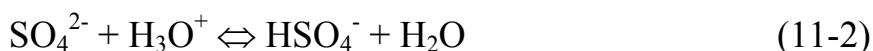


11 Solving Equilibrium Problems for Complex Systems

When water is saturated with sparingly soluble BaSO_4 :



1. if added $[\text{H}_3\text{O}^+]$: 11-2 \rightarrow shifted to the right,



2. if added acetate ions

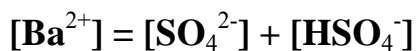
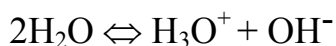
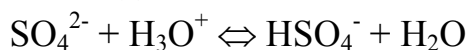
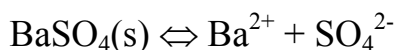


11A Solving Multiple-Equilibrium Problems by a Systematic Method

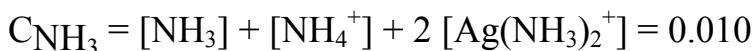
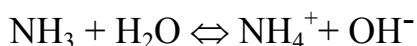
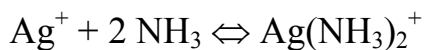
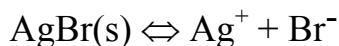
- equilibrium constant expressions
- mass-balance equations
- a single charge-balance equation

11A-1 Mass-Balance Equation

Ex. 11-1. Write mass-balance expressions for a 0.0100 M soln of HCl that is in equilibrium with an excess of solid BaSO_4 .



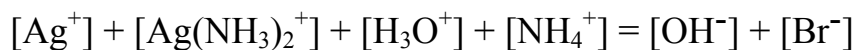
Ex. 11-2. Write mass-balance expressions for the system formed when a 0.010 M NH_3 solution is saturated with AgBr .



