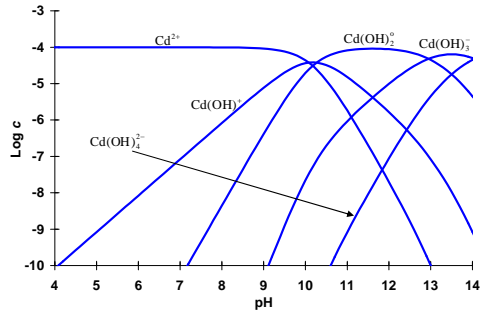
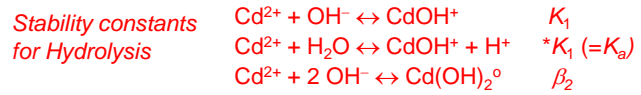


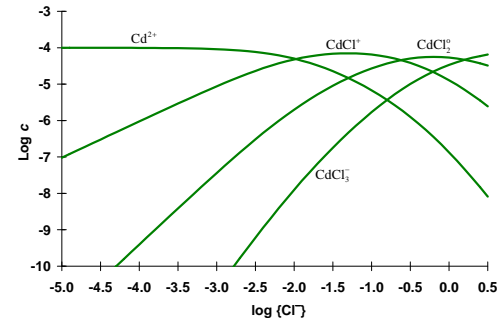
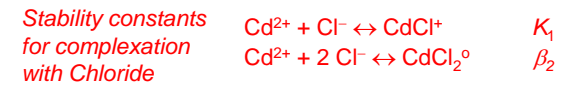
Aqueous Chemistry of Metals

How do metal ions interact with water and/or OH⁻?



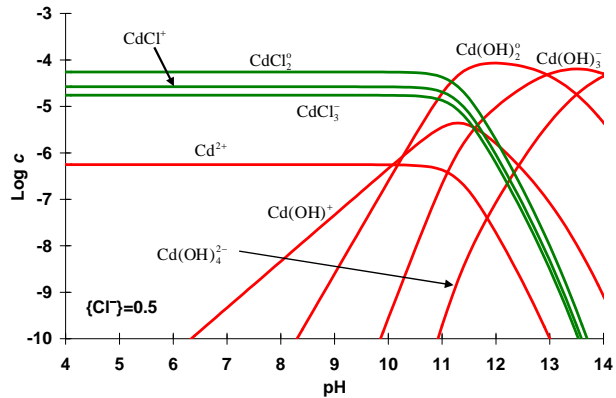
Aqueous Chemistry of Metals

How do metal ions interact with other solutes?



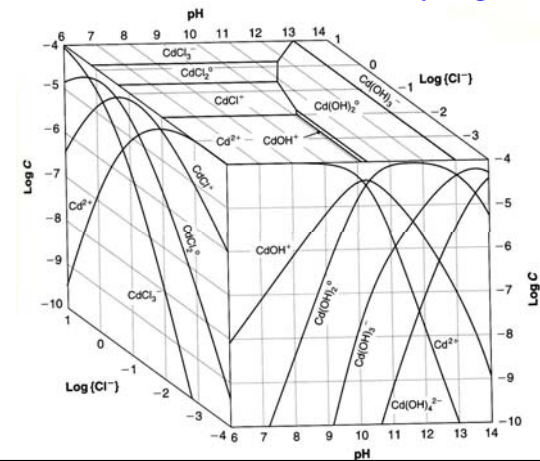
Aqueous Chemistry of Metals

How do metal ions interact with multiple ligands?



Aqueous Chemistry of Metals

How do metal ions interact with multiple ligands?





Equil. Species: H^+ , OH^- , NH_4^+ , NH_3 , Cu(OH)_y^{2-y} , $\text{Cu}_2(\text{OH})_2^0$, $\text{Cu(NH}_3)_x^{2+}$, CuCl^+ , Ca^{2+} , Cl^-

