Chapter 10

Effect of Electrolytes on Chemical Equilibria

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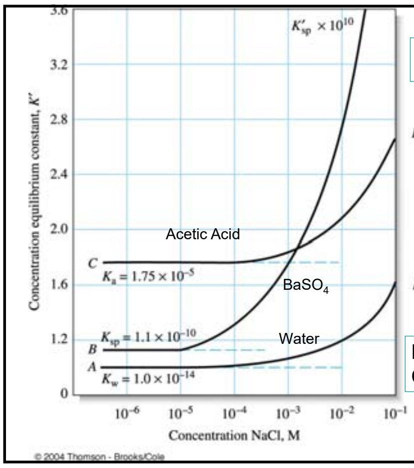

K'—**Concentration**-based Equilibrium constants

K*—*Thermodynamic Equilibrium constants

Effect of Electrolyte Concentration on *K'*

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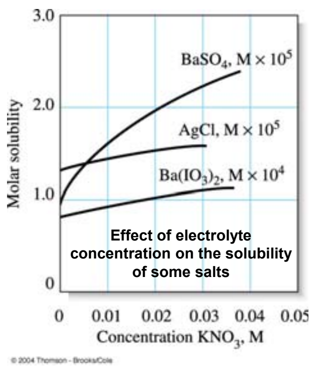
Effect of Ionic Charges on Equilibria



Effect of electrolyte concentration on the solubility of some salts

- Neutral species has essentially no effect
- The larger the ion charges, the bigger the equilibrium changes

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IONIC STRENGTH

- A measure of total ion concentration in solution.
- A quantity required to calculate activity coefficients.
- Attempts to account for effects of both concentration and charge of ion on activity coefficients.

$$\mu = \frac{1}{2}\sum_{i=1}^{n} c_i Z_i^2$$

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- Example: what is the ionic strength of a 0.050 M KCl solution?

$$\mu = \frac{1}{2}\left[\left(0.050 \text{ x } 1^2\right) + \left(0.050 \text{ x } (-1)^2\right)\right] = 0.050 \text{ M}$$

K^+ Cl^-

- Example: what is the ionic strength of a 0.050 M Na_2SO_4 solution?

$$\mu = \frac{1}{2}\left[\left(0.100 \text{ x } 1^2\right) + \left(0.050 \text{ x } (-2)^2\right)\right] = 0.15 \text{ M}$$

Na^+ SO_4^{2-}

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TABLE 10-1

Effect of Charge on Ionic Strength

Type Electrolyte	Example	Ionic Strength*
1:1	NaCl	c
1:2	$Ba(NO_3)_2$, NA_2SO_4	$3c$
1:3	$Al(NO_3)_3$, Na_3PO_4	$6c$
2:2	$MgSO_4$	$4c$

*c = molarity of the salt.

A strong electrolyte consisting solely of singly charged ions has the identical μ to its total molar concentration.

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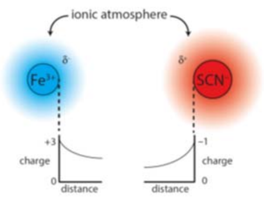
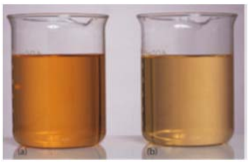
Ionic Atmosphere Affected by Added Electrolyte

$Fe^{3+}(aq) + SCN^{-}(aq) \xrightleftharpoons{+KNO_3?} Fe(SCN)^{2+}(aq)$

light yellow colorless redish-orange

n 1 (1.0 mM) : 1.5 (1.5 mM) ~ 0.5 mM range





No KNO_3 + 10 g KNO_3

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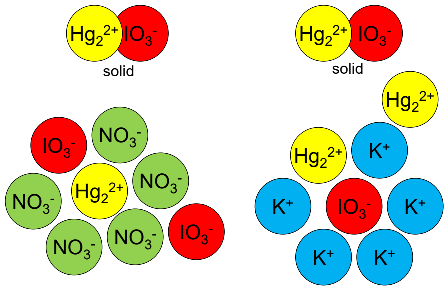
Salt (electrolyte) Effect
→Ionic Atmosphere



The effect is that the solubility increases.

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How do we apply this to the Equilibrium Expression?

- For the generic reaction:

$$aA + bB \longleftrightarrow cC + dD$$

- We have been writing the expression:

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

- A more accurate expression is:

$$\frac{a_C^c a_D^d}{a_A^a a_B^b} = K; \text{ where } a_i \text{ is the activity of } i.$$

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Activities

- For an aqueous species:

$a_i = [i]\gamma_i$; where $[i]$ is the concentration of i, and γ_i is the *activity coefficient*.