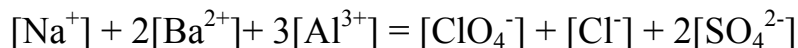
11A-2 Charge-Balance Equation

no. mol/L positive charge = no. mol /L negative charge

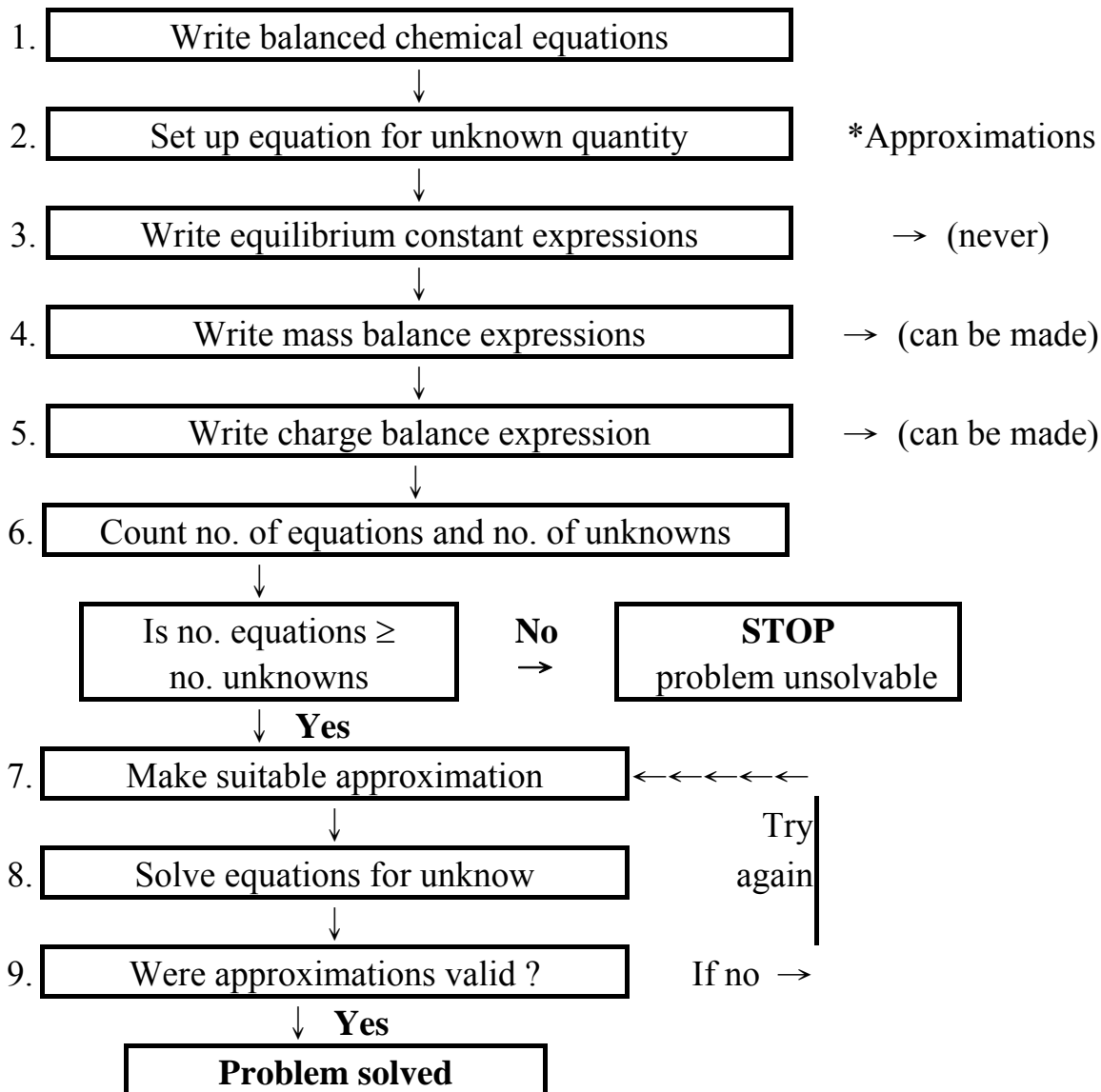
Ex. 11-3. Write a charge-balance equation for the system in Ex. 2.



Ex. 11-4. Neglecting the dissociation of water, write a charge-balance equation for a soln that contains NaCl, Ba(ClO₄)₂ & Al₂(SO₄)₃.



11A-3 Steps for solving problems involving several equilibria



***Approximations can be made only in charge-balance and mass-balance equations, → never in equilibrium-constant expressions.**

11B Calculating solubilities by the systematic method

11B-1 Solubility calculations

Ex. 11-5. Calculate the molar solubility of $\text{Mg}(\text{OH})_2$ in water.



$$\text{solubility } \text{Mg}(\text{OH})_2 = [\text{Mg}^{2+}], \quad [\text{OH}^-] = 2 [\text{Mg}^{2+}] + [\text{H}_3\text{O}^+]$$

$$\text{assume that } [\text{H}_3\text{O}^+] \ll [\text{Mg}^{2+}] \rightarrow [\text{OH}^-] \cong 2 [\text{Mg}^{2+}]$$

$$[\text{Mg}^{2+}](2[\text{Mg}^{2+}])^2 = 7.1 \times 10^{-12}, \quad [\text{Mg}^{2+}]^3 = \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12}$$

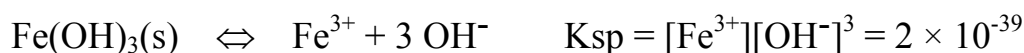
$$[\text{Mg}^{2+}] = \text{solubility} = 1.21 \times 10^{-4} = 1.2 \times 10^{-4} \text{ M}$$

Check of Assumptions:

$$[\text{OH}^-] = 2 \times 1.21 \times 10^{-4} = 2.42 \times 10^{-4} \text{ M}, \quad [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11} \text{ M}$$

The assumption that $4.1 \times 10^{-11} \ll 1.6 \times 10^{-4}$ is certainly valid.