| | H_2O | H^+ | Cu^{2+} | NH_3 | Ca^{2+} | Cl^- |
|---------------------------------|----------------------|--------------|------------------|---------------|------------------|---------------|
| H_2O | 1 | 0 | 0 | 0 | 0 | 0 |
| H^+ | 0 | 1 | 0 | 0 | 0 | 0 |
| Cu^{2+} | 0 | 0 | 1 | 0 | 0 | 0 |
| NH_3 | 0 | 0 | 0 | 1 | 0 | 0 |
| Ca^{2+} | 0 | 0 | 0 | 0 | 1 | 0 |
| Cl^- | 0 | 0 | 0 | 0 | 0 | 1 |
| OH^- | 1 | -1 | 0 | 0 | 0 | 0 |
| NH_4^+ | 0 | 1 | 0 | 1 | 0 | 0 |
| CuOH^+ | 1 | -1 | 1 | 0 | 0 | 0 |
| Cu(OH)_2^0 | 2 | -2 | 1 | 0 | 0 | 0 |
| Cu(OH)_3^- | 3 | -3 | 1 | 0 | 0 | 0 |
| Cu(OH)_4^{2-} | 4 | -4 | 1 | 0 | 0 | 0 |
| $\text{Cu}_2(\text{OH})_2^{2+}$ | 2 | -2 | 2 | 0 | 0 | 0 |
| $\text{Cu(NH}_3)_2^{2+}$ | 0 | 0 | 1 | 1 | 0 | 0 |
| $\text{Cu(NH}_3)_3^{2+}$ | 0 | 0 | 1 | 2 | 0 | 0 |
| $\text{Cu(NH}_3)_4^{2+}$ | 0 | 0 | 1 | 3 | 0 | 0 |
| $\text{Cu(NH}_3)_5^{2+}$ | 0 | 0 | 1 | 4 | 0 | 0 |
| CuCl^+ | 0 | 0 | 1 | 0 | 0 | 1 |

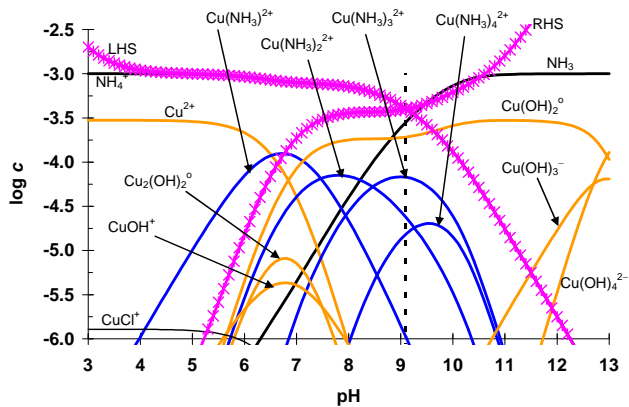


Input Species: NH_4Cl , CuCl_2 , Ca(OH)_2

| | H_2O | H^+ | Cu^{2+} | NH_3 | Ca^{2+} | Cl^- | Conc'n |
|------------------------|----------------------|--------------|------------------|---------------|------------------|---------------|--------------------|
| NH_4Cl | 0 | 1 | 0 | 1 | 0 | 1 | 10^{-3} |
| CuCl_2 | 0 | 0 | 1 | 0 | 0 | 2 | 3×10^{-4} |
| Ca(OH)_2 | 2 | -2 | 0 | 0 | 1 | 0 | 5×10^{-4} |

$$1(10^{-3}) + 0 - 2(5 \times 10^{-4}) = [\text{H}^+] - [\text{OH}^-] + [\text{NH}_4^+] - [\text{CuOH}^+] - 2[\text{Cu(OH)}_2^0] - 3[\text{Cu(OH)}_3^-] - 4[\text{Cu(OH)}_4^{2-}] - 2[\text{Cu}_2(\text{OH})_2^{2+}]$$

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{CuOH}^+] + 2[\text{Cu(OH)}_2^0] + 3[\text{Cu(OH)}_3^-] + 4[\text{Cu(OH)}_4^{2-}] + 2[\text{Cu}_2(\text{OH})_2^{2+}]$$



Equilibrium with Metal Solids

What defines formation of a solid?

What are the chemical characteristics of solids, in particular wrt their chemical activity?

What are the conventions for writing equilibrium reactions involving solids?

How does the presence of a solid affect the equilibrium activities of solutes, including free metal ions and complexes?

