# Aqueous Chemistry of Metals

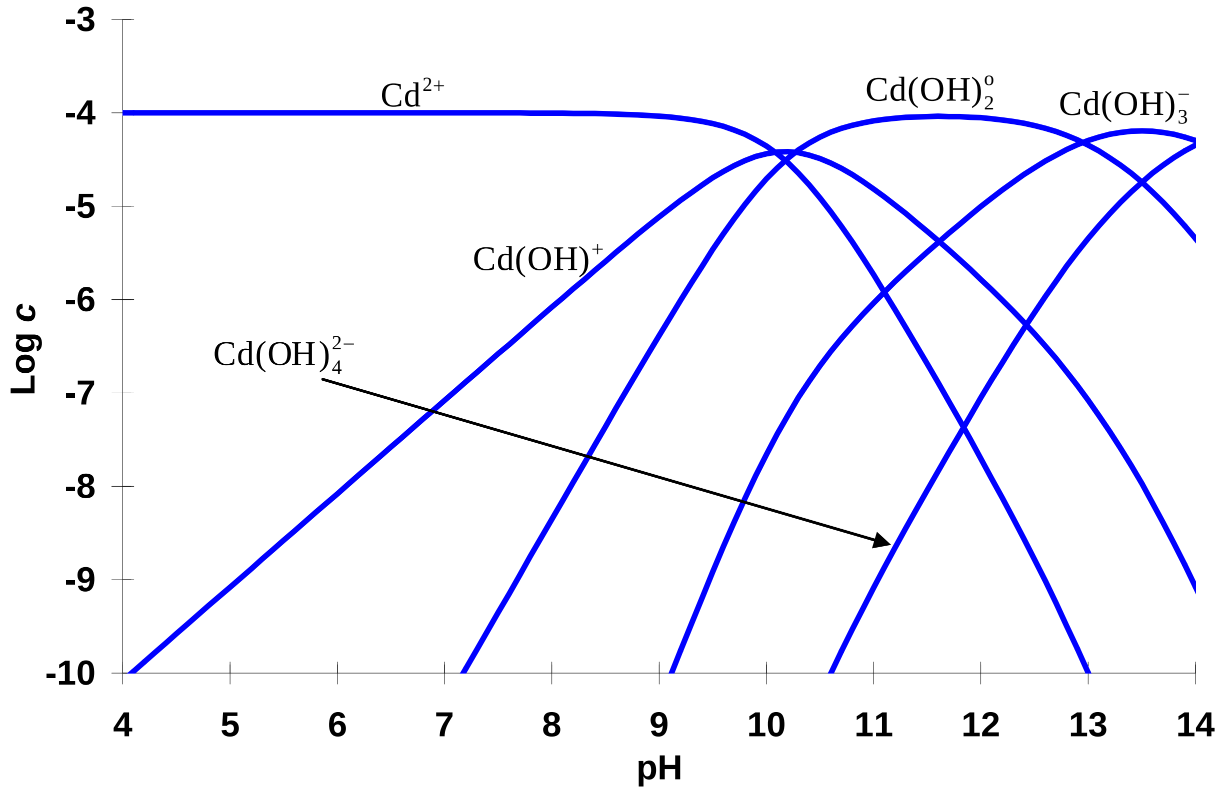
***How do metal ions interact with water and/or OH⁻?***

*Stability constants for Hydrolysis*

$Cd^{2+} + OH^{-} \leftrightarrow CdOH^{+}$ $\quad K_1$

$Cd^{2+} + H_2O \leftrightarrow CdOH^{+} + H^{+}$ $\quad {}^*K_1\ (=K_a)$

$Cd^{2+} + 2\,OH^{-} \leftrightarrow Cd(OH)_2^{o}$ $\quad \beta_2$



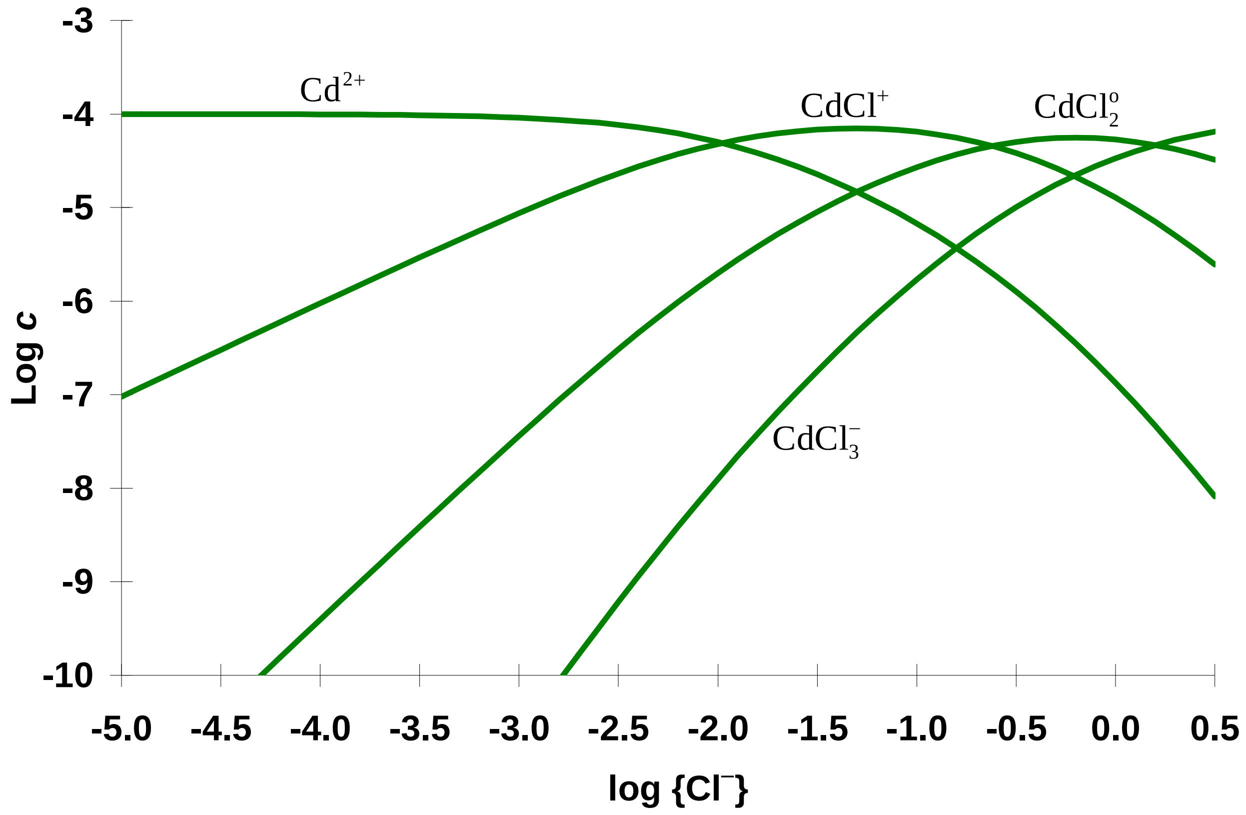
# Aqueous Chemistry of Metals

***How do metal ions interact with other solutes?***

*Stability constants for complexation with Chloride*

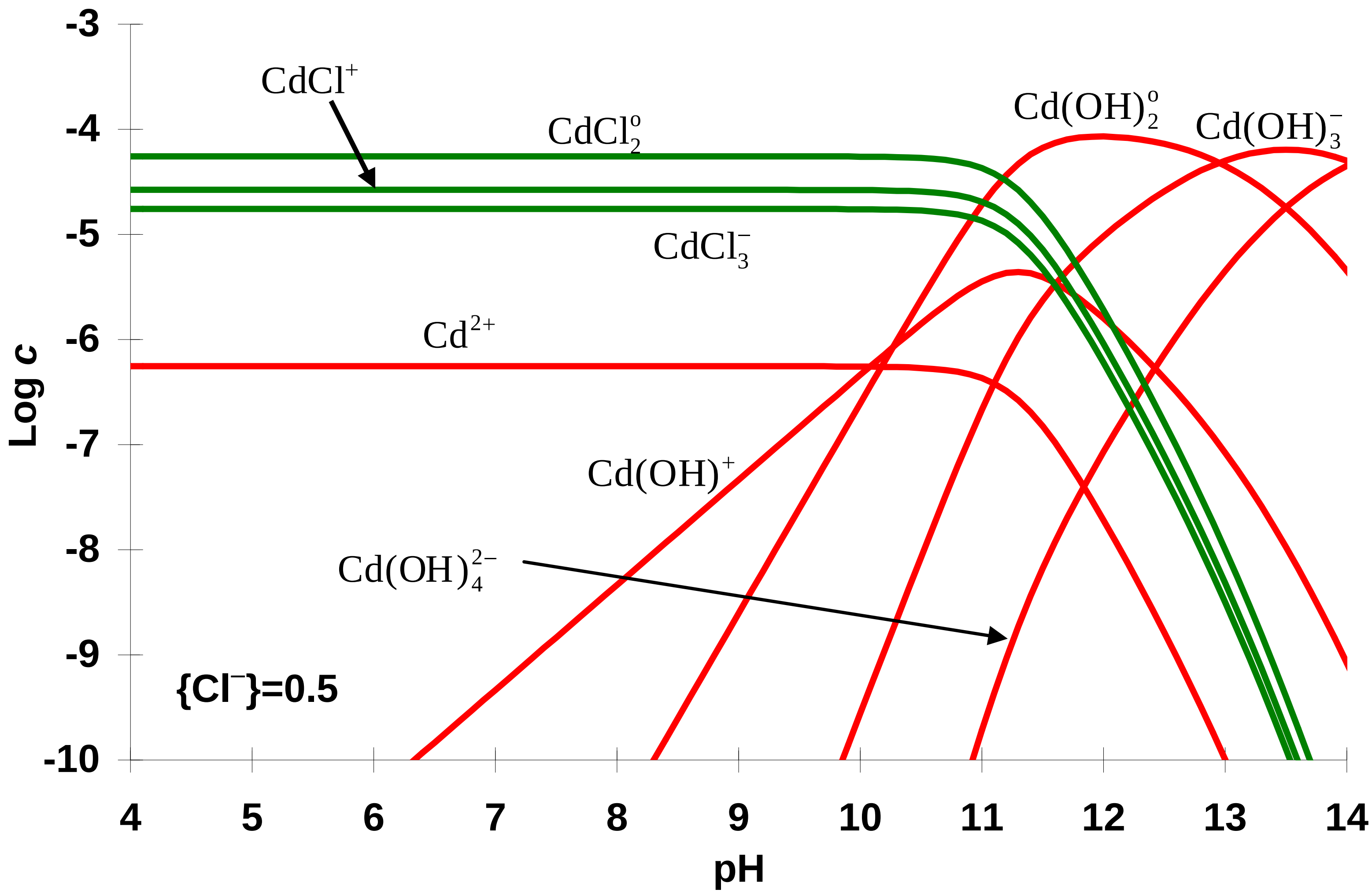
$Cd^{2+} + Cl^{-} \leftrightarrow CdCl^{+}$ $K_1$