Ex. 11-6. Calculate the solubility of $\text{Fe}(\text{OH})_3$ in water. Proceeding by the systematic approach used in Ex. 5 gives.



$$\text{solubility} = [\text{Fe}^{3+}], \quad [\text{OH}^-] = 3 [\text{Fe}^{3+}] + [\text{H}_3\text{O}^+]$$

$$\text{assume that } [\text{H}_3\text{O}^+] \ll 3 [\text{Fe}^{3+}] \rightarrow [\text{OH}^-] \approx 3 [\text{Fe}^{3+}], \quad [\text{Fe}^{3+}](3[\text{Fe}^{3+}])^3 = 2 \times 10^{-39}$$

$$\text{solubility} = [\text{Fe}^{3+}] = \sqrt[4]{\frac{2 \times 10^{-39}}{27}} = 9 \times 10^{-11} \text{ M}$$

Step 9. Check of Assumptions:

$$[\text{OH}^-] \approx 3 [\text{Fe}^{3+}] = 3 \times 9 \times 10^{-11} = 3 \times 10^{-10} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14}}{3 \times 10^{-10}} = 3 \times 10^{-5} \text{ M} \gg 3 [\text{Fe}^{3+}]$$

The assumption that $[\text{H}_3\text{O}^+] \ll 3[\text{Fe}^{3+}]$, was invalid and the provisional values for $[\text{Fe}^{3+}]$, $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ are all significantly in error.

$$\text{assume that } 3 [\text{Fe}^{3+}] \ll [\text{H}_3\text{O}^+], \quad [\text{OH}^-] = 3 [\text{Fe}^{3+}] + [\text{H}_3\text{O}^+]$$

$$\rightarrow [\text{OH}^-] = [\text{H}_3\text{O}^+] = 1 \times 10^{-7} \rightarrow [\text{Fe}^{3+}] = \frac{2 \times 10^{-39}}{(1 \times 10^{-7})^3} = 2 \times 10^{-18} \text{ M}$$

$$3 [\text{Fe}^{3+}] \ll [\text{H}_3\text{O}^+] \text{ or } 3 \times 2 \times 10^{-18} \ll 10^{-7}, \text{ the assumption is valid}$$

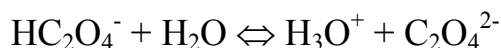
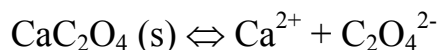
$$\text{solubility} = [\text{Fe}^{3+}] = 2 \times 10^{-18} \text{ M}$$

11B-2 The Effect of pH on Solubility

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

Solubility Calculations When the pH Is Constant

Ex. 11-7. Calculate the molar solubility of calcium oxalate in a soln that has been buffered so that its pH is constant and equal to 4.00.



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

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.7 \times 10^{-9} \quad (1)$$

$$\frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = K_1 = 5.60 \times 10^{-2} \quad (2)$$

$$\frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = K_2 = 5.42 \times 10^{-5} \quad (3)$$

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

$$[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] \quad (4)$$

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-4} \quad ; \quad [\text{OH}^-] = 1.00 \times 10^{-10}$$

Unknown \rightarrow $[\text{Ca}^{2+}]$, $[\text{C}_2\text{O}_4^{2-}]$, $[\text{HC}_2\text{O}_4^-]$ and $[\text{H}_2\text{C}_2\text{O}_4]$

$$[\text{HC}_2\text{O}_4^-] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{K_2} = \frac{1.00 \times 10^{-4} [\text{C}_2\text{O}_4^{2-}]}{5.42 \times 10^{-5}} = 1.85 [\text{C}_2\text{O}_4^{2-}]$$