Equilibrium with Metal Solids

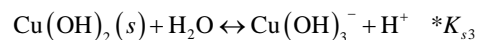
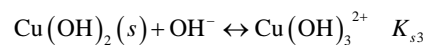
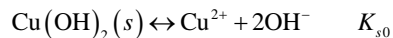
- **What defines formation of a solid?**
 - A solid is a non-aqueous phase; separate phases have different compositions and are separated by a well-defined interface
 - The properties of the interfacial region (a few layers on either side of the interface) are different from those in the bulk solid or liquid
 - *Colloids* are solids that are small enough that the interfacial region has a significant influence on the behavior of the whole particle (*my definition!*)

Equilibrium with Metal Solids

- **What are the chemical characteristics of solids, in particular wrt their chemical activity?**
 - The behavior of non-colloidal solids is dominated by the (uniform) environment in the bulk interior
 - Dissolution (or precipitation) of a molecule of a non-colloidal solid replaces one surface molecule with a different one; the net effect is exchange of a molecule from the bulk solid with one from the bulk solution
 - Because the environment in the interior is the same regardless of particle size, dissolution is analogous to discarding a portion of a solution, without changing its composition; i.e., the composition, Gibbs energy, and activity of the molecules are not affected. By convention, $a=1.0$.

Equilibrium with Metal Solids

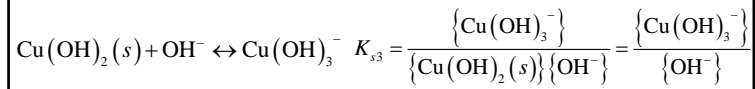
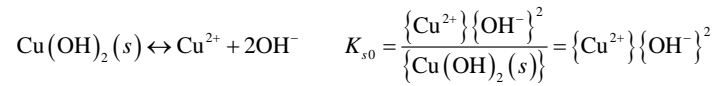
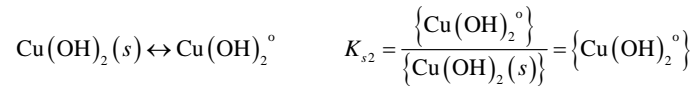
- **What are the conventions for writing equilibrium reactions involving solids?**
 - Reactions written for dissolution, with solid as reactant and free metal ion and ligands as products. Equilibrium constant designated K_{s0} (*solubility product, K_{sp}*)
 - If written with a complex containing i ligands as the product, equilibrium constant is designated K_{si} ; Ligands appear as reactants or products, depending on i . If ligands are protonated, add *



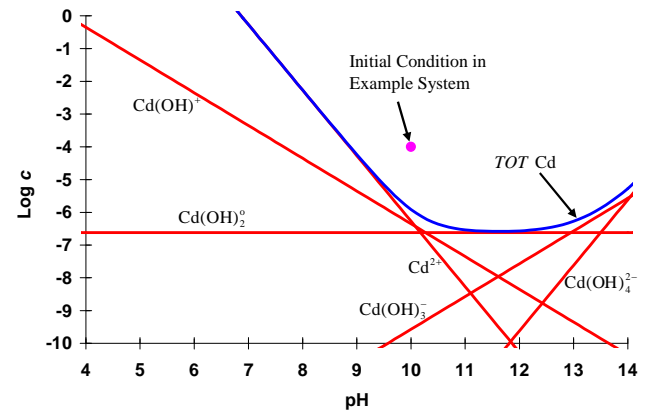
Equilibrium with Metal Solids

- **How does the presence of a solid affect the equilibrium activities of solutes, including free metal ions and complexes?**
 - Equilibrium with solid requires that the K_{si} expressions be satisfied. If one such equation and the K_i (stability constant) expressions are satisfied, all K_{si} expressions are satisfied
 - Essentially identical to equilibrium with a gas phase of known, constant composition
 - Solute with same composition as solid has activity that is independent of pH; more acidic or more basic solutes are characterized by straight lines on $\log c - \text{pH}$ diagrams

