

Chapter 10

Effect of Electrolytes on Chemical Equilibria

The equilibrium constants for chemical reactions should be written in terms of the activities of the participating species.

The activity of a species is related to its concentration by a factor called the activity coefficient.

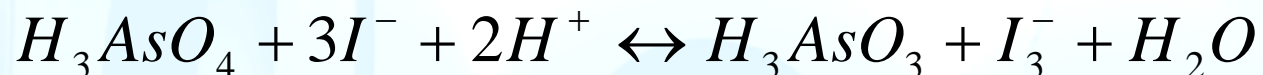
In some cases, the activity of a reactant is essentially equal to its concentration, and we can write the equilibrium constant in terms of the concentrations of the participating species.

In the case of ionic equilibria, however, activities and concentrations can be substantially different.

Such equilibria are also affected by the concentrations of electrolytes in solution that may not participate directly in the reaction.

10A The effect of electrolytes on chemical equilibria

The position of most solution equilibria depends on the electrolyte concentration of the medium, even when the added electrolyte contains no ion in common with those participating in the equilibrium.



If an electrolyte, such as barium nitrate, is added to this solution, the color of the triiodide ion becomes less intense, indicating that the concentration of I_3^- has decreased and that the equilibrium has been shifted to the left.

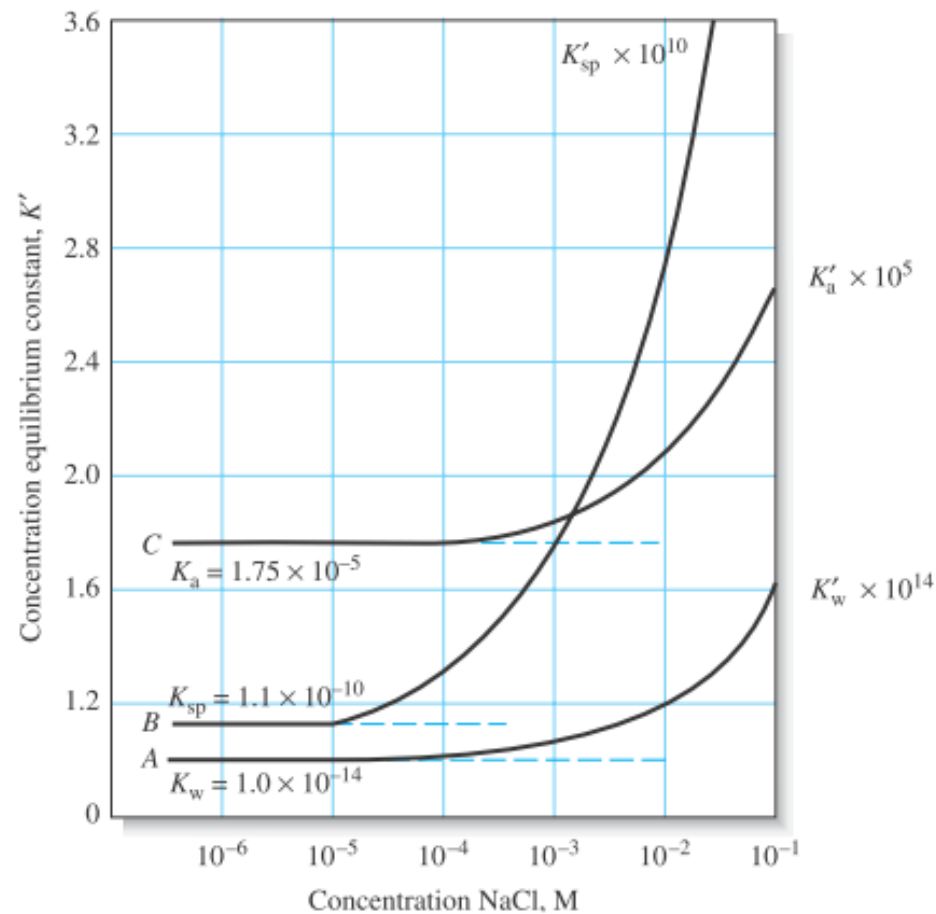
Concentration-based equilibrium constants are often indicated by adding a prime mark, for example, K_{rw}' , K_{rsp}' , K_{ra}' .

As the electrolyte concentration becomes very small, concentration-based equilibrium constants approach their thermodynamic values: K_w' , K_{sp}' , K_a' .

A relationship that approaches a constant value as some variable (in this instance, the electrolyte concentration) approaches zero is called a limiting law.