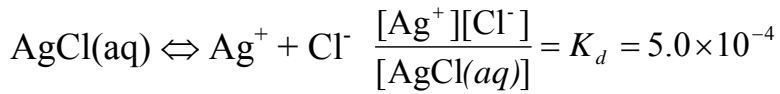
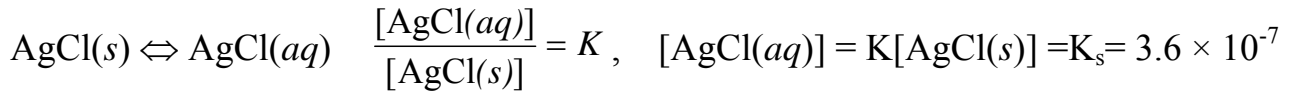
$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}] \times 1.85}{K_1} = \frac{1.85 \times 10^{-4} [\text{C}_2\text{O}_4^{2-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3} [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + 1.85 [\text{C}_2\text{O}_4^{2-}] + 3.30 \times 10^{-3} [\text{C}_2\text{O}_4^{2-}] = 2.85 [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{C}_2\text{O}_4^{2-}] = \frac{[\text{Ca}^{2+}]}{2.85} \quad ; \quad \frac{[\text{Ca}^{2+}][\text{Ca}^{2+}]}{2.85} = 1.7 \times 10^{-9}$$

$$[\text{Ca}^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5} \text{ M}$$

11B-3 The Effect of Undissociated Solutes on Precipitation Calculations



$$K_{sp} = K_d K_s = [\text{Ag}^+][\text{Cl}^-]$$

Ex. 11-8. Calculate the solubility of AgCl in distilled water.

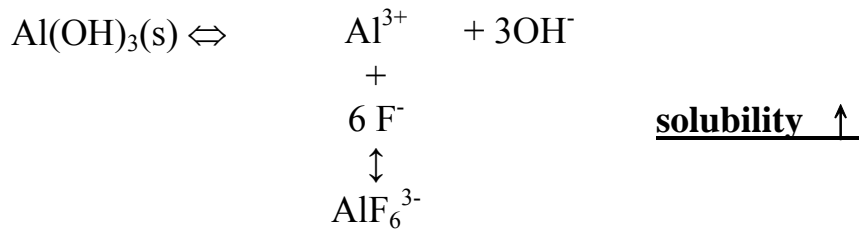
$$\text{solubility} = S = [\text{AgCl}(aq)] + [\text{Ag}^+]$$

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp} = 1.82 \times 10^{-10}$$

$$[\text{Ag}^+] = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5} \text{ M}$$

$$S = [\text{AgCl}(aq)] + [\text{Ag}^+] = 1.35 \times 10^{-5} + 3.6 \times 10^{-7} = 1.38 \times 10^{-5} \text{ M}$$

11B-4 The solubility of Precipitates in the presence of complexing agent

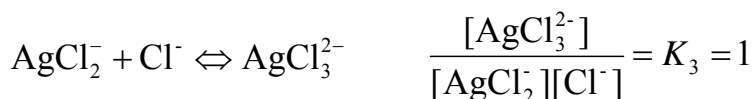
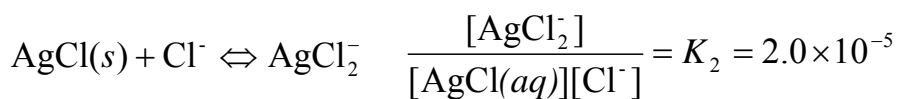
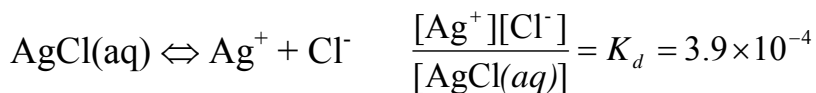


◆ Complex Formation with a common ion



Ex. 11-9 Derive an equation that describes the effect of the analytical concentration of KCl on the solubility of AgCl in an aqueous solution. Calculate the concentration of KCl at which the solubility is a minimum.