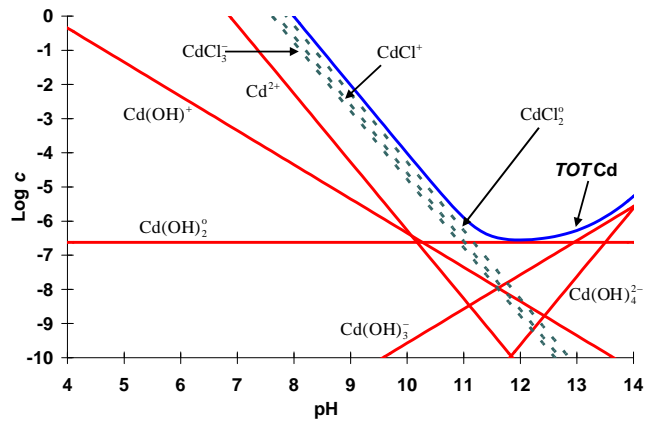
Equilibrium with Metal Hydroxides



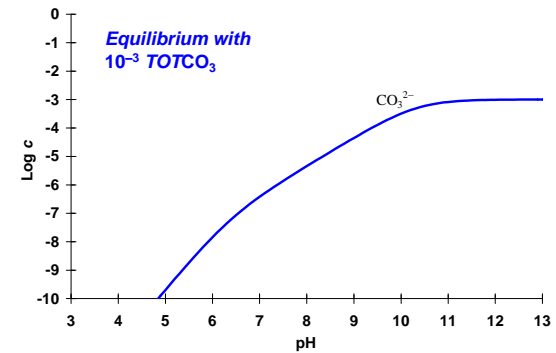
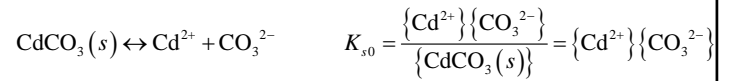
Equilibrium with Metal Hydroxides



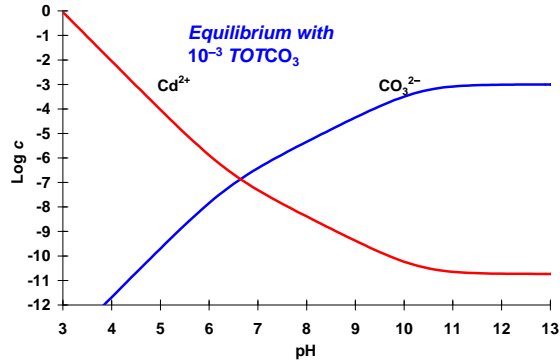
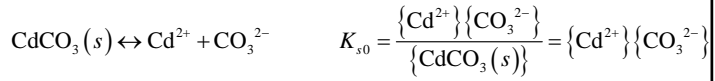
Equilibrium with Metal Hydroxides



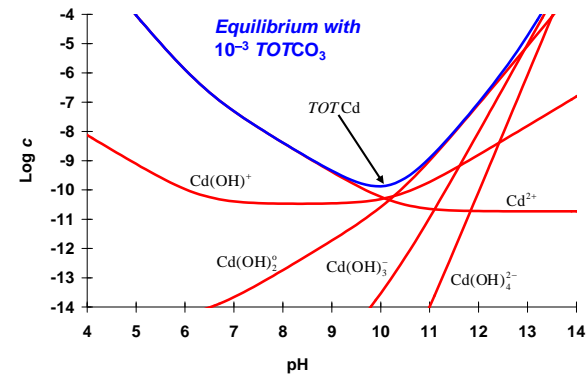
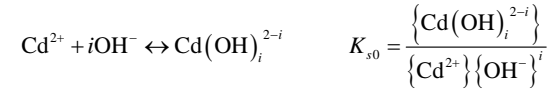
Equilibrium with Metal Carbonates