- For the reaction:

$$aA + bB \longleftrightarrow cC + dD$$

- We can write the expression:

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

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Properties of Activity Coefficients

- As $\mu \rightarrow 0$, $\gamma_x \rightarrow 1$, $a_x \rightarrow [x]$, and $K' \rightarrow K$.
- In solutions that are not too concentrated, $\gamma_x = f(\mu)$.
- For a given μ, γ_x decreases as the ion charge increses.
- For neutral species, $\gamma_x \rightarrow 1$
- For a given μ, approximately same γ_x values for the same charge ions

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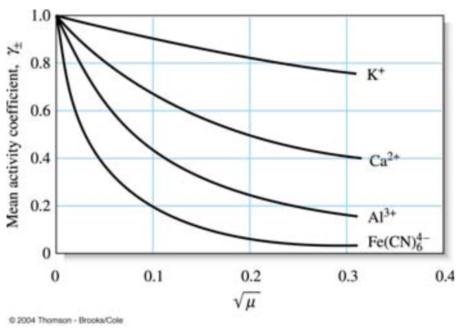
Effect of μ on γ_x



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Calculating Activity Coefficients

- The three factors (ionic strength, ionic charge, and ionic radius) are related by the Debye-Hückel equation (valid to ~ 0.1 M):

$$\log \gamma_x = \frac{-0.51 z_x^2 \sqrt{\mu}}{1+\left(3.3\alpha_x\sqrt{\mu}\right)} \quad \text{at } 25^{\circ}\text{C}$$

where γ_x is the activity of an ion x with charge z and hydrated radius α (in nm) in a solution with an ionic strength of μ.

- Table 10-2 in the text gives activity coefficients for many common ions at various ionic strengths.

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TABLE 10-2
Activity Coefficients for Ions at 25°C

Ion	α_X, nm	Activity Coefficient at Indicated Ionic Strength: 0.001	0.005	0.01	0.05	0.1
H_3O^+	0.9	0.967	0.934	0.913	0.85	0.83
Li^+, $C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-	0.35	0.965	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.965	0.925	0.899	0.81	0.75
Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+	0.25	0.965	0.925	0.897	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.756	0.690	0.52	0.44
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Phthalate^{2-}	0.6	0.870	0.748	0.676	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.869	0.743	0.668	0.46	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, $C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	0.40	0.867	0.738	0.661	0.44	0.35
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.737	0.540	0.443	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.587	0.348	0.252	0.10	0.063
$Fe(CN)_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020

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Use Excel to calculate the activity coefficients of various ions in different ionic strength solutions

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An Example:

- What is the solubility of $Hg_2(IO_3)_2(s)$ in pure water and in 0.050 M KNO_3?

$$Hg_2(IO_3)_{2(s)} \longleftrightarrow Hg_{2(aq)}^{2+} + 2IO_{3(aq)}^-$$

$$[Hg_2^{2+}][IO_3^-]^2 = 1.3\text{x}10^{-18}$$

	Hg_2^{2+}	IO_3^-
Initial	0	0
Change	+x	+2x
End	x	2x

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$$[x][2x]^2 = 1.3x10^{-18}$$
$$4x^3 = 1.3x10^{-18}$$
$$x = 6.9x10^{-7} M$$

Solubility of $Hg_2(IO_3)_2$ in pure H_2O

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- the solubility of $Hg_2(IO_3)_2$ in 0.050 M KNO_3.
  - The ionic strength of 0.050 M KNO_3:

$$\mu = \frac{1}{2}\left[\left(0.050 \text{ x } 1^2\right) + \left(0.050 \text{ x } (-1)^2\right)\right] = 0.050 \text{ M}$$

  - From table 10-2:
    - The activity coefficient for Hg_2^{2+} = 0.44
    - The activity coefficient for IO_3^- = 0.82

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- The expression:

$$[Hg_2^{2+}][IO_3^-]^2 = 1.3x10^{-18}$$

becomes:

$$[Hg_2^{2+}]\gamma_{Hg_2^{2+}}[IO_3^-]^2\gamma_{IO_3^-}^2 = 1.3x10^{-18}$$
$$[x](0.44)[2x]^2(0.82)^2 = 1.3x10^{-18}$$
$$x = 1.0x10^{-6}$$

versus $6.9x10^{-7}$ in pure water

About 1.4X greater than in pure water
Relative Error = -31%

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Using Activity Coefficients

- We will normally not consider activity coefficients.
  - Usually, we are working at concentrations where γ is nearly 1.0
  - Usually, the difference that accounting for activity introduces is smaller than we can precisely measure.

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Class Practice –Chapter 10

- Calculate the molar solubility of Hg_2Cl_2 in 0.10 M NaCl, taking into account the effect of ionic strength. Compare your answer to that in which you ignore the effect of ionic strength (K_{sp} = 1.2 e-18). [hint: Hg_2Cl_2 (s) = Hg_2^{2+} (aq) + 2Cl^- (aq)]

(6.1e-16 M vs 1.2 e-16 M, 5X difference)

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Chapter 10 Summary

- Activity of a species
- Activity vs concentration
- Activity coefficient and the influence of ionic charge
- Calculate ionic strength of solutions
- Salt/electrolyte effect
- Use activities in chemical equilibria

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Important Equations

Ionic strength

$$\mu = \frac{1}{2}\sum_{i=1}^{n} c_i Z_i^2 = \frac{1}{2}([A]Z_A{}^{2+} + [B]Z_B{}^{2+} + [C]Z_C{}^{2+} + ...)$$

Activity

$$a_x = [X]\gamma_x$$

For $X_mY_n(s) \rightleftharpoons mX + nY$

$$K_{sp} = a_X^m a_Y^n = \{[X]^m[Y]^n\} \bullet (\gamma_X^m \gamma_Y^n) = K_{sp}^{'} \bullet (\gamma_X^m \gamma_Y^n)$$

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