$$\text{solubility} = S = [\text{AgCl}(aq)] + [\text{Ag}^+] + [\text{AgCl}_2^-] + [\text{AgCl}_3^{2-}]$$



$$[\text{Cl}^-] = c_{\text{KCl}} + [\text{Ag}^+] - [\text{AgCl}_2^-] - 2[\text{AgCl}_3^{2-}]$$

Assumption: $c_{\text{KCl}} \gg [\text{Ag}^+] - [\text{AgCl}_2^-] - 2[\text{AgCl}_3^{2-}] \Rightarrow [\text{Cl}^-] = c_{\text{KCl}}$

$$\frac{[\text{AgCl}_3^{2-}]}{[\text{Cl}^-]^2} = K_2 K_3 = 2.0 \times 10^{-5} \times 1 = 2.0 \times 10^{-5}$$

$$[\text{AgCl}(aq)] = \frac{K_{sp}}{K_d} = \frac{1.82 \times 10^{-10}}{3.9 \times 10^{-4}} = 4.7 \times 10^{-7}$$

$$S = \frac{K_{sp}}{K_d} + \frac{K_{sp}}{[\text{Cl}^-]} + K_2[\text{Cl}^-] + K_2 K_3 [\text{Cl}^-]^2 = \frac{K_{sp}}{K_d} + \frac{K_{sp}}{c_{\text{KCl}}} + K_2 c_{\text{KCl}} + K_2 K_3 c_{\text{KCl}}^2$$

$$\frac{dS}{dc_{\text{KCl}}} = 0 = + \frac{K_{sp}}{c_{\text{KCl}}^2} + K_2 + 2K_2 K_3 c_{\text{KCl}} \Rightarrow 2K_2 K_3 c_{\text{KCl}}^3 + c_{\text{KCl}}^2 K_2 - K_{sp} = 0$$

$$(4.0 \times 10^{-5})c_{\text{KCl}}^3 + (2.0 \times 10^{-5})c_{\text{KCl}}^2 - 1.82 \times 10^{-10} = 0 \Rightarrow c_{\text{KCl}} = 0.0030 = [\text{Cl}^-]$$

Check: $[\text{Ag}^+] = (1.82 \times 10^{-10})/0.0030 = 6.1 \times 10^{-8} \text{ M} \ll c_{\text{KCl}}$

$$[\text{AgCl}_2^-] = 2.0 \times 10^{-5} \times 0.0030 = 6.0 \times 10^{-8} \text{ M} \ll c_{\text{KCl}}$$

$$[\text{AgCl}_3^{2-}] = 2.0 \times 10^{-5} \times 0.0030^2 = 1.8 \times 10^{-10} \text{ M} \ll c_{\text{KCl}}$$

$$S = 64.7 \times 10^{-7} + 6.1 \times 10^{-8} + 6.0 \times 10^{-8} + 1.8 \times 10^{-10} = 5.9 \times 10^{-7} \text{ M}$$

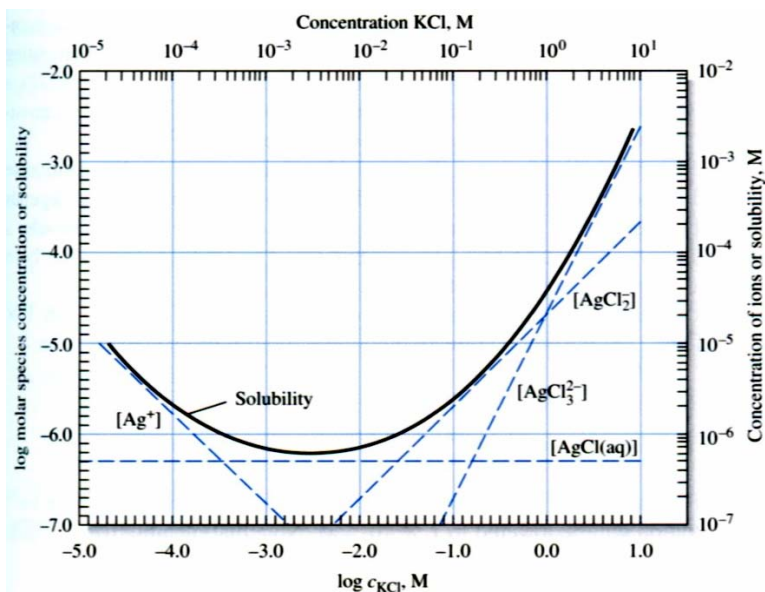
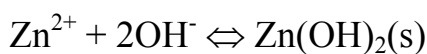