The constant numerical value observed at this limit is referred to as a limiting value.

Figure 10-1 Effect of electrolyte concentration on concentration-based equilibrium constants.



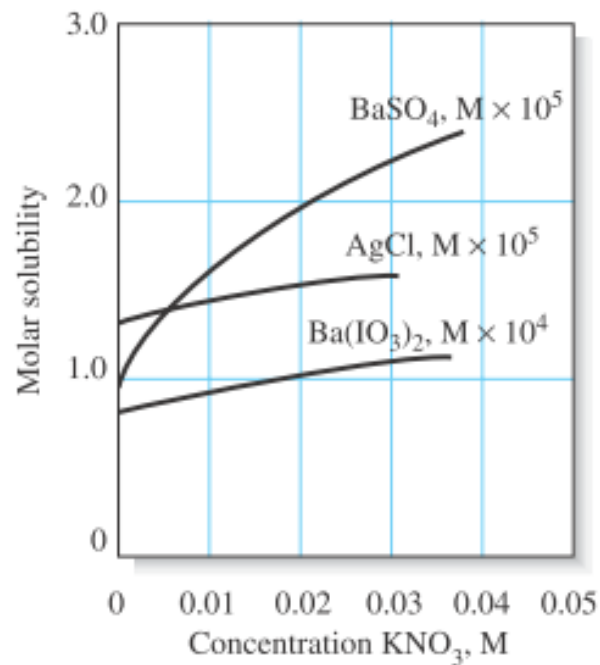
The Effect of Ionic Charges on Equilibria

The magnitude of the electrolyte effect is highly dependent on the charges of the participants in an equilibrium.

When only neutral species are involved, the position of equilibrium is essentially independent of electrolyte concentration.

With ionic participants, the magnitude of the electrolyte effect increases with charge.

Figure 10-2 Effect of electrolyte concentration on the solubility of some salts for compounds containing ions of different charge.



The Effect of Ionic Strength

The effect of added electrolyte on equilibria is independent of the chemical nature of the electrolyte but depends on a property of the solution called the ionic strength, which is defined as

$$\text{ionic strength} = \mu = \frac{1}{2} ([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + \dots)$$

where $[A]$, $[B]$, $[C]$, . . . represent the species molar concentrations of ions A, B, C, . . . and Z_A , Z_B , Z_C , . . . are their charges.

EXAMPLE 10-1

Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4 .

Solution

(a) For the KNO_3 solution, $[\text{K}^+]$ and $[\text{NO}_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1 \text{ M} \times 1^2 + 0.1 \text{ M} \times 1^2) = 0.1 \text{ M}$$

(b) For the Na_2SO_4 solution, $[\text{Na}^+] = 0.2 \text{ M}$ and $[\text{SO}_4^{2-}] = 0.1 \text{ M}$. Therefore,

$$\mu = \frac{1}{2}(0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2) = 0.3 \text{ M}$$

EXAMPLE 10-2

What is the ionic strength of a solution that is 0.05 M in KNO_3 and 0.1 M in Na_2SO_4 ?

Solution

$$\mu = \frac{1}{2}(0.05 \text{ M} \times 1^2 + 0.05 \text{ M} \times 1^2 + 0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2) = 0.35 \text{ M}$$

The ionic strength of a solution of a strong electrolyte consisting solely of singly charged ions is identical to its total molar salt concentration.

For solutions with ionic strengths of 0.1 M or less, the electrolyte effect is independent of the kind of ions and dependent only on the ionic strength.

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 ₂ SO ₄	$3c$
1:3	Al(NO ₃) ₃ , Na ₃ PO ₄	$6c$
2:2	MgSO ₄	$4c$

* c = molar concentration of the salt.

The Salt Effect

The electrolyte effect (salt effect) results from the electrostatic attractive and repulsive forces between the ions of an electrolyte and the ions involved in an equilibrium.

These forces cause each ion from the dissociated reactant to be surrounded by a sheath of solution that contains a slight excess of electrolyte ions of opposite charge.

10 B Activity coefficients

The activity, or effective concentration, of species X depends on the ionic strength of the medium and is defined by

$$a_x = [X] \gamma_x$$

where a_x is the activity of the species X, $[X]$ is its molar concentration, and γ_x is a dimensionless quantity called the activity coefficient.

The activity of a species is a measure of its effective concentration as determined by colligative properties.