$Cd^{2+} + 2\ Cl^{-} \leftrightarrow CdCl_2^{o}$ $\beta_2$



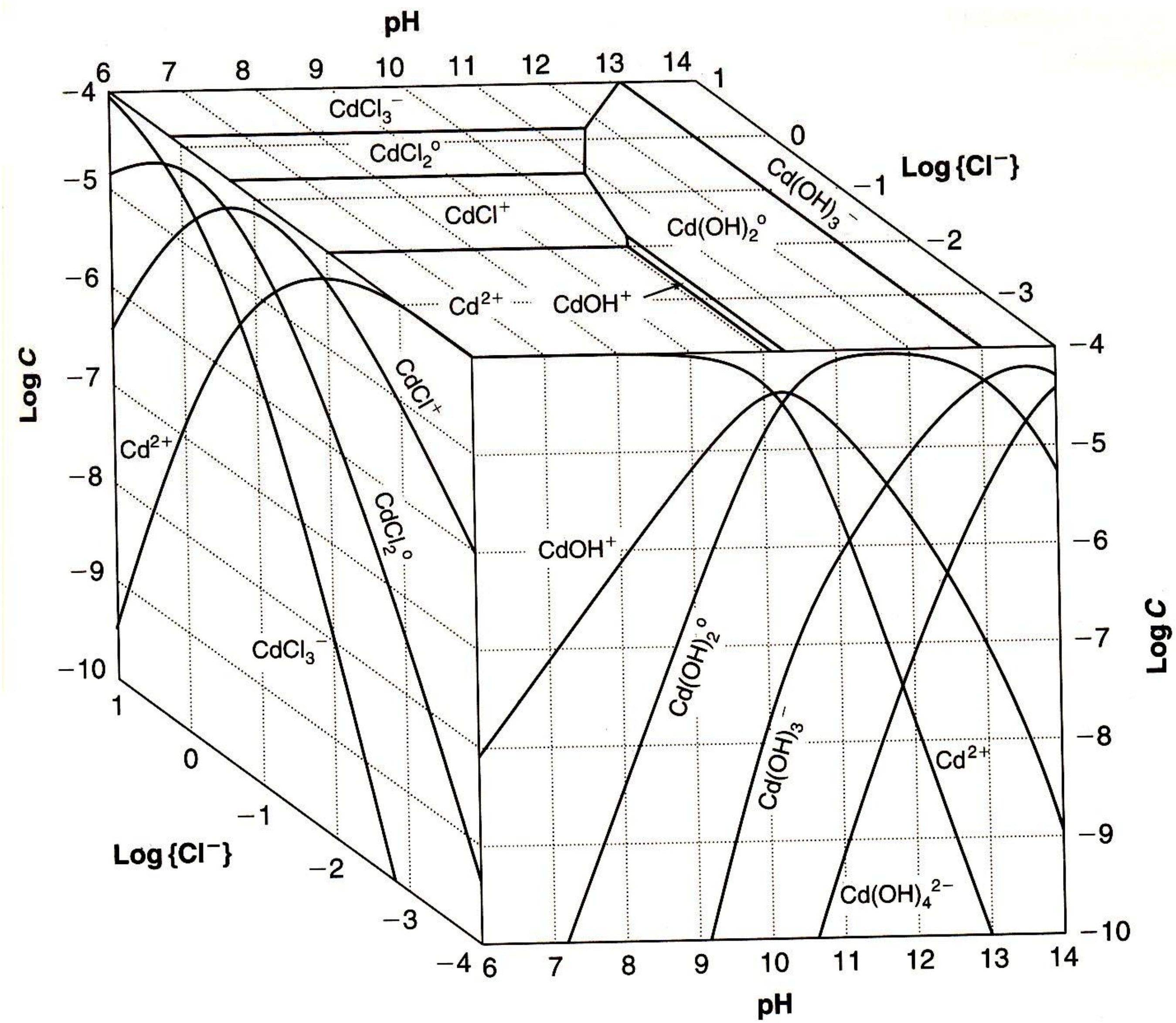
# Aqueous Chemistry of Metals

*How do metal ions interact with multiple ligands?*



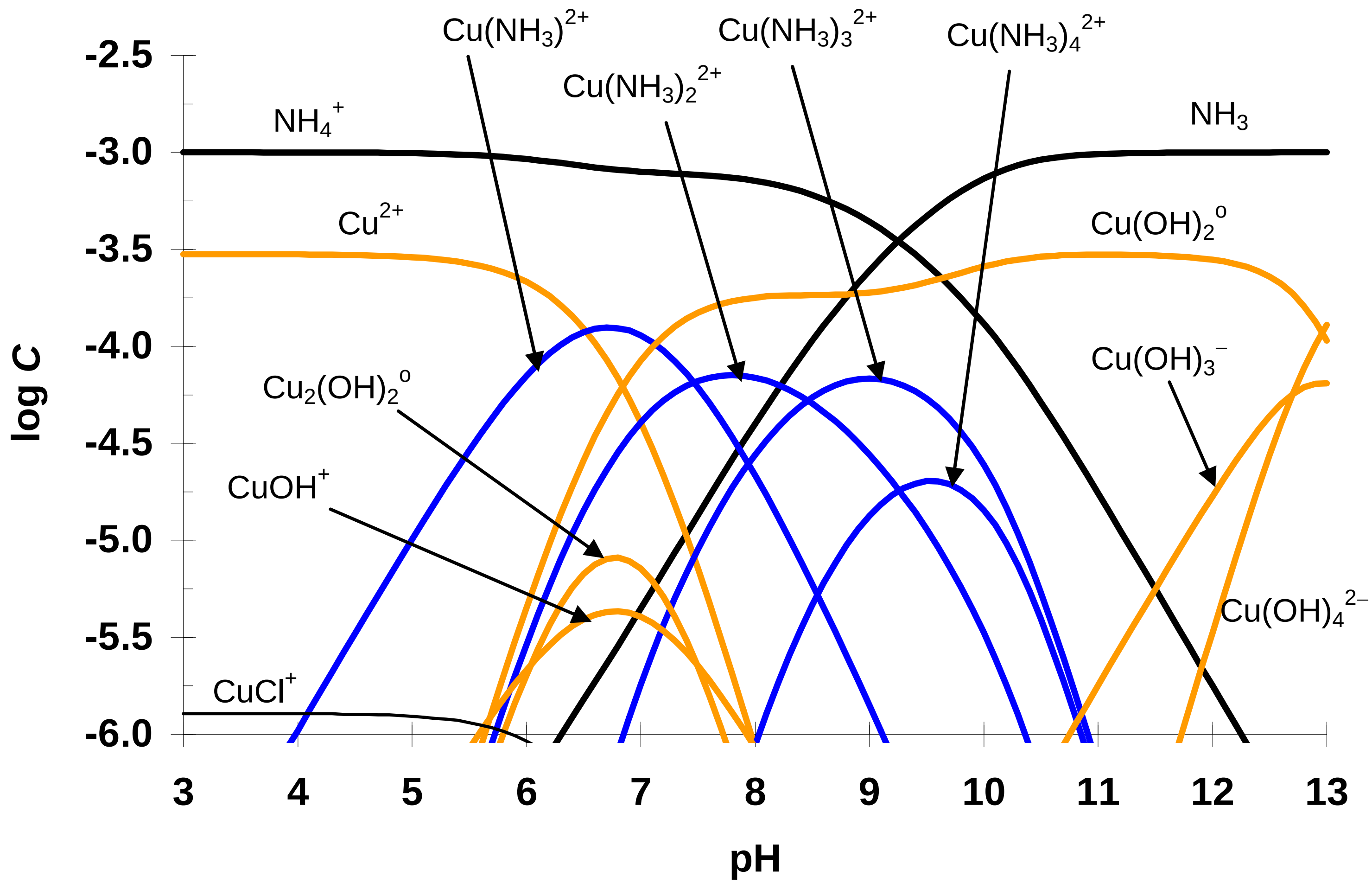
# Aqueous Chemistry of Metals

***How do metal ions interact with multiple ligands?***



# Aqueous Chemistry of Metals

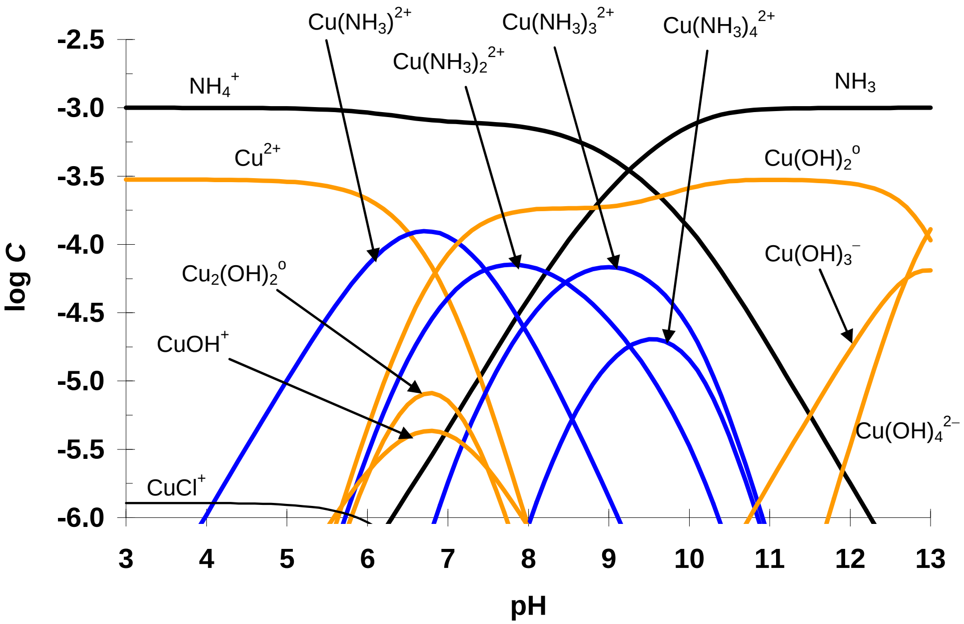
***Exercise: This plot is for a system with $3 \times 10^{-4}$ TOTCu + $10^{-3}$ $TOTNH_4$. What is log $\beta_2$ for $Cu^{2+}$-$NH_3$ complexes?***



# Aqueous Chemistry of Metals

$$Cu^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_2^{\ 2+}$$

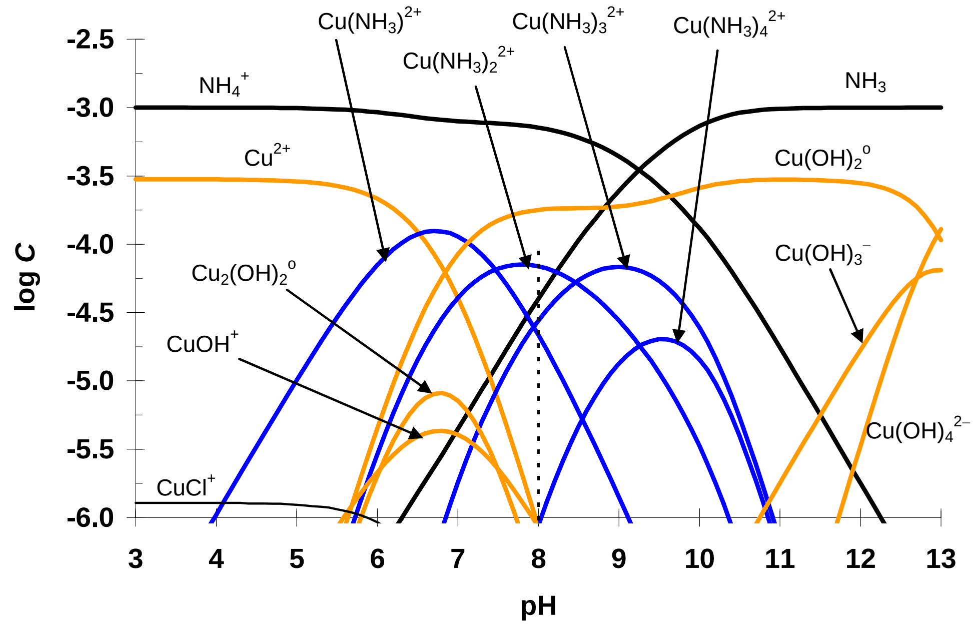
$$\beta_2 = \frac{\{Cu(NH_3)_2^{\ 2+}\}}{\{Cu^{2+}\}\{NH_3\}^2}$$




*Can we use the above equation in conjunction with the graph to determine $\beta_2$? At what pH?*

# Aqueous Chemistry of Metals

$$Cu^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_2^{\;2+}$$

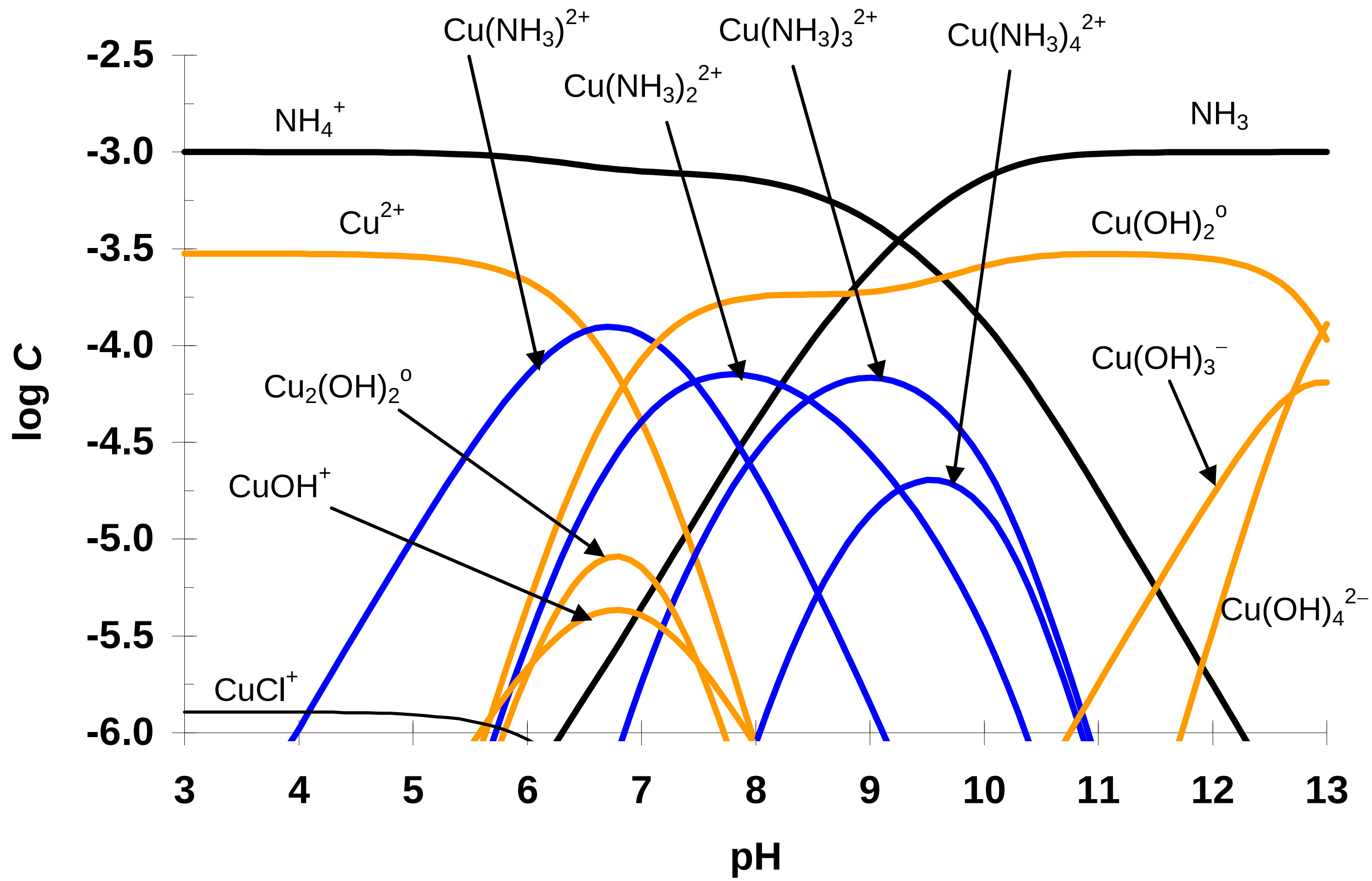



$$\beta_2 = \frac{\{Cu(NH_3)_2^{\;2+}\}}{\{Cu^{2+}\}\{NH_3\}^2}$$

$$\beta_2 = \frac{\{Cu(NH_3)_2^{\;2+}\}}{\{Cu^{2+}\}\{NH_3\}^2} = \frac{10^{-4.16}}{(10^{-6.07})(10^{-4.40})^2} = 10^{10.71}$$