Fig. 11-2 The Effect of $[\text{Cl}^-]$ on the solubility of AgCl . The solid curve shows the total concentration of dissolved AgCl . The broken lines show the concentration of the various silver-containing species.



11C Separation of Ions by Control of the Concentration of the Precipitating Agent

11C-1 Calculation of the Feasibility of Separations

Ex. 11-10 Can Fe^{3+} and Mg^{2+} be separated quantitatively as hydroxide from a solution that is 0.10 M in each cation? If the separation is possible, what range of $[\text{OH}^-]$ is permissible?

$[\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}$ $[\text{Mg}^{2+}][\text{OH}^-]^2 = 7.1 \times 10^{-12}$	Quantitative separation: (1) 99.9% Fe^{3+} will be precipitated and (2) Mg^{2+} not precipitated.
---	---

quantitative: $> 99\%$ precipitation $\Rightarrow < 0.1\%$ remained $\Rightarrow [\text{Fe}^{3+}] \ll 1.0 \times 10^{-4} \text{ M}$

$$1. (1.0 \times 10^{-4})[\text{OH}^-]^3 = 2 \times 10^{-39} \Rightarrow [\text{OH}^-] = \sqrt[3]{\frac{2 \times 10^{-39}}{1.0 \times 10^{-4}}} = 3 \times 10^{-12} \text{ M}$$

$$2. 0.1[\text{OH}^-]^2 = 7.1 \times 10^{-12} \Rightarrow [\text{OH}^-] = \sqrt{\frac{7.1 \times 10^{-12}}{0.1}} = 8.4 \times 10^{-6} \text{ M}$$

\therefore By maintaining $[\text{OH}^-]$ between $3 \times 10^{-12} \text{ M}$ and $8.4 \times 10^{-6} \text{ M}$. In practice, $[\text{OH}^-]$ is kept as low as practical—often about 10^{-10} M

11C-2 Sulfide Separations

Solubility differences : \rightarrow control pH \rightarrow control active reagent conc.

reagents in which the anion is the conjugate base of a weak acid

Ex: S^{2-} (conjugate base of H_2S), OH^- (conjugate base of H_2O) and the anions of several organic weak acids.

MS : ($K_{\text{sp}}: 10^{-10} \sim 10^{-50}$ or small)

$[\text{S}^{2-}]$: $0.1 \sim 10^{-22} \text{ M}$

$\text{MS}(\text{s}) \Leftrightarrow \text{M}^{2+} + \text{S}^{2-}, \quad [\text{M}^{2+}][\text{S}^{2-}] = K_{\text{sp}}$

$\text{H}_2\text{S} + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{HS}^-, \quad \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = K_1 = 9.6 \times 10^{-8}$

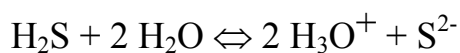
$\text{HS}^- + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{S}^{2-}, \quad \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = K_2 = 1.3 \times 10^{-14}$