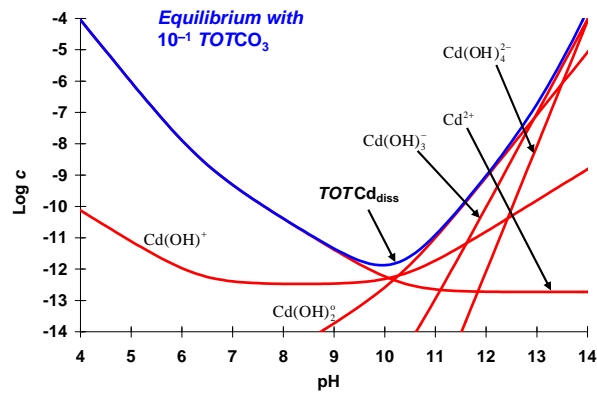
Equilibrium with Metal Carbonates



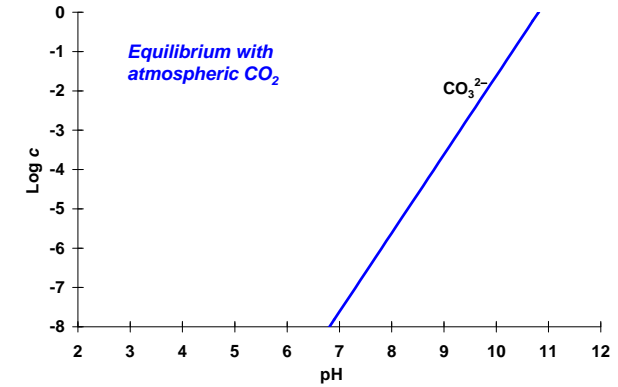
Equilibrium with Metal Carbonates



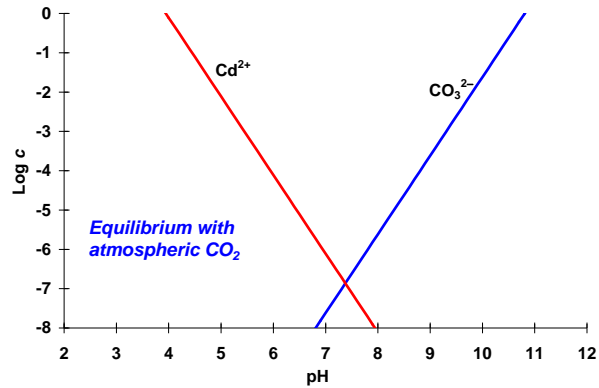
Equilibrium with Metal Carbonates



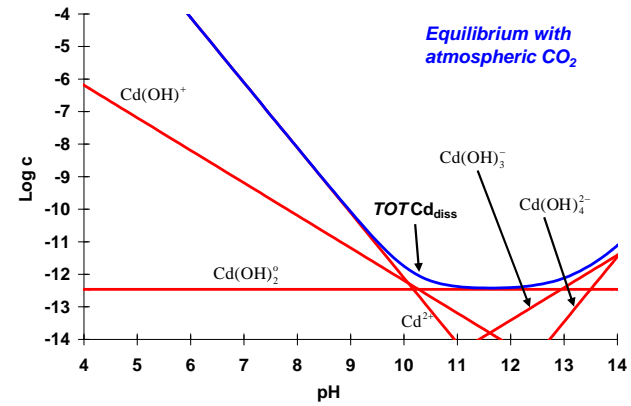
Equilibrium with Metal Carbonates



Equilibrium with Metal Carbonates



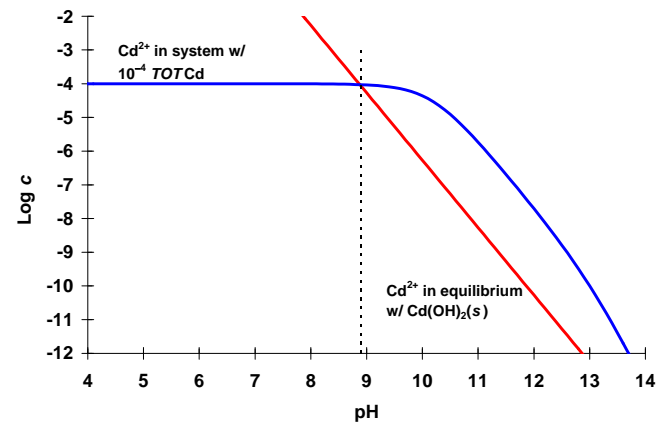
Equilibrium with Metal Carbonates



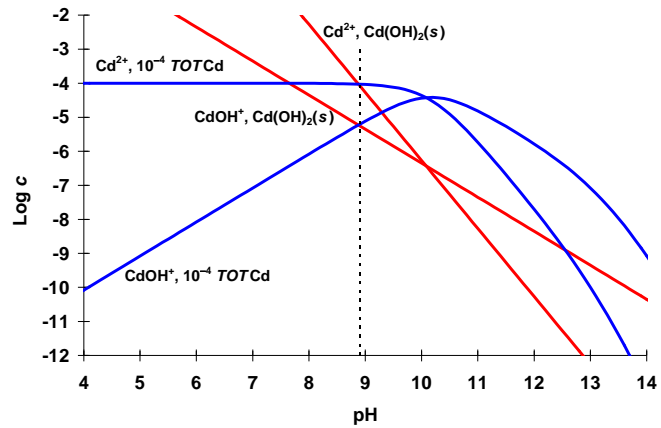
Equilibrium with Metal Solids

- Under what conditions will a solid form? Dissolve?*
- How much solid will be present at equilibrium?*
- If multiple solids can form, which one(s) dominate, and what is the solution composition?*
- How do complexing ligands affect solubility?*