# Aqueous Chemistry of Metals

***Example. Find pH of a solution of $3x10^{-4}$ $CuCl_2$ + $10^{-3}$ $NH_4Cl$ + $5x10^{-4}$ $Ca(OH)_2$, given following log C – pH diagram.***



***$3x10^{-4}$ $CuCl_2$ + $10^{-3}$ $NH_4Cl$ + $5x10^{-4}$ $Ca(OH)_2$***

*Equil. Species:* $H^+$, $OH^-$, $NH_4^+$, $NH_3$, $Cu(OH)_y^{2-y}$, $Cu_2(OH)_2^o$, $Cu(NH_3)_x^{2+}$, $CuCl^+$, $Ca^{2+}$, $Cl^-$

| | $H_2O$ | $H^+$ | $Cu^{2+}$ | $NH_3$ | $Ca^{2+}$ | $Cl^-$ |
|---|---|---|---|---|---|---|
| $H_2O$ | 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 |
| $Cu(OH)_2^o$ | 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 |
| $Cu_2(OH)_2^{2+}$ | 2 | –2 | 2 | 0 | 0 | 0 |
| $Cu(NH_3)^{2+}$ | 0 | 0 | 1 | 1 | 0 | 0 |
| $Cu(NH_3)_2^{2+}$ | 0 | 0 | 1 | 2 | 0 | 0 |
| $Cu(NH_3)_3^{2+}$ | 0 | 0 | 1 | 3 | 0 | 0 |
| $Cu(NH_3)_4^{2+}$ | 0 | 0 | 1 | 4 | 0 | 0 |
| $CuCl^+$ | 0 | 0 | 1 | 0 | 0 | 1 |

***$3x10^{-4}$ $CuCl_2$ + $10^{-3}$ $NH_4Cl$ + $5x10^{-4}$ $Ca(OH)_2$***

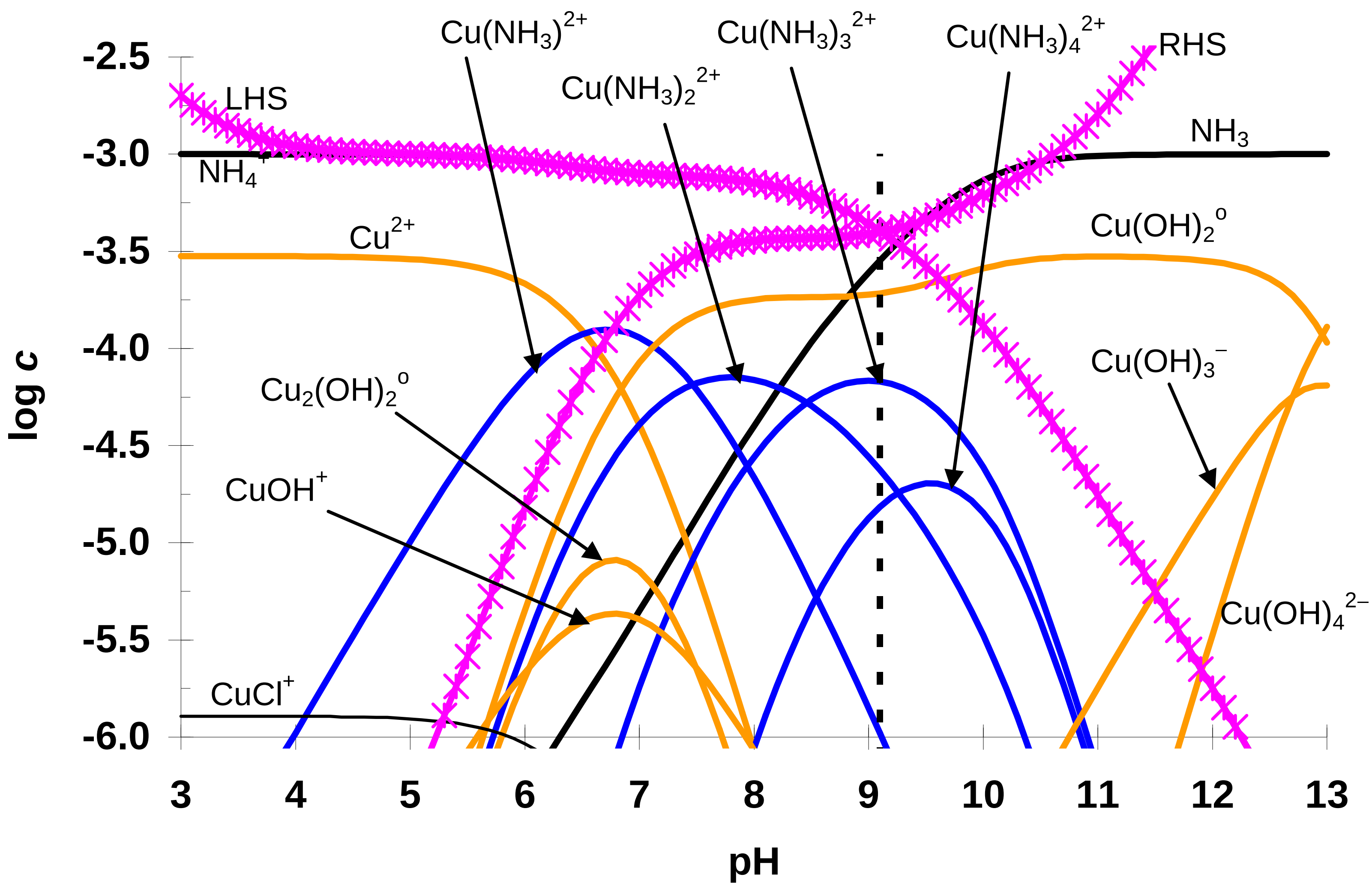
*Input Species:* $NH_4Cl$, $CuCl_2$, $Ca(OH)_2$

| | $H_2O$ | $H^+$ | $Cu^{2+}$ | $NH_3$ | $Ca^{2+}$ | $Cl^-$ | Conc'n |
|---|---|---|---|---|---|---|---|
| $NH_4Cl$ | 0 | 1 | 0 | 1 | 0 | 1 | $10^{-3}$ |
| $CuCl_2$ | 0 | 0 | 1 | 0 | 0 | 2 | $3x10^{-4}$ |
| $Ca(OH)_2$ | 2 | –2 | 0 | 0 | 1 | 0 | $5x10^{-4}$ |

$$1\left(10^{-3}\right)+0-2\left(5x10^{-4}\right)=\left[H^+\right]-\left[OH^-\right]+\left[NH_4^+\right]-\left[CuOH^+\right]-2\left[Cu\left(OH\right)_2^o\right]$$
$$-3\left[Cu\left(OH\right)_3^-\right]-4\left[Cu\left(OH\right)_4^{2-}\right]-2\left[Cu_2\left(OH\right)_2^{\;2+}\right]$$

$$\left[H^+\right]+\left[NH_4^+\right]=\left[OH^-\right]+\left[CuOH^+\right]+2\left[Cu\left(OH\right)_2^o\right]+3\left[Cu\left(OH\right)_3^-\right]$$
$$+4\left[Cu\left(OH\right)_4^{2-}\right]+2\left[Cu_2\left(OH\right)_2^{\;2+}\right]$$

# $3x10^{-4}$ $CuCl_2$ + $10^{-3}$ $NH_4Cl$ + $5x10^{-4}$ $Ca(OH)_2$



# 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, $a_i$=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 *

$$\mathrm{Cu(OH)_2}(s) \leftrightarrow \mathrm{Cu^{2+}} + 2\mathrm{OH^-} \qquad K_{s0}$$

$$\mathrm{Cu(OH)_2}(s) + \mathrm{OH^-} \leftrightarrow \mathrm{Cu(OH)_3}^{2+} \qquad K_{s3}$$

$$\mathrm{Cu(OH)_2}(s) + \mathrm{H_2O} \leftrightarrow \mathrm{Cu(OH)_3}^{-} + \mathrm{H^+} \qquad {}^{*}K_{s3}$$

# 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 by 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 $c$ – pH diagrams

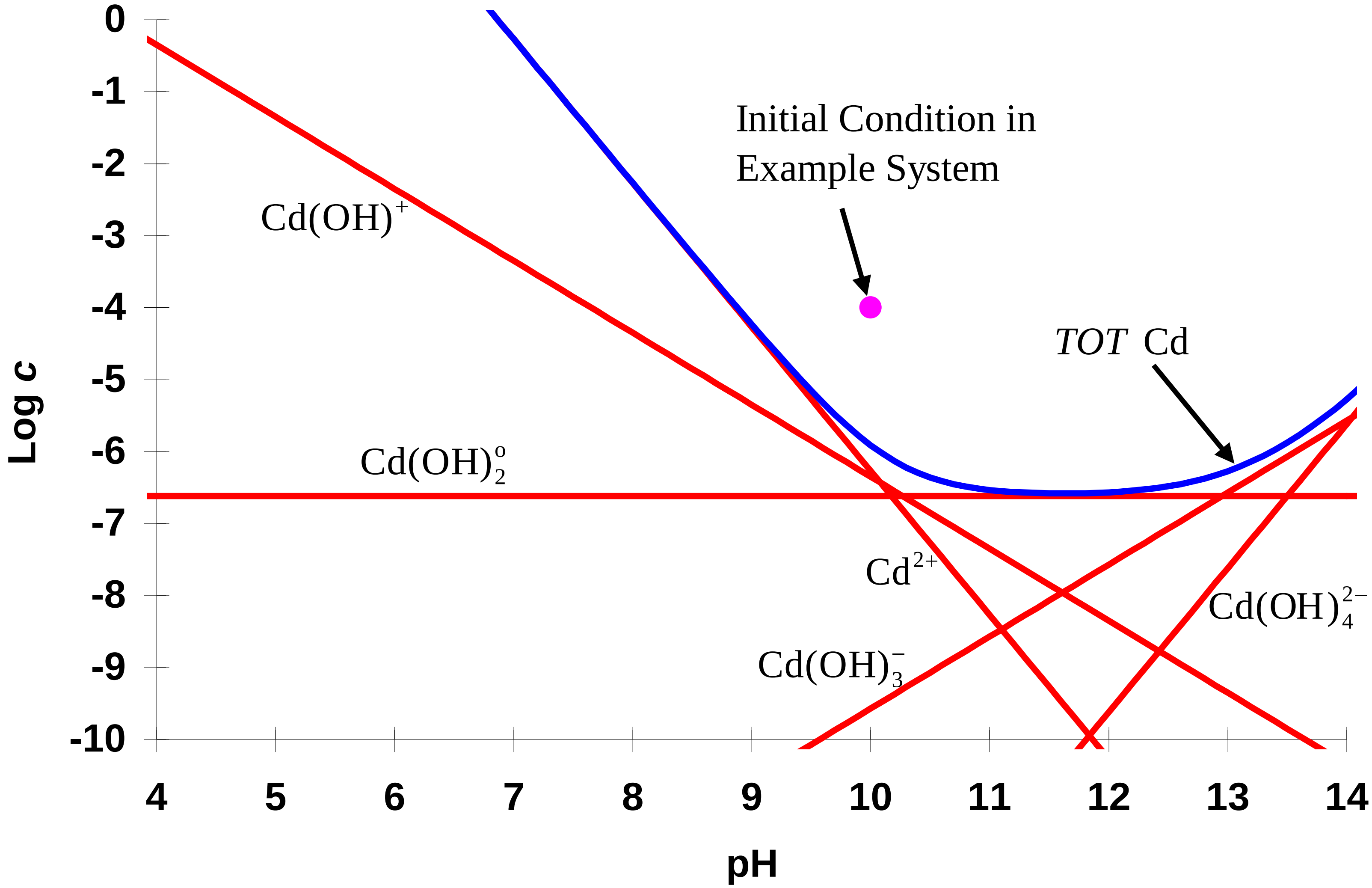
# Equilibrium with Metal Hydroxides

$$\mathrm{Cu(OH)_2}(s) \leftrightarrow \mathrm{Cu(OH)_2}^{\mathrm{o}} \qquad K_{s2} = \frac{\left\{\mathrm{Cu(OH)_2}^{\mathrm{o}}\right\}}{\left\{\mathrm{Cu(OH)_2}(s)\right\}} = \left\{\mathrm{Cu(OH)_2}^{\mathrm{o}}\right\}$$