If we substitute a_x for $[X]$ in any equilibrium-constant expression, we find that the equilibrium constant is then independent of the ionic strength.

To illustrate this point, if X_mY_n is a precipitate, the thermodynamic solubility product expression is defined by the equation:

$$K_{sp} = a_X^m \cdot a_Y^n$$

$$K_{sp} = [X]^m [Y]^n \cdot \gamma_X^m \gamma_Y^n = K'_{sp} \cdot \gamma_X^m \gamma_Y^n$$

K'_{sp} is the concentration solubility product constant, and K_{sp} is the thermodynamic equilibrium constant.

Properties of Activity Coefficients

Activity coefficients have the following properties:

1. The activity coefficient of a species is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant.

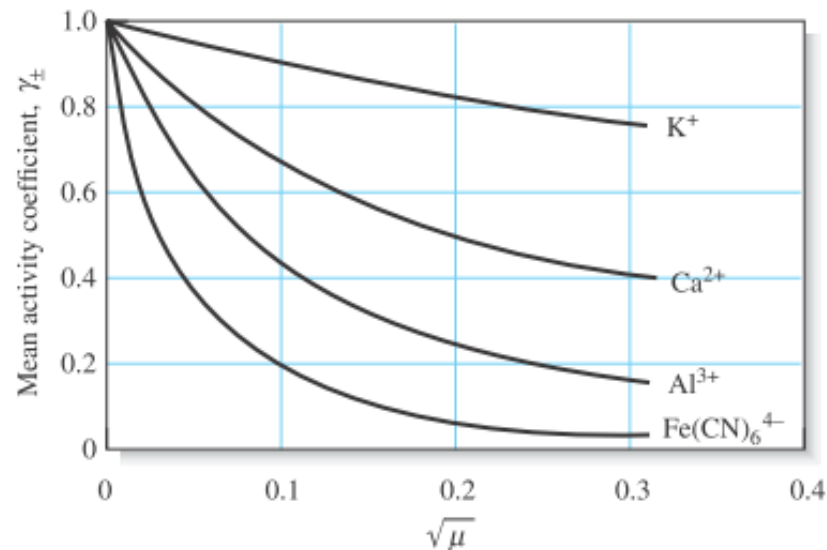
In very dilute solutions in which the ionic strength is minimal, this effectiveness becomes constant, and the activity coefficient is unity.

Under these circumstances, the activity and the molar concentration are identical. As the ionic strength increases, an ion loses some of its effectiveness, and its activity coefficient decreases.

As $\mu \rightarrow -\infty$, $\gamma_X \rightarrow 1$, $a_X \rightarrow [X]$, and $K'_{sp} \rightarrow K_{sp}$

2. In solutions that are not too concentrated, the activity coefficient for a given species is independent of the nature of the electrolyte and dependent only on the ionic strength.
3. For a given ionic strength, the activity coefficient of an ion decreases more dramatically from unity as the charge on the species increases.

Figure 10-3 Effect of ionic strength on activity coefficients.



4. The activity coefficient of an uncharged molecule is approximately unity, no matter what the level of ionic strength.
5. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal. The small variations among ions of the same charge can be correlated with the effective diameter of the hydrated ions.

The activity coefficient of a given ion describes its effective behavior in all equilibria in which it participates.

At a given ionic strength, a single activity coefficient for cyanide ion describes the influence of that species on any of the following equilibria:



The Debye-Hückel Equation

This equation that permits the calculation of activity coefficients of ions from their charge and their average size.

$$-\log \gamma_x = \frac{0.51 Z_x^2 \sqrt{\mu}}{1 + 3.3 \alpha_x \sqrt{\mu}}$$

Where, γ_x is the activity coefficient of the species X ;

Z_x is the charge on the species X

μ is the ionic strength of the solution

α_x is the effective diameter of the hydrated ion X in nanometers (10^{-9} m).

When $\mu < 0.01 \text{ M}$, $1 + \sqrt{\mu} \approx 1$, the equation becomes

$$-\log \gamma_X = 0.51 Z_X^2 \sqrt{\mu}$$

This equation is referred to as the Debye-Hückel Limiting Law (DhLL).

In solutions of very low ionic strength ($\mu < 0.01 \text{ M}$), the DhLL can be used to calculate approximate activity coefficients.