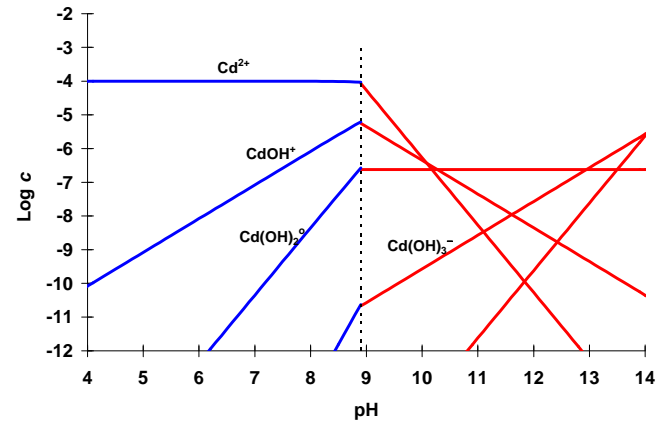
Considering Whether a Solid Will Form



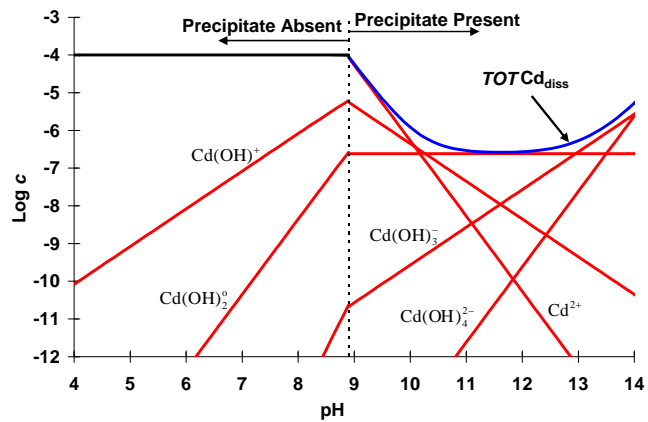
Considering Whether a Solid Will Form



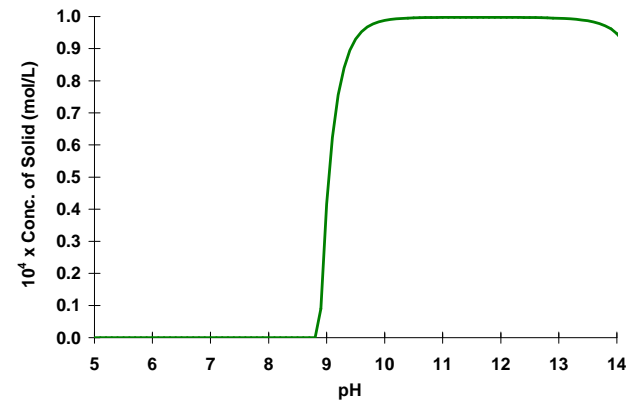
Considering Whether a Solid Will Form



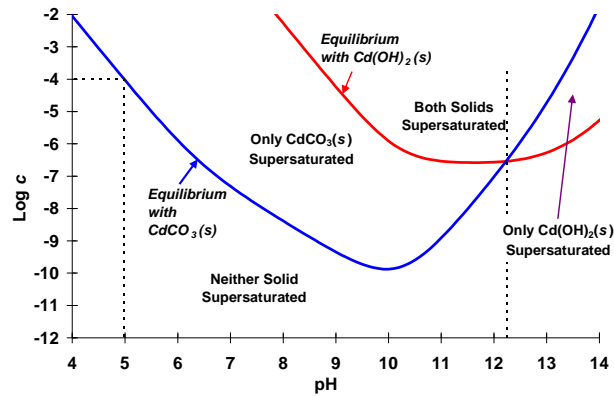
Considering Whether a Solid Will Form



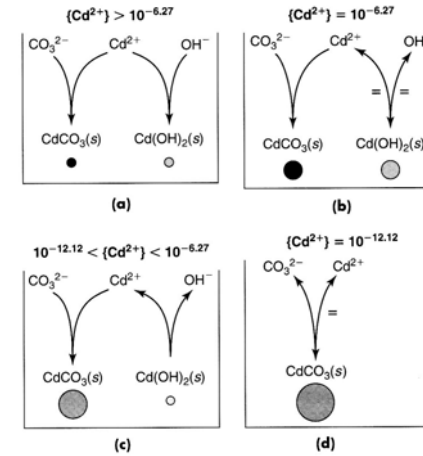
How Much Solid Will Form?