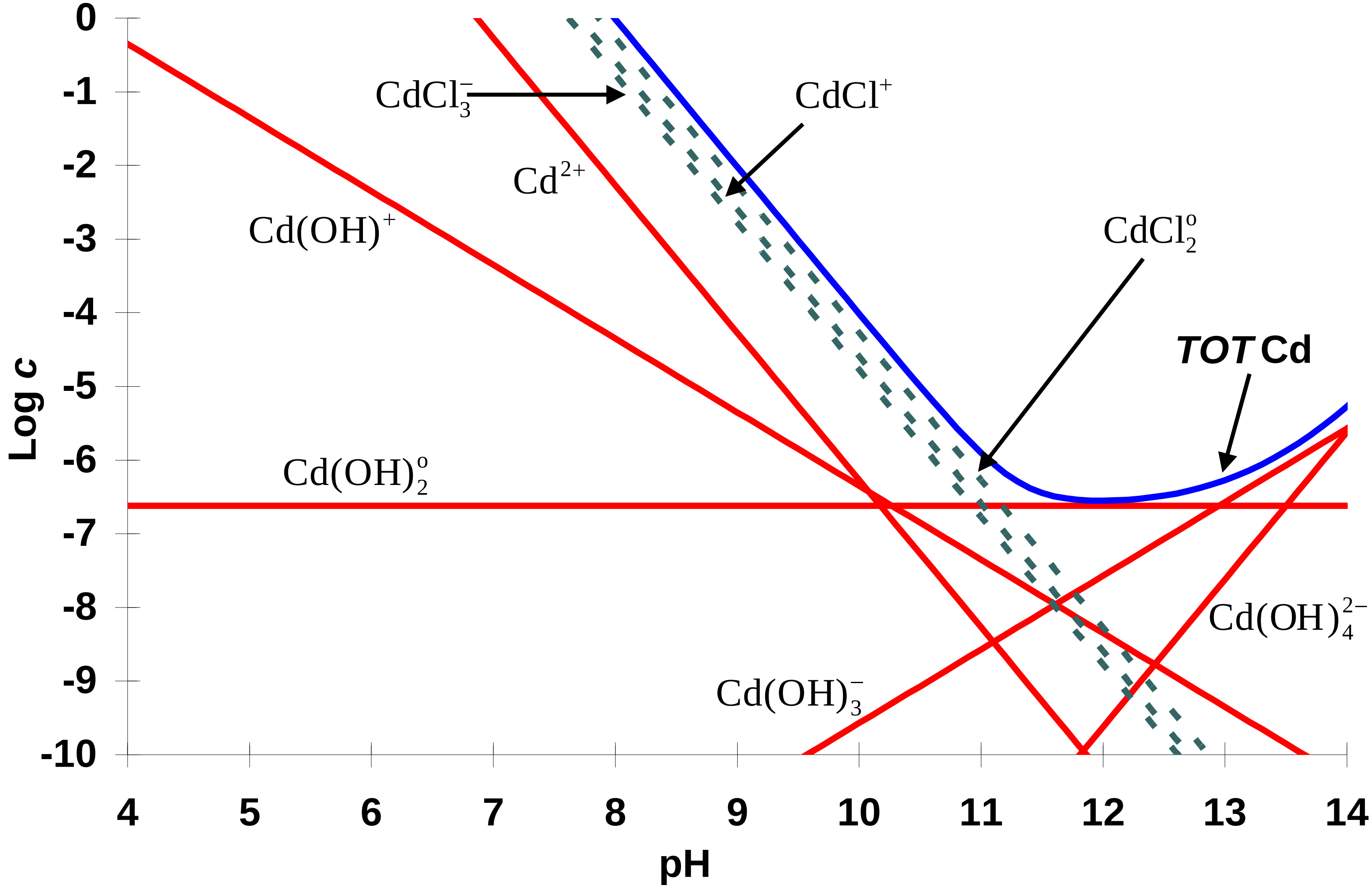
$$\mathrm{Cu(OH)_2}(s) \leftrightarrow \mathrm{Cu}^{2+} + 2\mathrm{OH}^- \qquad K_{s0} = \frac{\left\{\mathrm{Cu}^{2+}\right\}\left\{\mathrm{OH}^-\right\}^2}{\left\{\mathrm{Cu(OH)_2}(s)\right\}} = \left\{\mathrm{Cu}^{2+}\right\}\left\{\mathrm{OH}^-\right\}^2$$

$$\mathrm{Cu(OH)_2}(s) + \mathrm{OH}^- \leftrightarrow \mathrm{Cu(OH)_3}^- \qquad K_{s3} = \frac{\left\{\mathrm{Cu(OH)_3}^-\right\}}{\left\{\mathrm{Cu(OH)_2}(s)\right\}\left\{\mathrm{OH}^-\right\}} = \frac{\left\{\mathrm{Cu(OH)_3}^-\right\}}{\left\{\mathrm{OH}^-\right\}}$$

# Equilibrium with Metal Hydroxides



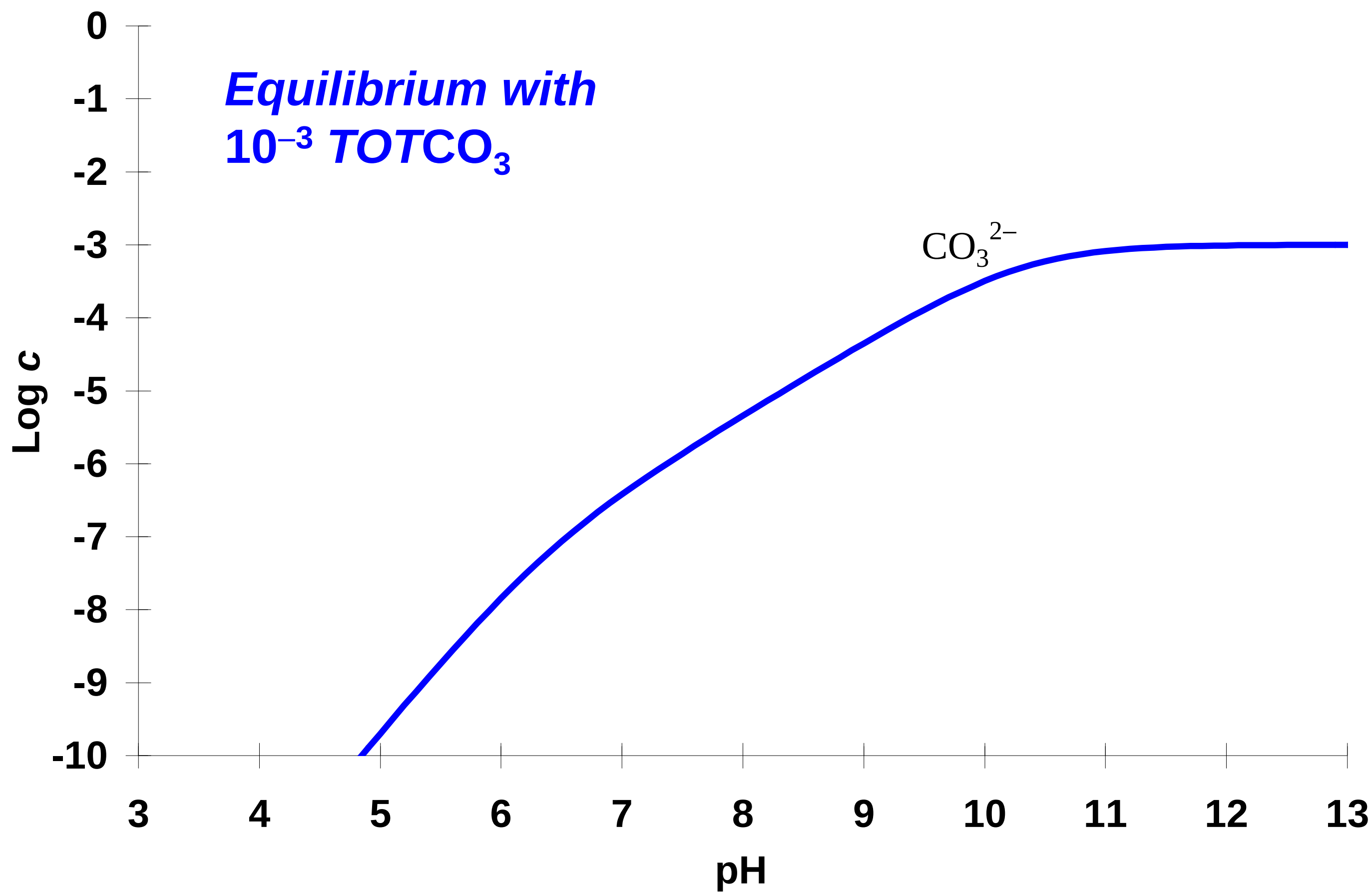
# Equilibrium with Metal Hydroxides



# Equilibrium with Metal Carbonates

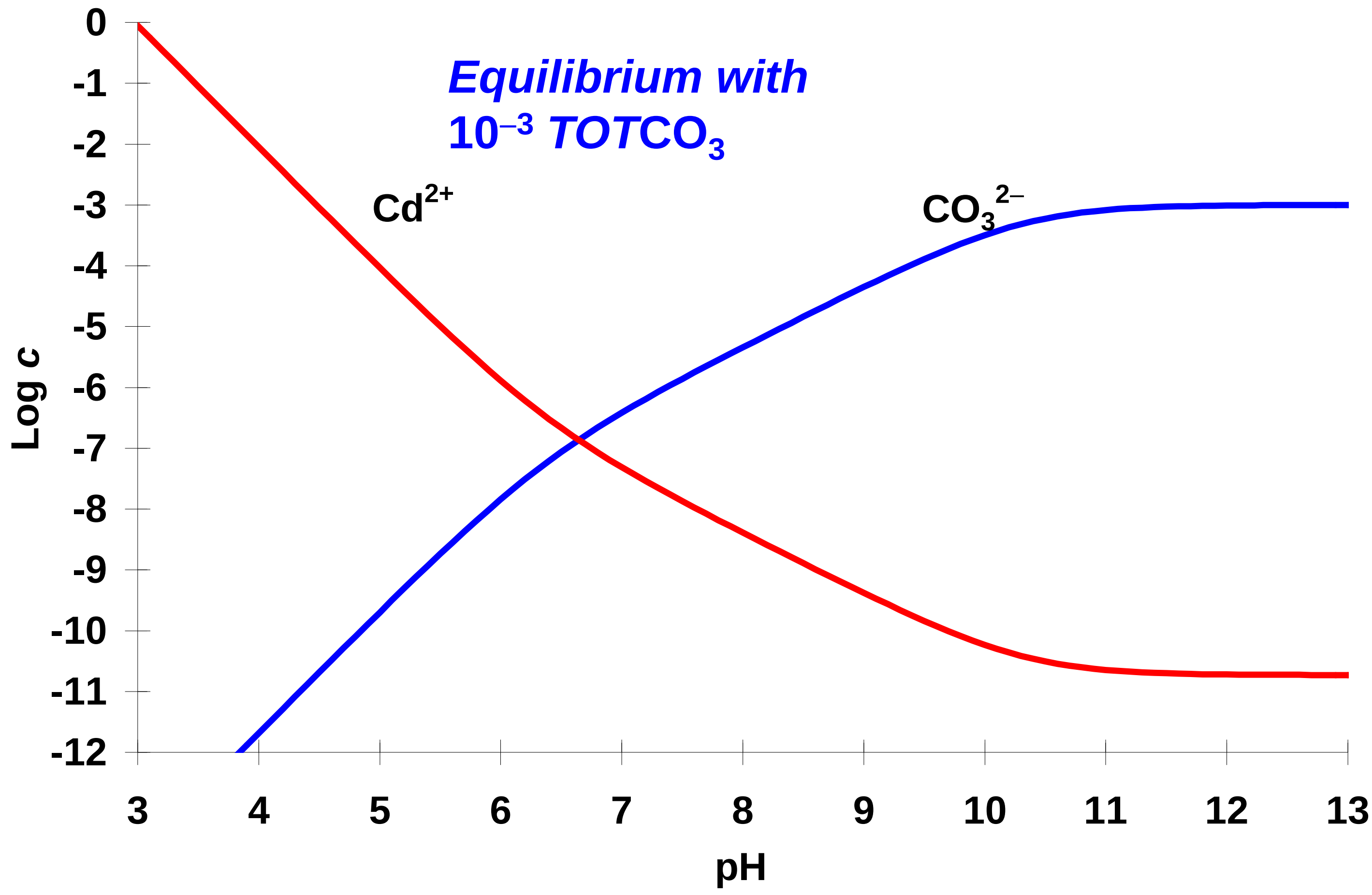
$$CdCO_3(s) \leftrightarrow Cd^{2+} + CO_3^{2-}$$

$$K_{s0} = \frac{\{Cd^{2+}\}\{CO_3^{2-}\}}{\{CdCO_3(s)\}} = \{Cd^{2+}\}\{CO_3^{2-}\}$$