TABLE 10-2

Activity Coefficients for Ions at 25°C

Ion	Activity Coefficient at Indicated Ionic Strength					
	α_X , nm	0.001	0.005	0.01	0.05	0.1
H ₃ O ⁺	0.9	0.967	0.934	0.913	0.85	0.83
Li ⁺ , C ₆ H ₅ COO ⁻	0.6	0.966	0.930	0.907	0.83	0.80
Na ⁺ , IO ₃ ⁻ , HSO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , H ₂ AsO 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 ₃ ⁻ , 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 ⁺ , TI ⁺ , 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 ₂ O ₄ ²⁻	0.45	0.868	0.741	0.665	0.45	0.36
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , Cr 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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The Debye-Hückel limiting law is usually assumed to be accurate at values of m up to about 0.01 for singly charged ions.

EXAMPLE 10-3

(a) Use Equation 10-5 to calculate the activity coefficient for Hg^{2+} in a solution that has an ionic strength of 0.085 M. Use 0.5 nm for the effective diameter of the ion. (b) Compare the value obtained in (a) with the activity coefficient obtained by linear interpolation of the data in Table 10-2 for coefficients of the ion at ionic strengths of 0.1 M and 0.05 M.

Solution

$$\begin{aligned}\text{(a)} \quad -\log \gamma_{\text{Hg}^{2+}} &= \frac{(0.51)(2)^2 \sqrt{0.085}}{1 + (3.3)(0.5) \sqrt{0.085}} \approx 0.4016 \\ \gamma_{\text{Hg}^{2+}} &= 10^{-0.4016} = 0.397 \approx 0.40\end{aligned}$$

(b) From Table 10-1

μ	$\gamma_{\text{Hg}^{2+}}$
0.1M	0.38
0.05M	0.46

Thus, when $\Delta\mu = (0.10 \text{ M} - 0.05 \text{ M}) = 0.05 \text{ M}$, $\Delta\gamma_{\text{Hg}^{2+}} = 0.46 - 0.38 = 0.08$.
At an ionic strength of 0.085 M,

$$\Delta\mu = (0.100 \text{ M} - 0.085 \text{ M}) = 0.015 \text{ M}$$

and

$$\Delta\gamma_{\text{Hg}^{2+}} = \frac{0.015}{0.05} \times 0.08 = 0.024$$

Thus,

$$\Delta\gamma_{\text{Hg}^{2+}} = 0.38 + 0.024 = 0.404 \approx 0.40$$

Equilibrium Calculations Using Activity Coefficients

EXAMPLE 10-4

Find the relative error introduced by neglecting activities in calculating the solubility of $\text{Ba}(\text{IO}_3)_2$ in a 0.033 M solution of $\text{Mg}(\text{IO}_3)_2$. The thermodynamic solubility product for $\text{Ba}(\text{IO}_3)_2$ is 1.57×10^{-9} (see Appendix 2).

Solution

First, we write the solubility-product expression in terms of activities:

$$K_{\text{sp}} = a_{\text{Ba}^{2+}} \cdot a_{\text{IO}_3^-}^2 = 1.57 \times 10^{-9}$$

where $a_{\text{Ba}^{2+}}$ and $a_{\text{IO}_3^-}$ are the activities of barium and iodate ions. Replacing activities in this equation with activity coefficients and concentrations from Equation 10-2 yields

$$K_{\text{sp}} = \gamma_{\text{Ba}^{2+}} [\text{Ba}^{2+}] \cdot \gamma_{\text{IO}_3^-}^2 [\text{IO}_3^-]^2 \quad (10-6)$$

where $\gamma_{\text{Ba}^{2+}}$ and $\gamma_{\text{IO}_3^-}$ are the activity coefficients for the two ions. Rearranging this expression gives

$$K'_{\text{sp}} = \frac{K_{\text{sp}}}{\gamma_{\text{Ba}^{2+}} \gamma_{\text{IO}_3^-}^2} = [\text{Ba}^{2+}] [\text{IO}_3^-]^2$$

where K'_{sp} is the *concentration-based solubility product*.

The ionic strength of the solution is obtained by substituting into Equation 10-1:

$$\begin{aligned} \mu &= \frac{1}{2} ([\text{Mg}^{2+}] \times 2^2 + [\text{IO}_3^-] \times 1^2) \\ &= \frac{1}{2} (0.033 \text{ M} \times 4 + 0.066 \text{ M} \times 1) = 0.099 \text{ M} \approx 0.1 \text{ M} \end{aligned}$$

In calculating μ , we have assumed that the Ba^{2+} and IO_3^- ions from the precipitate do not contribute significantly to the ionic strength of the solution. This simplification seems justified considering the low solubility of barium iodate and the relatively high concentration of $\text{Mg}(\text{IO}_3)_2$. In situations in which it is not possible to make such an assumption, the concentrations of the two ions can be approximated by solubility calculation in which activities and concentrations are assumed to be identical (as in Examples 9-3, 9-4, and 9-5). These concentrations can then be introduced to give a better value for μ (see spreadsheet summary).