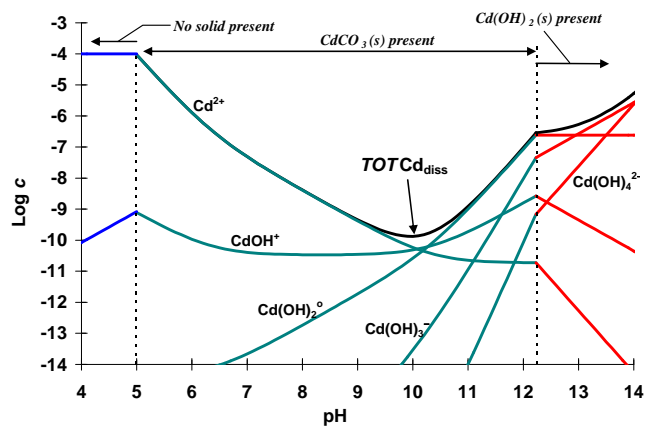
Systems with Two Possible Precipitates



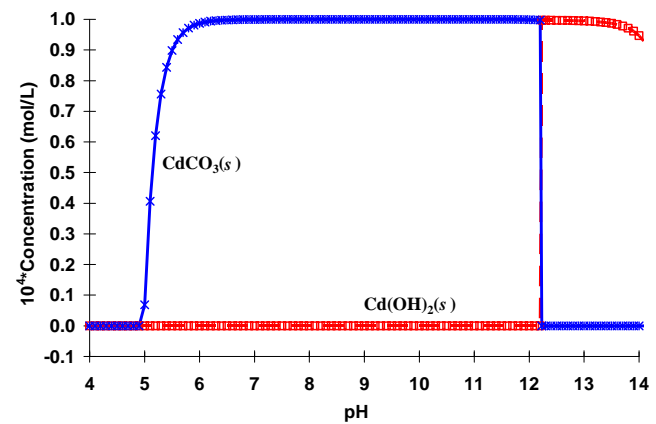
Systems with Two Possible Precipitates



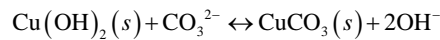
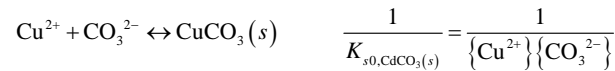
Systems with Two Possible Precipitates



Systems with Two Possible Precipitates

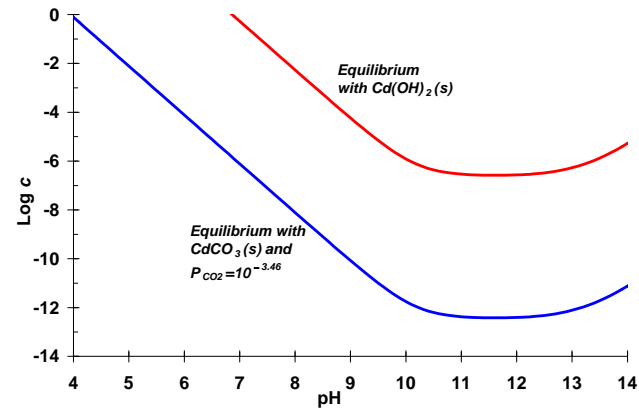


Simultaneous Equilibrium with Two Solids



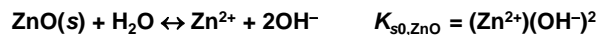
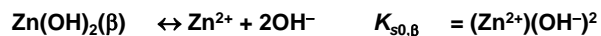
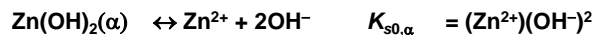
$$K_{eq} = \frac{\{\text{CuCO}_3(s)\} \{\text{OH}^-\}^2}{\{\text{Cu}(\text{OH})_2(s)\} \{\text{CO}_3^{2-}\}} = \frac{\{\text{OH}^-\}^2}{\{\text{CO}_3^{2-}\}}$$

Systems with Two Possible Precipitates



Multiple Solids with Identical Dissolution Stoichiometries (Polymorphs)

Solids that differ only in their crystallography and/or the extent of hydration of the solid have K_{s0} expressions with the same form:



Solid polymorphs might have different values of K_{s0} , in which case the solid with the smallest K_{s0} is the only one that can be present at equilibrium. Nevertheless, the others are sometimes found as pseudo-stable phases.

Equilibrium with Metal Solids

Under what conditions will a solid form? Dissolve?

Solids are present at equilibrium if and only if the composition of the solution can equilibrate with them. If insufficient metal or ligand is present to satisfy K_{s0} , no solid will be present.