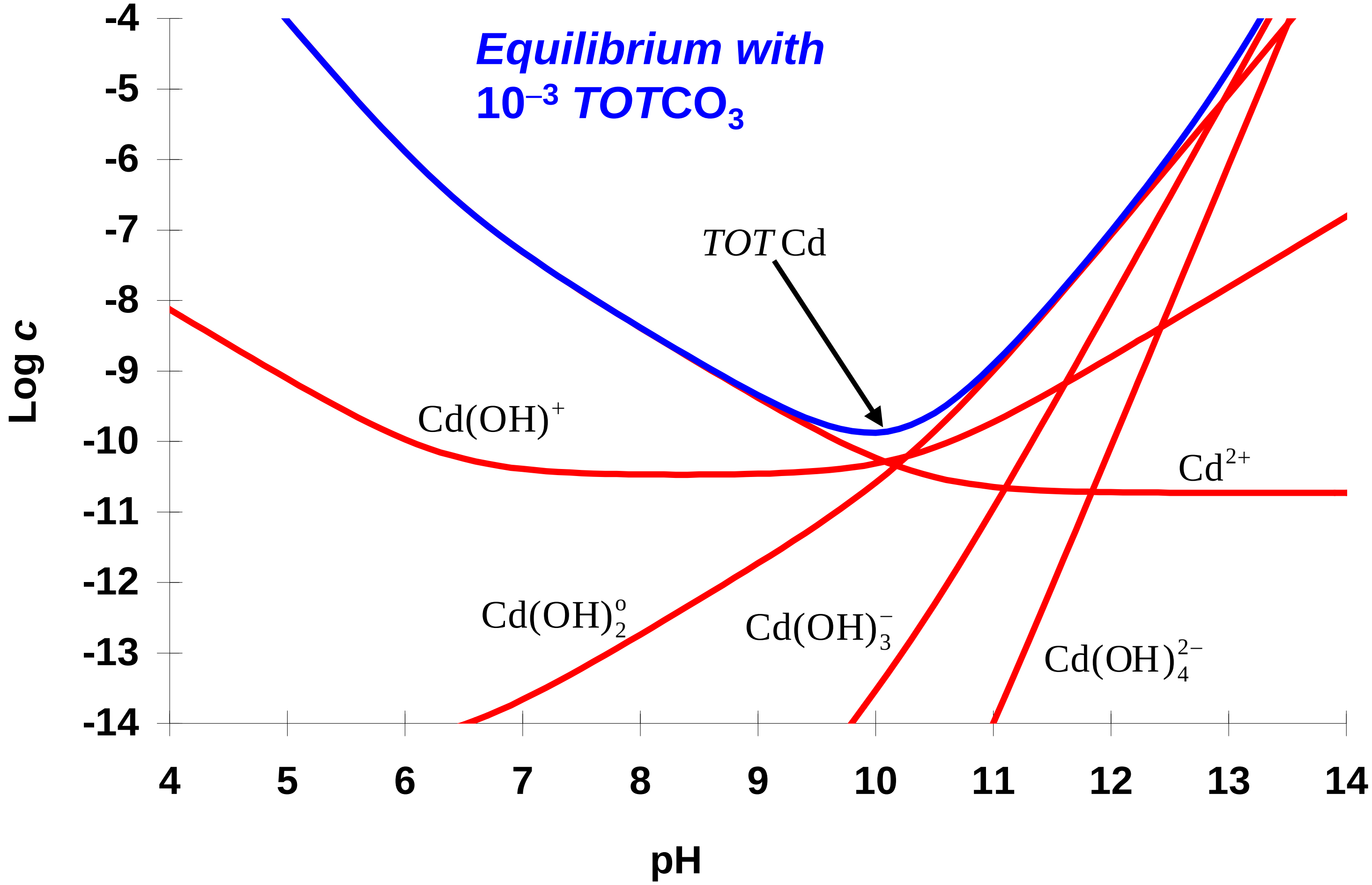
# Equilibrium with Metal Carbonates

$$CdCO_3(s) \leftrightarrow Cd^{2+} + CO_3^{2-} \qquad K_{s0} = \frac{\{Cd^{2+}\}\{CO_3^{2-}\}}{\{CdCO_3(s)\}} = \{Cd^{2+}\}\{CO_3^{2-}\}$$



# Equilibrium with Metal Carbonates

$$Cd^{2+} + iOH^{-} \leftrightarrow Cd(OH)_i^{2-i} \qquad K_{s0} = \frac{\{Cd(OH)_i^{2-i}\}}{\{Cd^{2+}\}\{OH^{-}\}^i}$$



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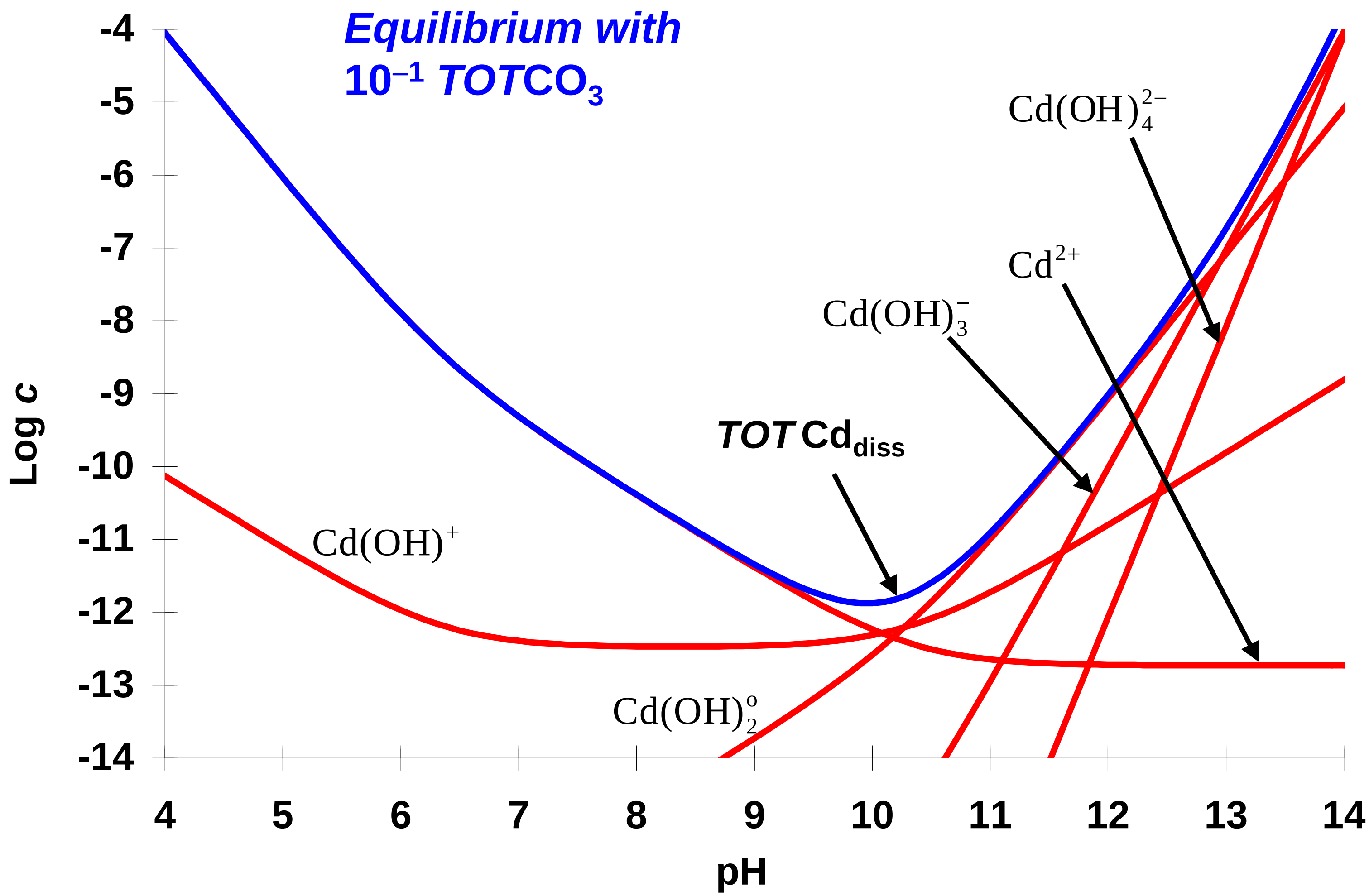

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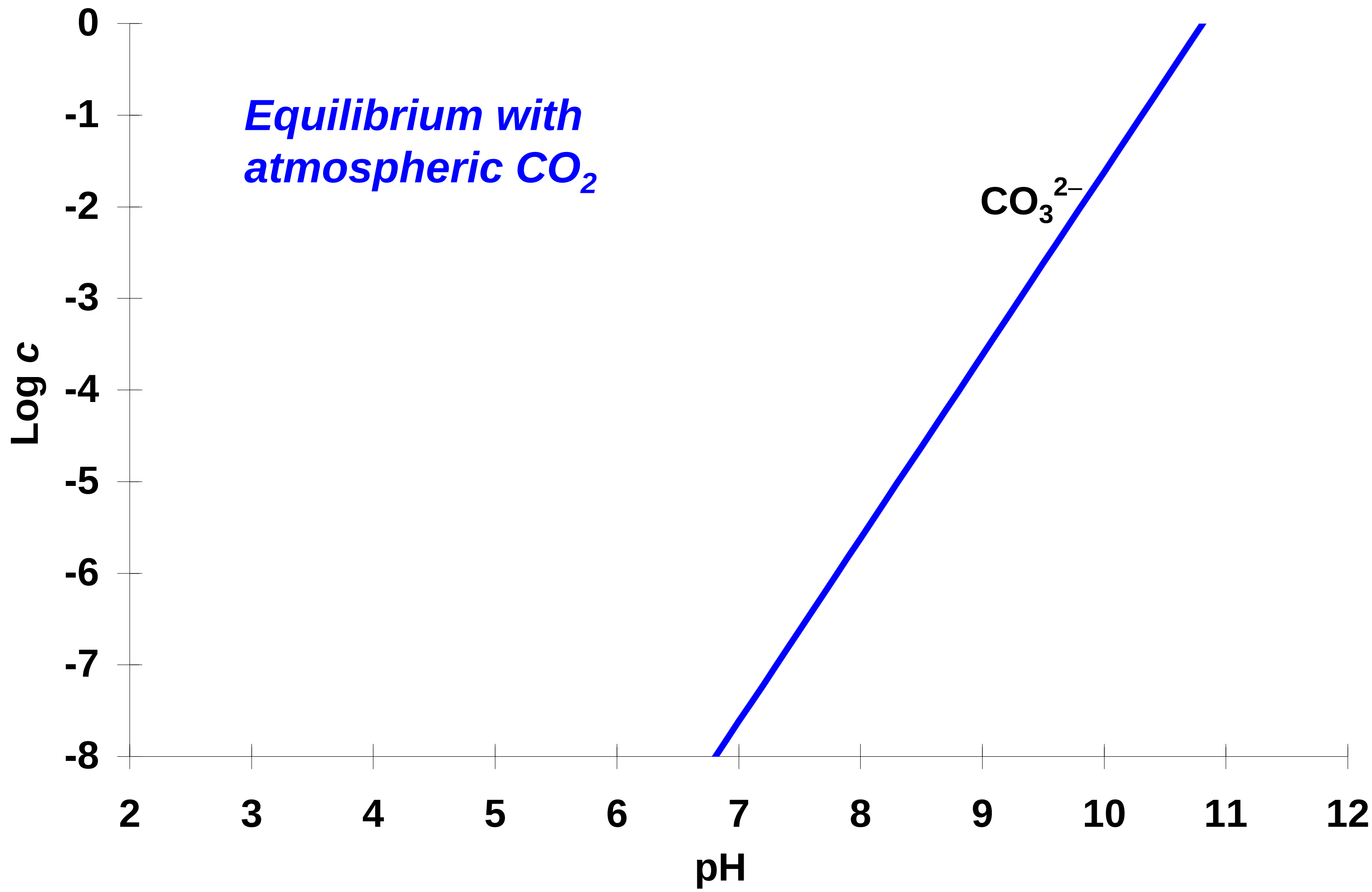