Turning now to Table 10-2, we find that at an ionic strength of 0.1 M,

$$\gamma_{\text{Ba}^{2+}} = 0.38 \quad \gamma_{\text{IO}_3^-} = 0.77$$

If the calculated ionic strength did not match that of one of the columns in the table, $\gamma_{\text{Ba}^{2+}}$ and $\gamma_{\text{IO}_3^-}$ could be calculated from Equation 10-5.

Substituting into the thermodynamic solubility-product expression gives

$$K'_{\text{sp}} = \frac{1.57 \times 10^{-9}}{(0.38)(0.77)^2} = 6.97 \times 10^{-9}$$

$$[\text{Ba}^{2+}][\text{IO}_3^-]^2 = 6.97 \times 10^{-9}$$

Proceeding now as in earlier solubility calculations,

$$\text{solubility} = [\text{Ba}^{2+}]$$

$$[\text{IO}_3^-] = 2 \times 0.033 \text{ M} + 2[\text{Ba}^{2+}] \approx 0.066 \text{ M}$$

$$[\text{Ba}^{2+}](0.066)^2 = 6.97 \times 10^{-9}$$

$$[\text{Ba}^{2+}] = \text{solubility} = 1.60 \times 10^{-6} \text{ M}$$

If we neglect activities, we find the solubility as follows:

$$[\text{Ba}^{2+}](0.066)^2 = 1.57 \times 10^{-9}$$

$$[\text{Ba}^{2+}] = \text{solubility} = 3.60 \times 10^{-7} \text{ M}$$

$$\text{relative error} = \frac{3.60 \times 10^{-7} - 1.60 \times 10^{-6}}{1.60 \times 10^{-6}} \times 100\% = -77\%$$

EXAMPLE 10-5

Use activities to calculate the hydronium ion concentration in a 0.120 M solution of HNO_2 that is also 0.050 M in NaCl. What is the relative percent error incurred by neglecting activity corrections?

Solution

The ionic strength of this solution is

$$\mu = \frac{1}{2} (0.0500 \text{ M} \times 1^2 + 0.0500 \text{ M} \times 1^2) = 0.0500 \text{ M}$$

In Table 10-2, at ionic strength 0.050 M, we find

$$\gamma_{\text{H}_3\text{O}^+} = 0.85 \quad \gamma_{\text{NO}_2^-} = 0.81$$

Also, from Rule 4 (page 240), we can write

$$\gamma_{\text{HNO}_2} = 1.0$$

These three values for γ permit us to calculate the concentration-based dissociation constant from the thermodynamic constant of 7.1×10^{-4} (see Appendix 3).

$$K'_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{K_a \cdot \gamma_{\text{HNO}_2}}{\gamma_{\text{H}_3\text{O}^+} \gamma_{\text{NO}_2^-}} = \frac{7.1 \times 10^{-4} \times 1.0}{0.85 \times 0.81} = 1.03 \times 10^{-3}$$

Proceeding as in Example 9-7, we write

$$[\text{H}_3\text{O}^+] = \sqrt{K'_a \times c_a} = \sqrt{1.03 \times 10^{-3} \times 0.120} = 1.11 \times 10^{-2} \text{ M}$$

Note that assuming unit activity coefficients gives $[\text{H}_3\text{O}^+] = 9.2 \times 10^{-3} \text{ M}$.

$$\text{relative error} = \frac{9.2 \times 10^{-3} - 1.11 \times 10^{-2}}{1.11 \times 10^{-2}} \times 100\% = -17\%$$

Omitting Activity Coefficients in Equilibrium Calculations

Activity coefficients are usually neglected and molar concentrations are used in applications of the equilibrium law. This approximation simplifies the calculations and greatly decreases the amount of data needed. For most purposes, the error introduced by the assumption of unity for the activity coefficient is not large enough to lead to false conclusions.

Significant discrepancies occur when the ionic strength is large (0.01 M or larger) or when the participating ions have multiple charges.

With dilute solutions ($\mu < 0.01$ M) of nonelectrolytes or of singly charged ions, mass-law calculations using concentrations are often reasonably accurate.