How much solid will be present at equilibrium?

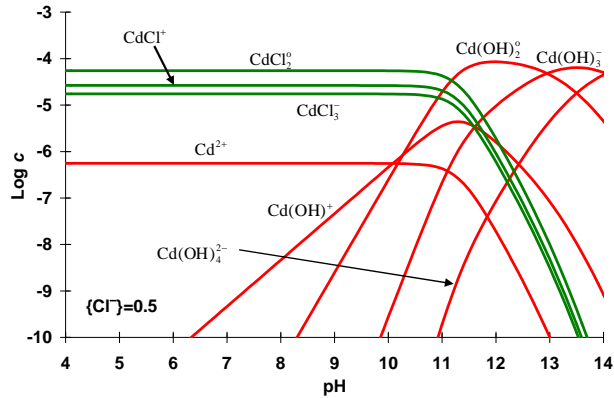
The amount of metal that is present as a solid at equilibrium is the difference between $\text{TOTMe}_{\text{init}}$ and $\text{TOTMe}_{\text{fin}}$; the amount of solid present depends on this difference and the MW of the solid.

If multiple solids can form, which one(s) will dominate, and what will the solution composition be?

In general, the phase that limits the metal concentration to the lowest value (considering all possible reactions) will control $\text{TOTMe}_{\text{diss}}$.

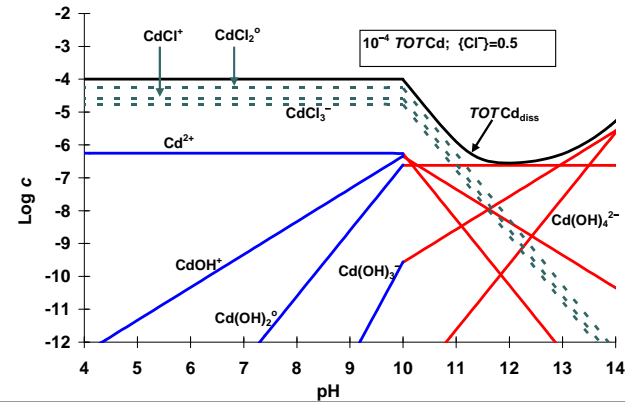
Equilibrium with Metal Solids

How do metal ions interact with ligands?



Aqueous Chemistry of Metals

How do complexing ligands affect solubility?



Equilibrium with Metal Solids

How do complexing ligands affect solubility?

Complexes form whenever ligands are present. The K_{si} relationships are unaffected by ligands. Since addition of ligands reduces the activity of the other dissolved metal species (e.g., the free ion), they interfere with precipitation; i.e., the solution can retain more TOTMe without precipitation occurring or, if a solid is present, more of it can dissolve in the presence of ligands than in their absence.

Modeling Solid/Liquid Equilibrium in Visual Minteq

Stoichiometry and Log K values for inputting solids

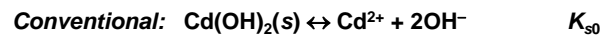
Specifying whether the solution is forced to be in equilibrium with the solid, or whether the solution can be undersaturated

Determining how much solid precipitates, if the inputs cause the solution to be supersaturated

Modeling Solid/Liquid Equilibrium in Minteq

Stoichiometry and Log K values for inputting solids

Solids are input into Minteq following the same formalism as for other Species, i.e., as the product of a reaction in which all other reactants and products are Components. Note that these reactions are different from the reactions used to describe solid/solution equilibrium in other contexts.



Specifying whether the solution is forced to be in equilibrium with the solid, or whether the solution can be undersaturated

- The input option to specify the presence of an infinite amount of the solid assures that the solution will be in equilibrium with the solid; the program adds or removes the components of the solid to the solution in the appropriate stoichiometric ratio until the solution is saturated with the solid*
- Alternatively, specifying the presence of a fixed amount of solid (including zero, if appropriate) in the initial system allows the solid to be present at equilibrium, but only if the inputs support that outcome (i.e., if the solution would be supersaturated in the absence of the solid)*

Determining how much solid precipitates, if the inputs cause the solution to be supersaturated

As for other, similar situations, the concentration of solids formed (mol/L) can be computed based on the difference between the total input of metal and the total dissolved metal in the equilibrated solution:

$$\text{TOTMe}_{\text{solid}} = \text{TOTMe}_{\text{input}} - \text{TOTMe}_{\text{diss,eq}}$$