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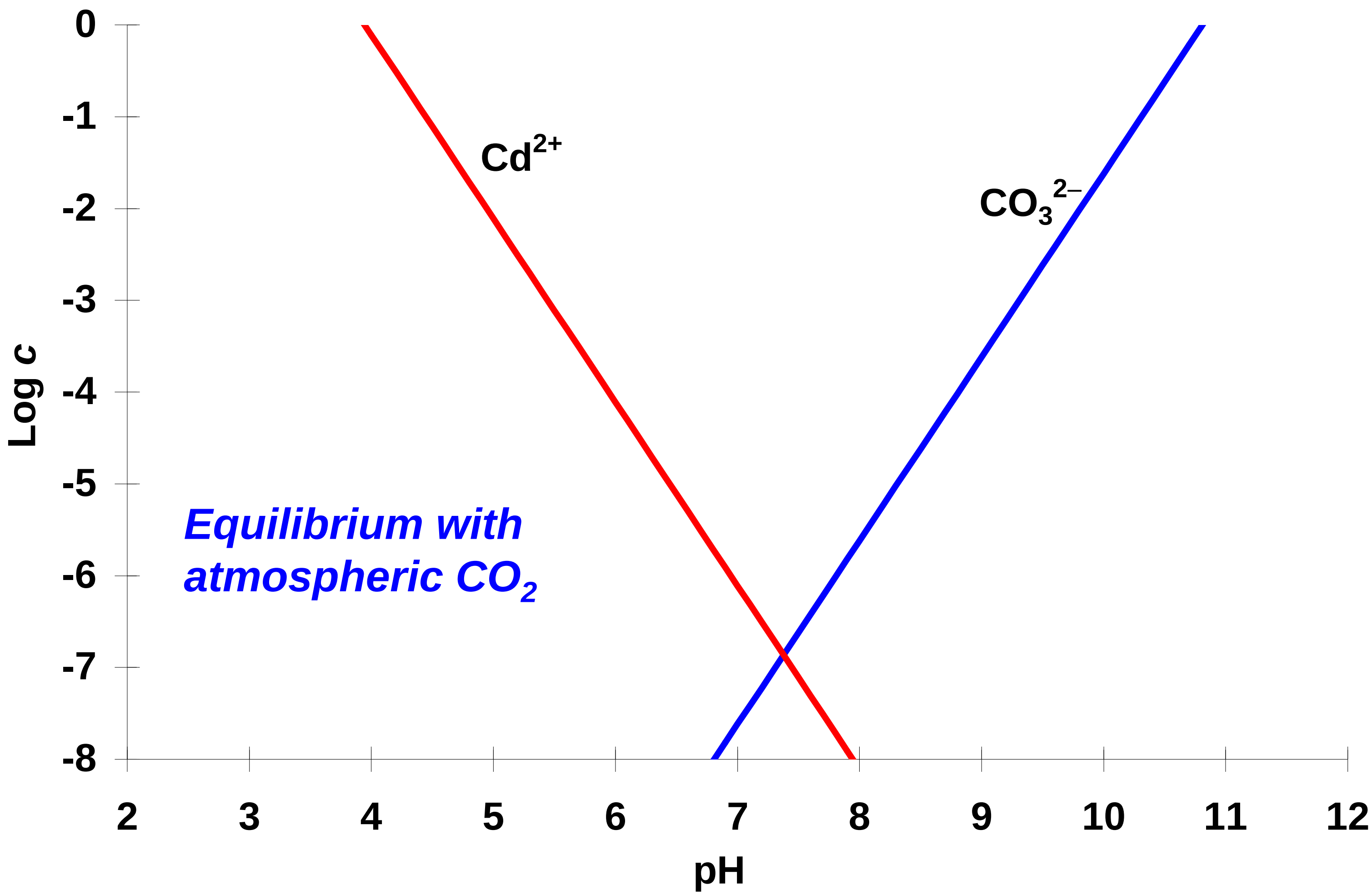
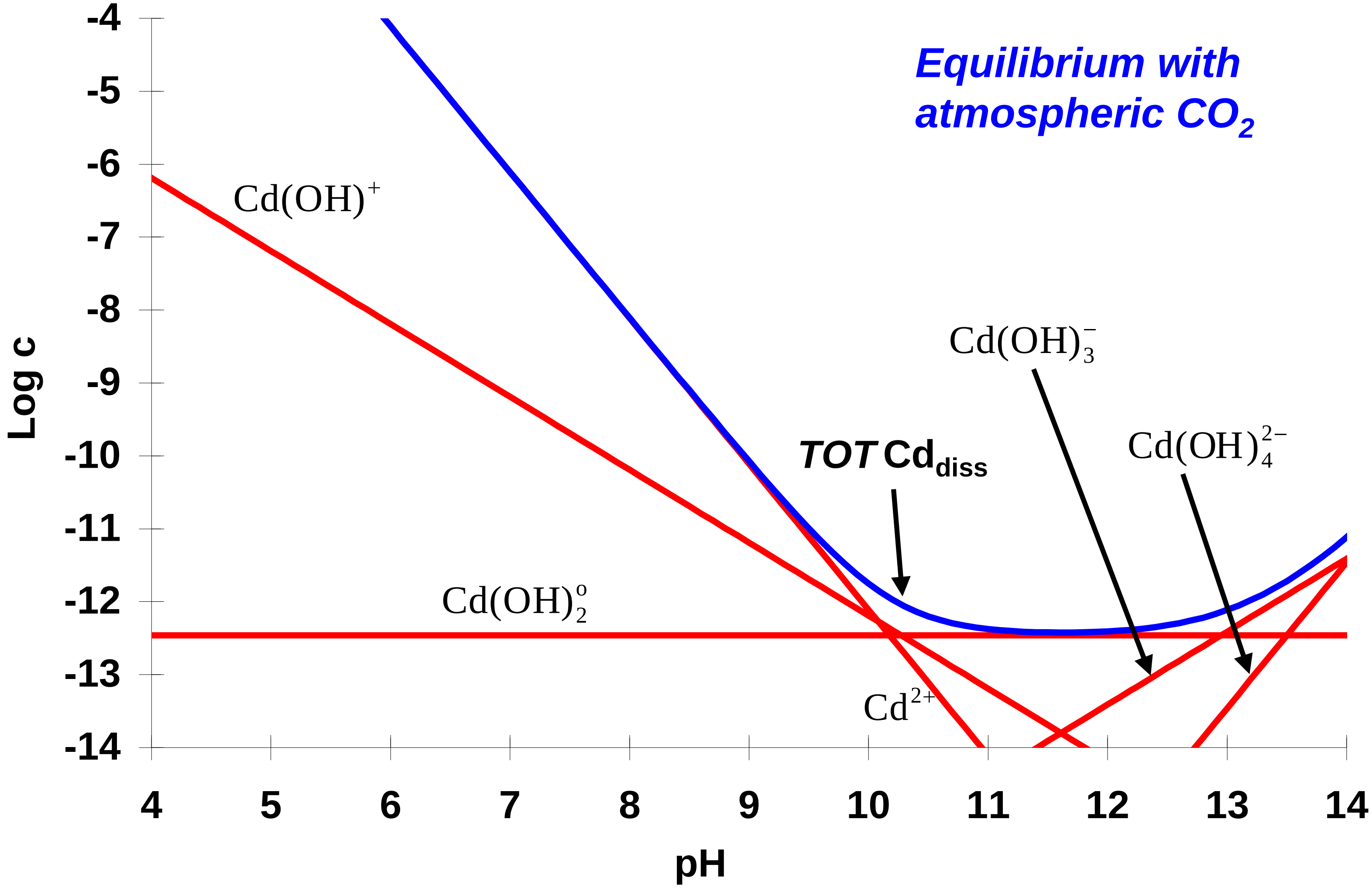


# Equilibrium with Metal Carbonates



# Equilibrium with Metal Solids

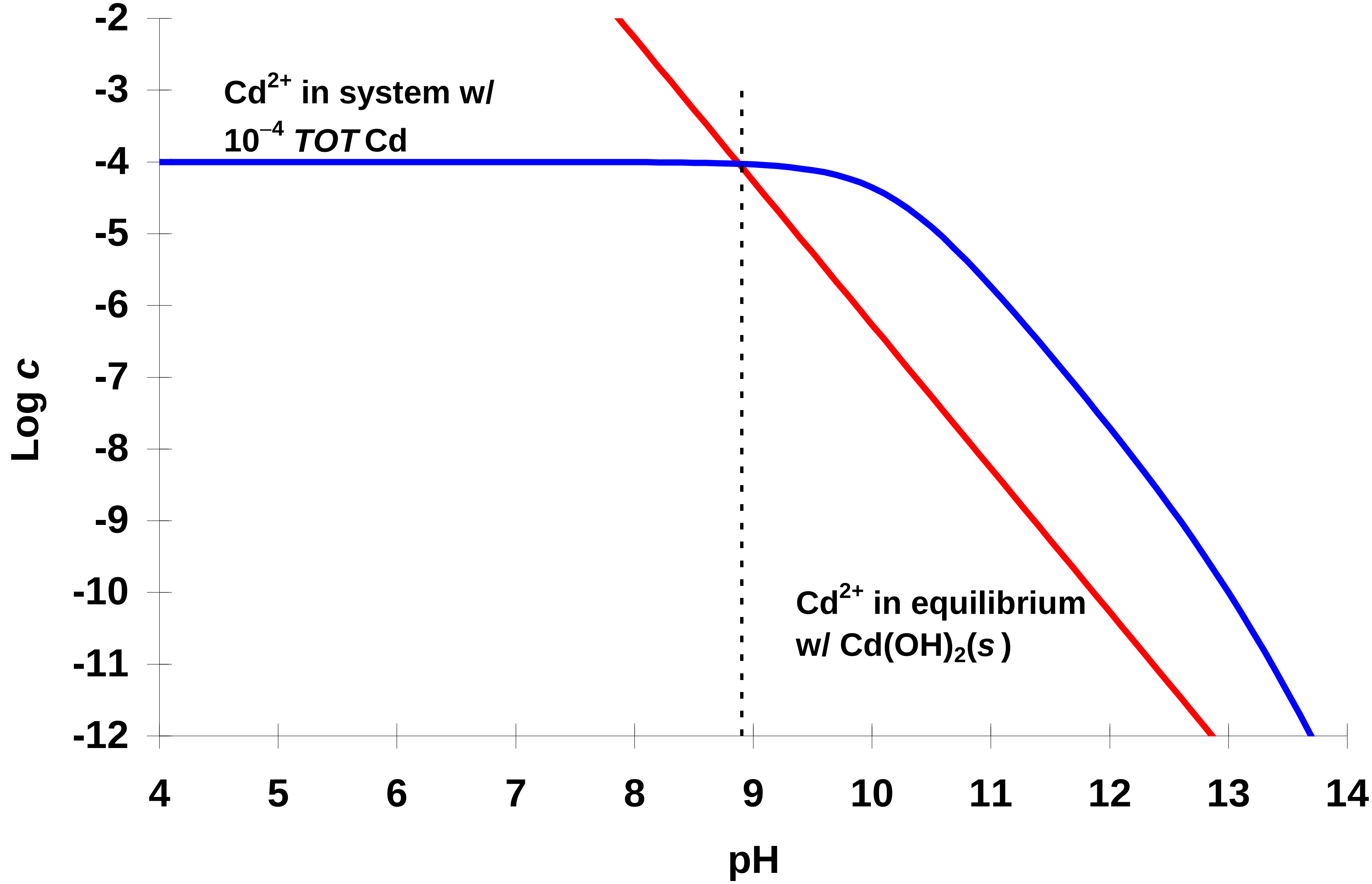
*Under what conditions will a solid form? Dissolve?*

*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



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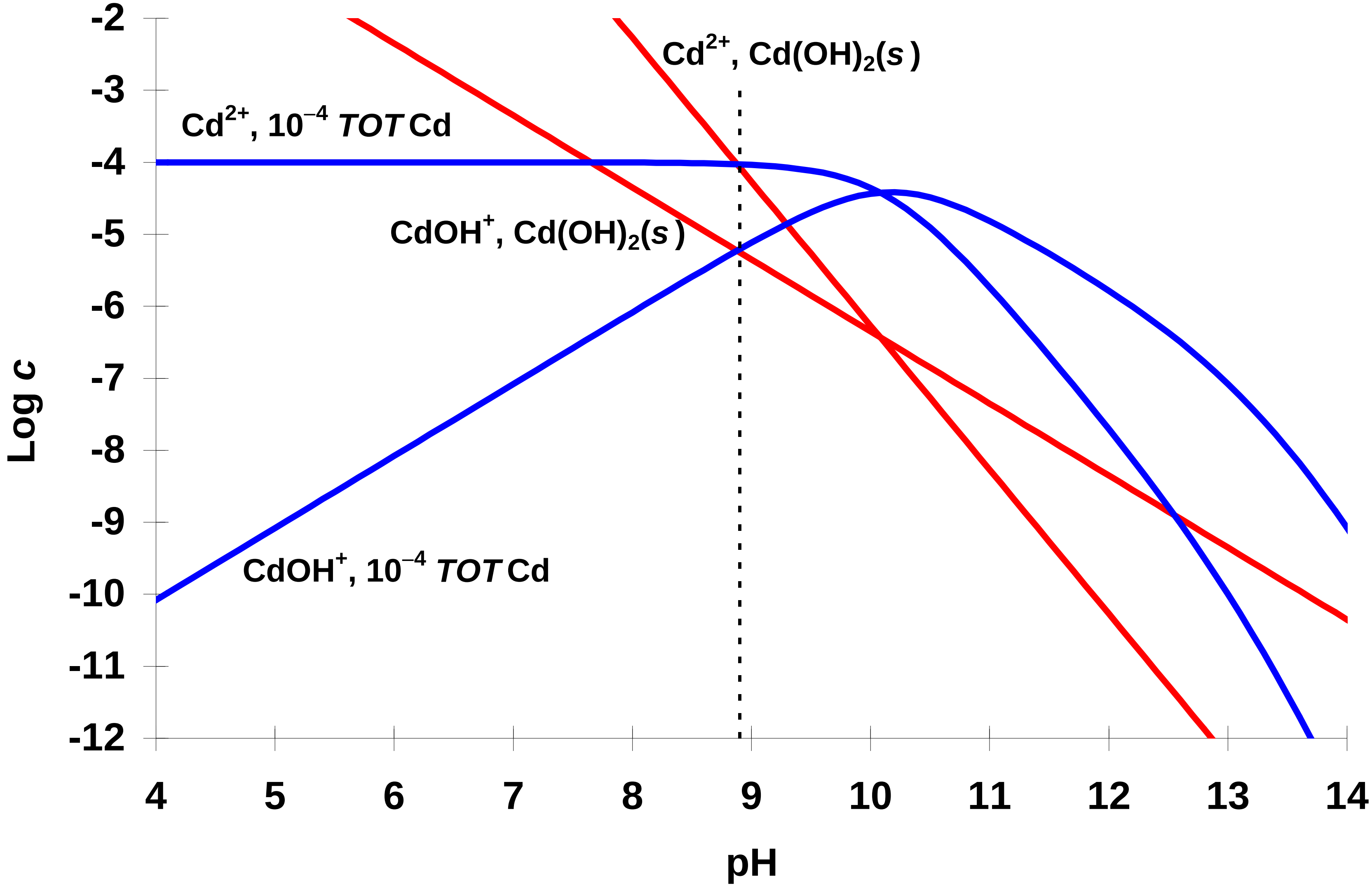

