * G4/F4					
24					I4 =	\$B\$6 * H4/F4					
25					J4 =	\$B\$4 / G4					
26					K4 =	2*J4 + E4 - 2*G4 - H4 - F4					