Solubility = $[\text{M}^{2+}]$

The $[\text{H}_2\text{S}]$ in a saturated soln is $\approx 0.1 \text{ M}$

$$[\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}] = 0.1$$

assuming that $([\text{S}^{2-}] + [\text{HS}^-]) \ll [\text{H}_2\text{S}] \Rightarrow [\text{H}_2\text{S}] \cong 0.10 \text{ M}$



$$\frac{[\text{H}_3\text{O}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} = K_1K_2 = 1.2 \times 10^{-21}$$

$$\frac{[\text{H}_3\text{O}^+]^2[\text{S}^{2-}]}{0.10} = 1.2 \times 10^{-21}$$

$$[\text{S}^{2-}] = \frac{1.2 \times 10^{-22}}{[\text{H}_3\text{O}^+]^2}$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{1.2 \times 10^{-22}}{[\text{S}^{2-}]}}$$

$$K_{sp} = \frac{[\text{M}^{2+}] \times 1.2 \times 10^{-22}}{[\text{H}_3\text{O}^+]^2}$$

$$[\text{M}^{2+}] = \text{solubility} = \frac{[\text{H}_3\text{O}^+]^2 K_{sp}}{1.2 \times 10^{-22}}$$

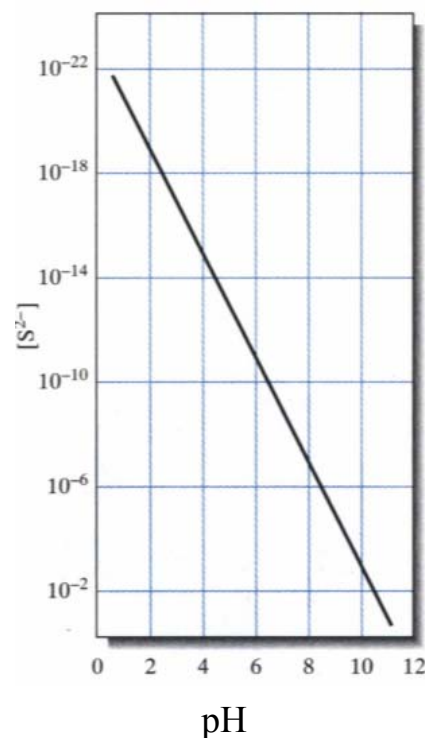
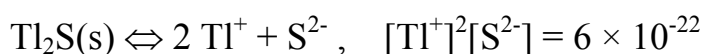
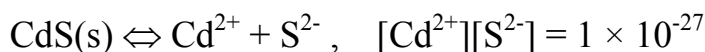


Fig.11-3 $[\text{H}_2\text{S}]$ as a function of pH in a saturated H_2S solution.

Ex.11-11. CdS is less soluble than Tl_2S . Find the conditions under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively with H_2S from a solution that is 0.1 M in each cation.



Consider a separation to be quantitative when all but 1 part in 1000 of the Cd^{2+} has been removed, or, when the conc. of the cation has been reduced to 1.00×10^{-4} M

$$10^{-4} [\text{S}^{2-}] > 1 \times 10^{-27}, \quad [\text{S}^{2-}] > \mathbf{1 \times 10^{-23}} \quad (\text{Min})$$

$$(0.1)^2 [\text{S}^{2-}] < 6 \times 10^{-22}, \quad [\text{S}^{2-}] < \mathbf{6 \times 10^{-20}} \quad (\text{Max})$$

$$[\text{H}_3\text{O}^+]^2 < \frac{1.2 \times 10^{-22}}{1 \times 10^{-23}} = 12, \quad [\text{H}_3\text{O}^+] < \mathbf{3.5 \text{ M}} \quad (\text{Max})$$

$$[\text{H}_3\text{O}^+]^2 > \frac{1.2 \times 10^{-22}}{6 \times 10^{-20}} = 2.0 \times 10^{-3}, \quad [\text{H}_3\text{O}^+] > \mathbf{0.045 \text{ M}} \quad (\text{Min})$$

maintaining $[\text{H}_3\text{O}^+]$ between 0.045 and 3.5 M