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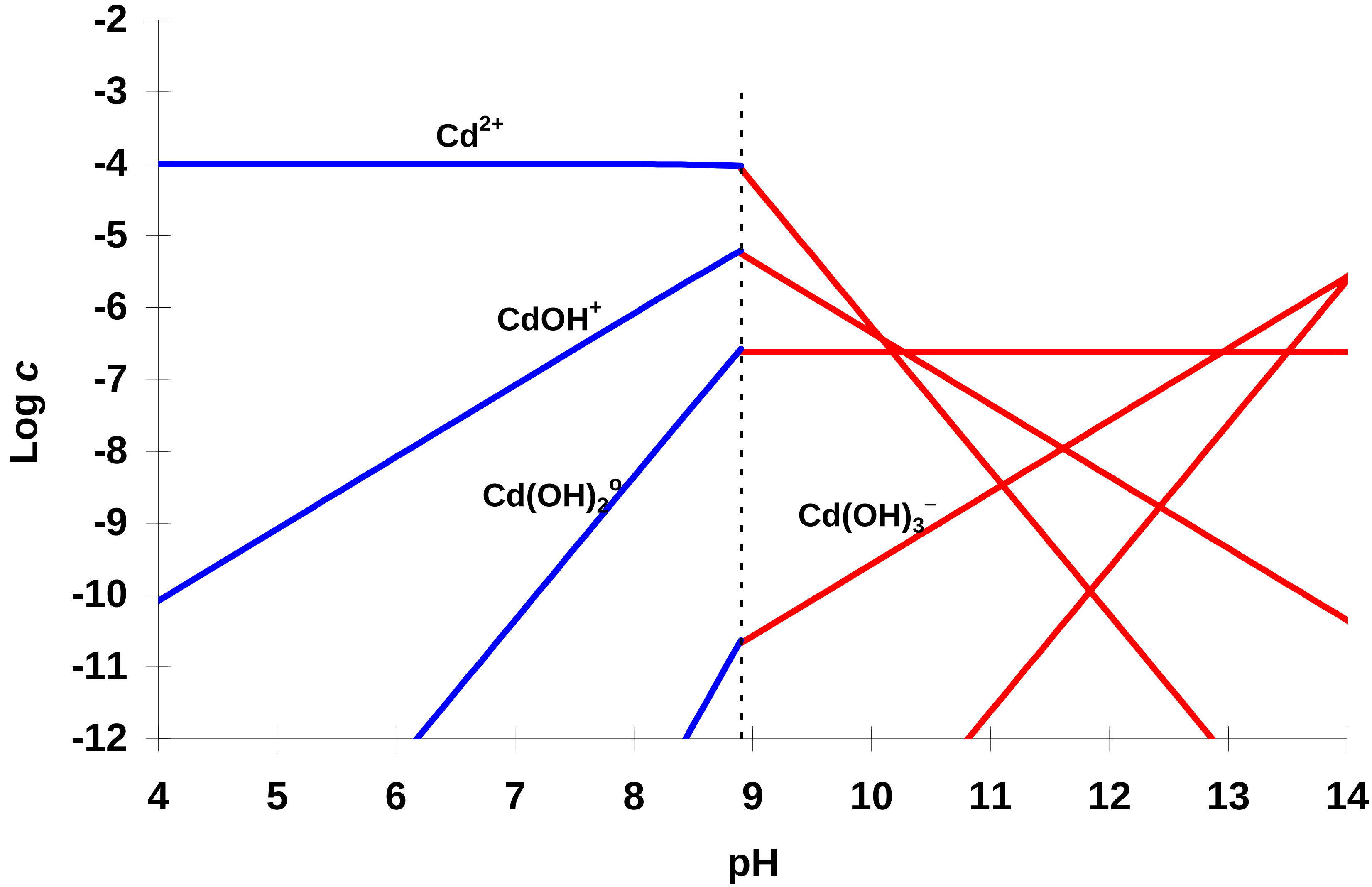

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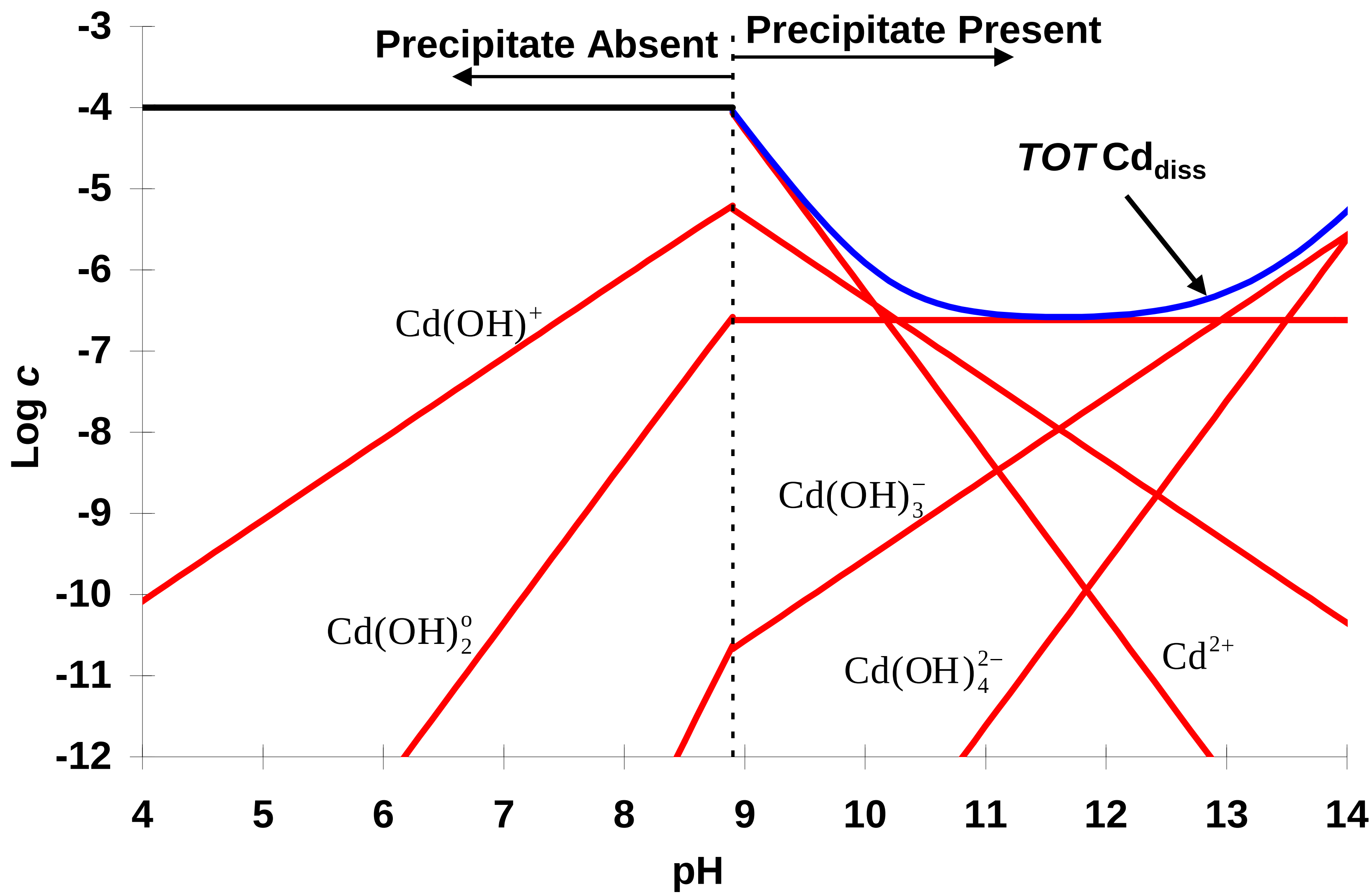
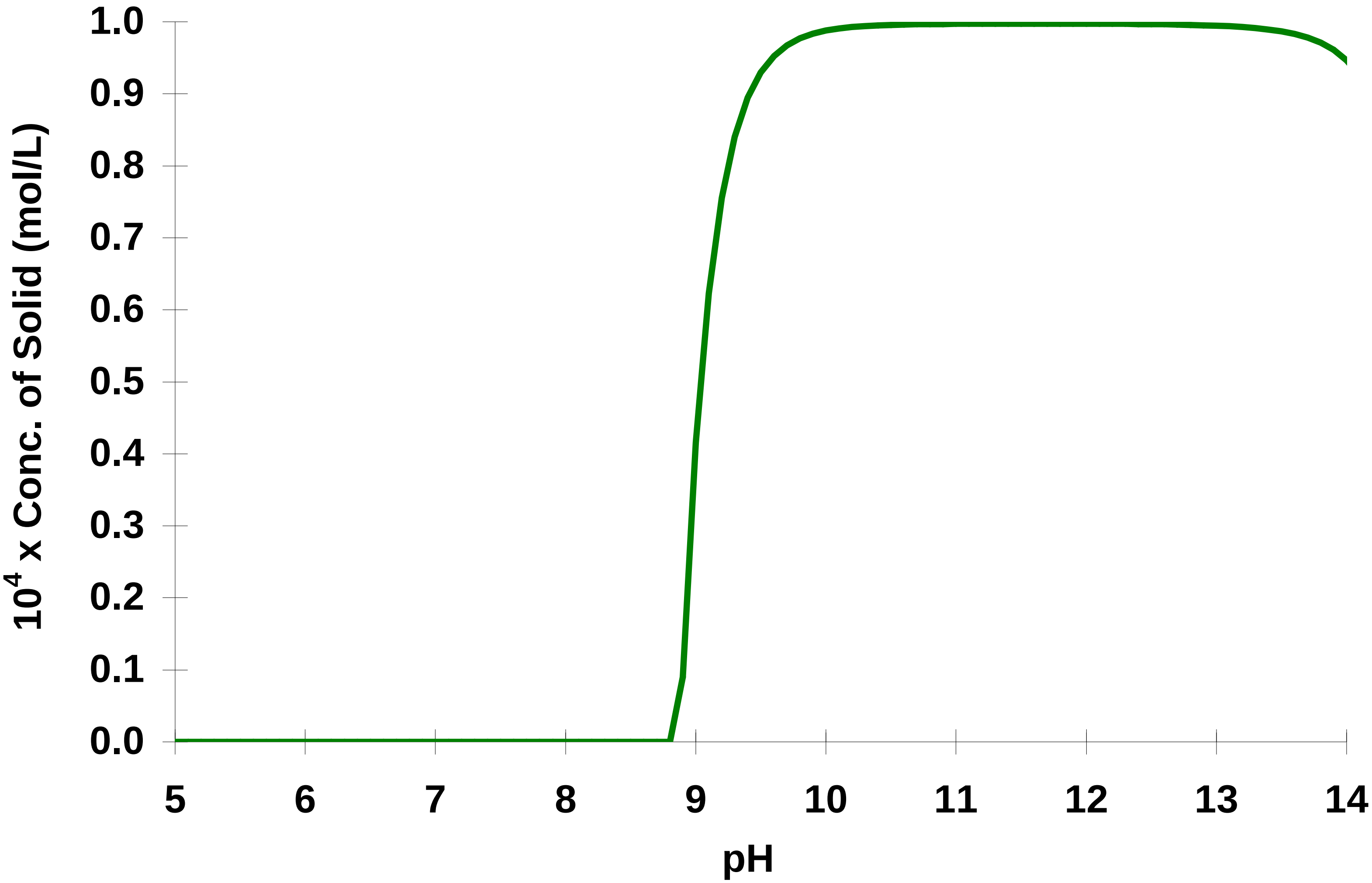
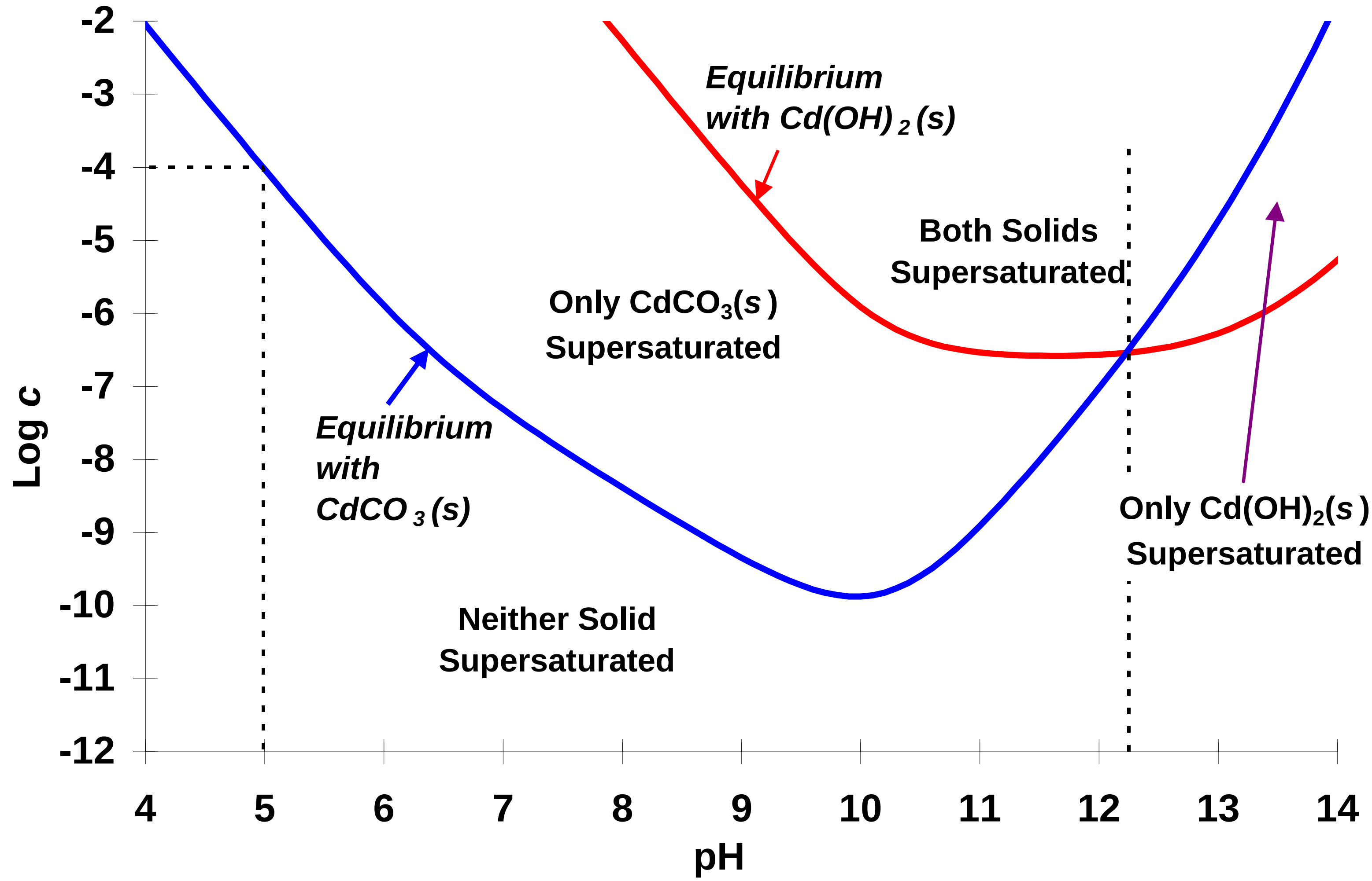


