

ANALYTICAL CHEMISTRY

Read the details of the information given below from Skoog and West's "Fundamentals of Analytical Chemistry" book, which is recommended as a reference.

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Solving Equilibrium Problems for Complex Systems

Solving Multiple-Equilibrium Problems Using a Systematic Method

Calculating Solubilities by the Systematic Method

11A Solving multiple-equilibrium problems using a systematic method

Write as many independent equations as there are chemical species in the system being studied.

Types of algebraic equations to solve multiple-equilibrium problems:

- Equilibrium-constant expressions
- *Mass-balance* equations
- *Single charge-balance* equation

11A-1 Mass-balance equations

Relate the *equilibrium concentrations* of various species in a solution to one another and to the *analytical concentrations* of the various solutes.



$$c_{\text{HA}} = [\text{HA}] + [\text{A}^-]$$

$$[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{HA}} + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}}$$

$$[\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-]$$

11A-2 Charge-balance equation

For any solution containing electrolytes,

$$\text{no. moles/L positive charge} = \text{no. moles/L negative charge}$$



This equation represents the charge-balance condition and is called the **charge-balance equation**.

Using approximations to solve equilibrium calculations

Approximations can be made only in charge-balance and mass-balance equations.



only in these equations do the concentration terms appear as sums or differences rather than as products or quotients.

11B Calculating solubilities by the systematic method

- The solubility of metal hydroxides
- The effect of pH on solubility
- The effect of undissociated solutes on precipitation calculations
- The solubility of precipitates in the presence of complexing agents

Calculate the molar solubility of $\text{Mg}(\text{OH})_2$ in water.

1. Write equations for the pertinent equilibria
2. Define the unknown
3. Write all equilibrium-constant expressions
4. Write mass-balance expressions
5. Write the charge-balance expression
6. Count the number of independent equations and unknowns
7. Make approximations
8. Solve the equations
9. Check the assumptions

The effect of pH on solubility

All precipitates containing an anion that is the conjugate base of a weak acid are more soluble at low than at high pH.

The solubility of precipitates in the presence of complexing agents

The solubility of a precipitate always increases in the presence of a complexing agent that reacts with the cation of the precipitate.