# How Much Solid Will Form?



# Systems with Two Possible Precipitates



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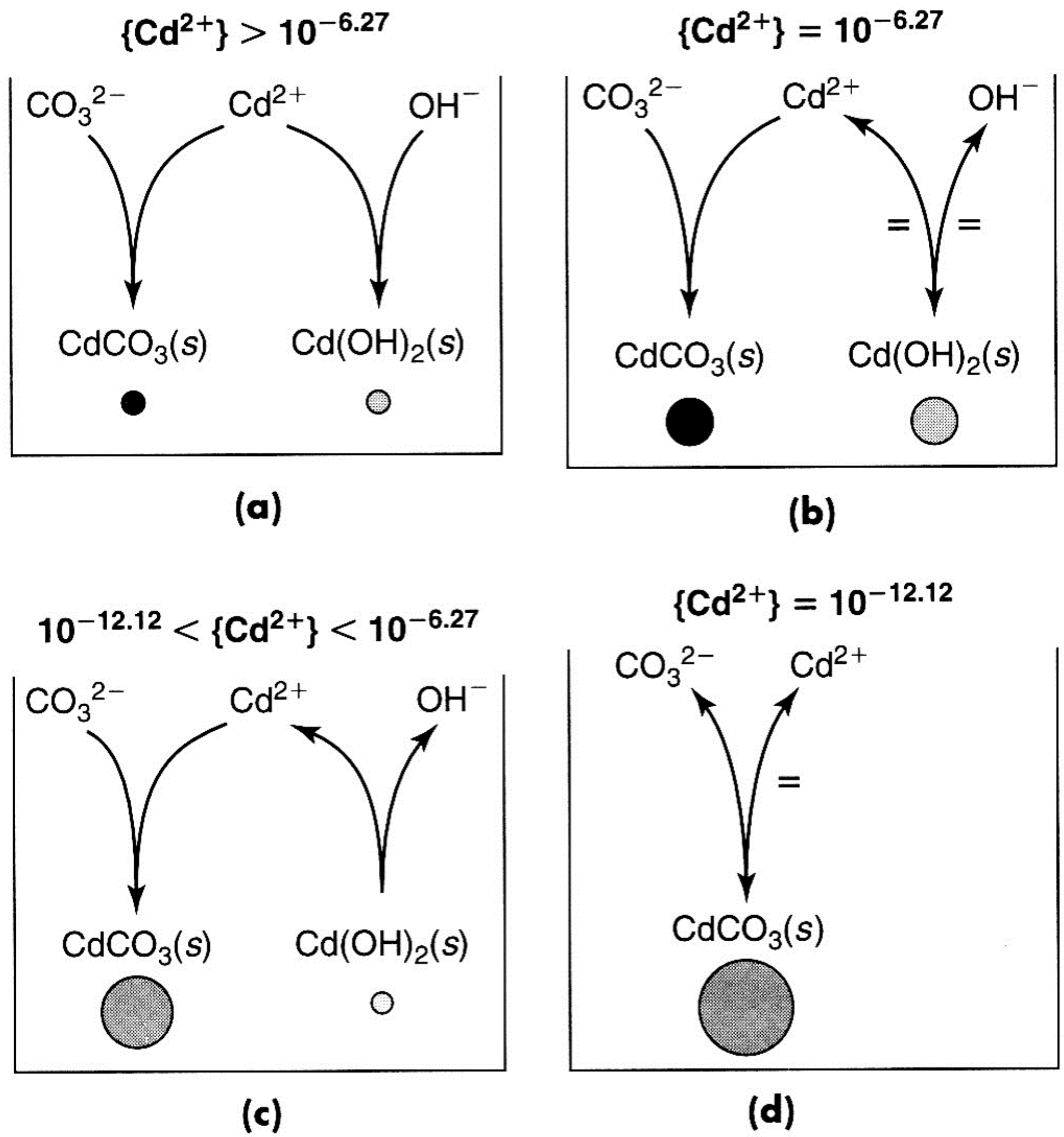

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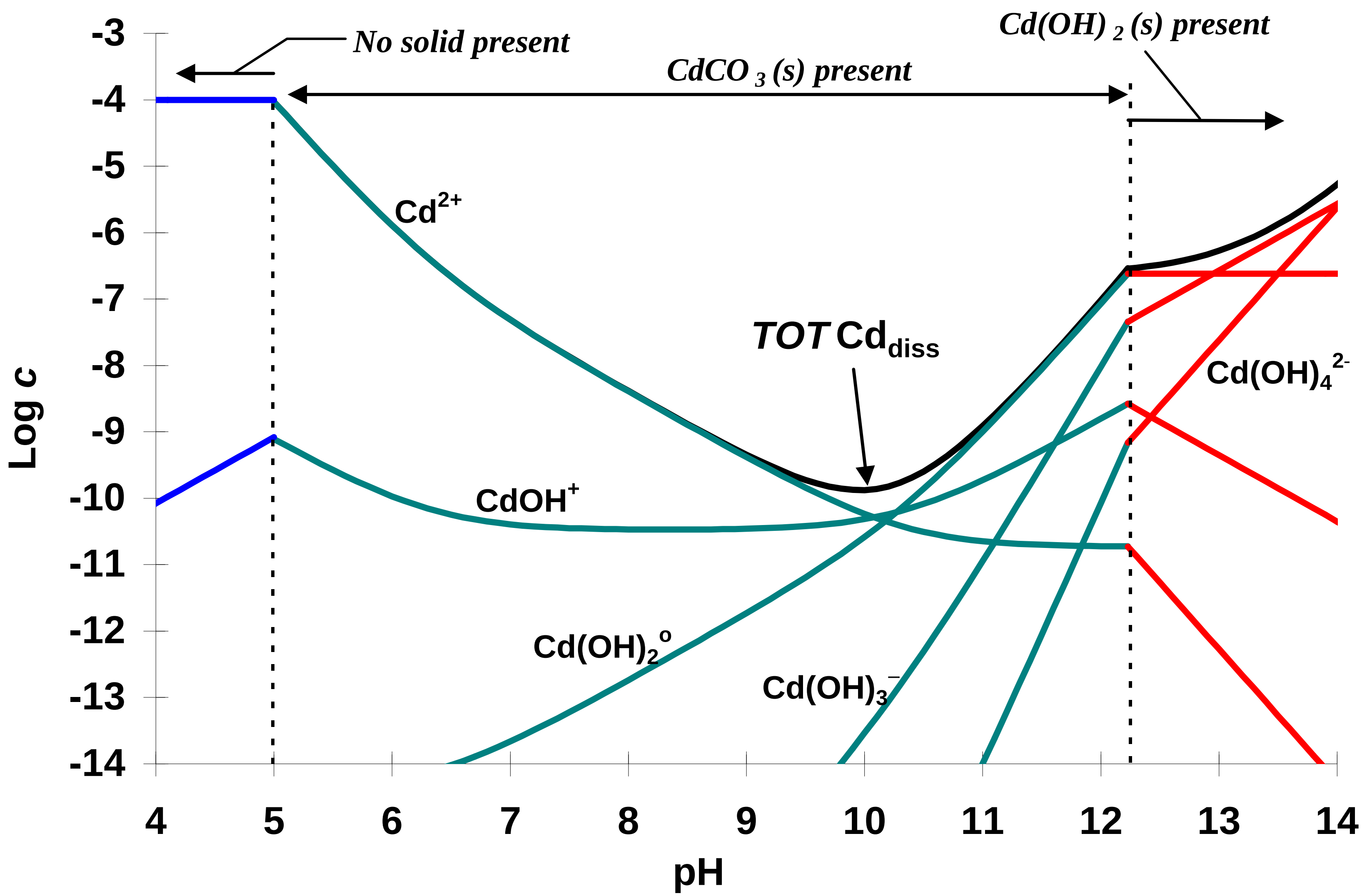
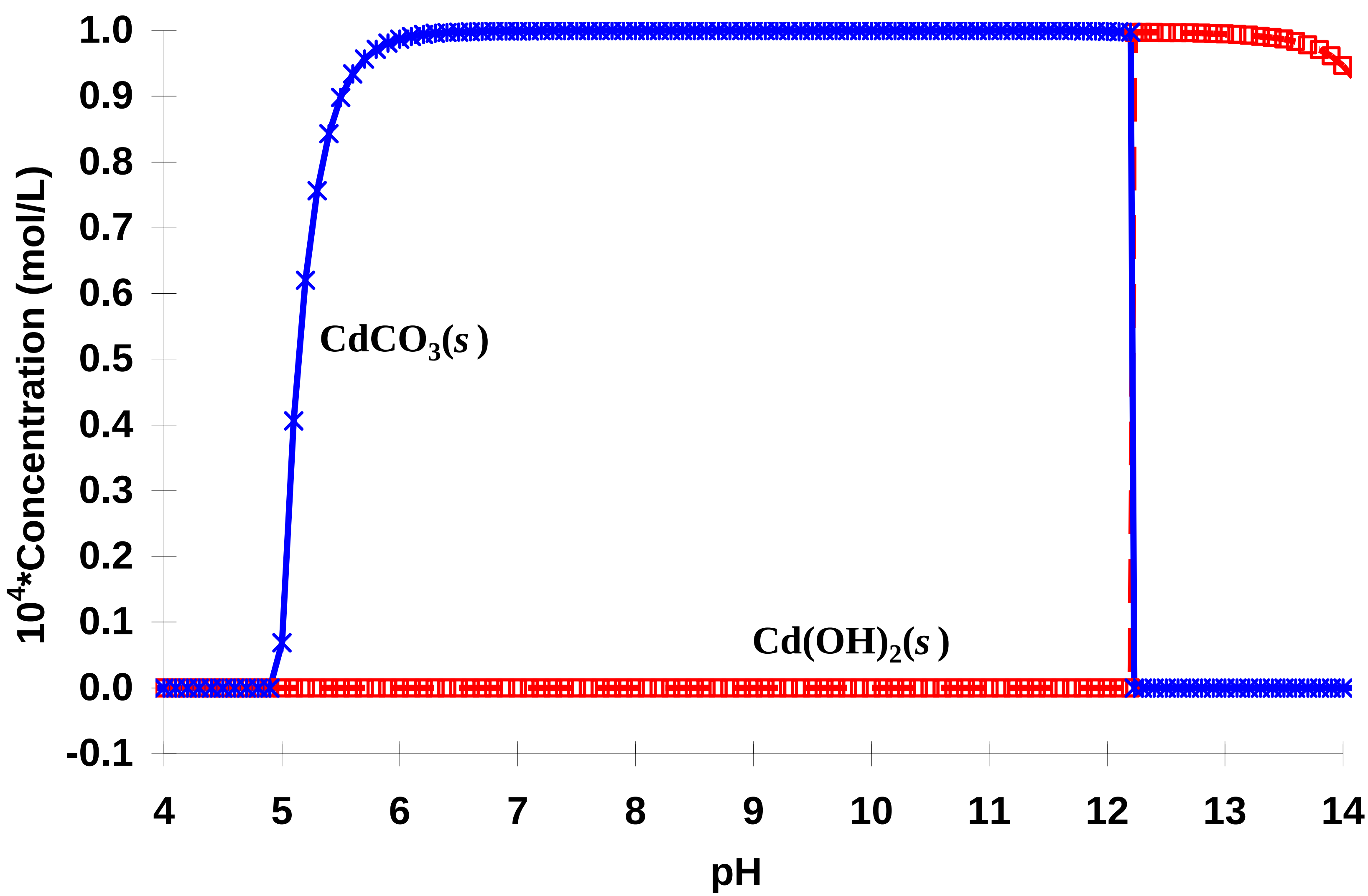


# Systems with Two Possible Precipitates



# Simultaneous Equilibrium with Two Solids

$$Cu(OH)_2(s) \leftrightarrow Cu^{2+} + 2OH^- \qquad K_{s0,Cu(OH)_2(s)} = \{Cu^{2+}\}\{OH^-\}^2$$

$$Cu^{2+} + CO_3^{2-} \leftrightarrow CuCO_3(s) \qquad \frac{1}{K_{s0,CdCO_3(s)}} = \frac{1}{\{Cu^{2+}\}\{CO_3^{2-}\}}$$

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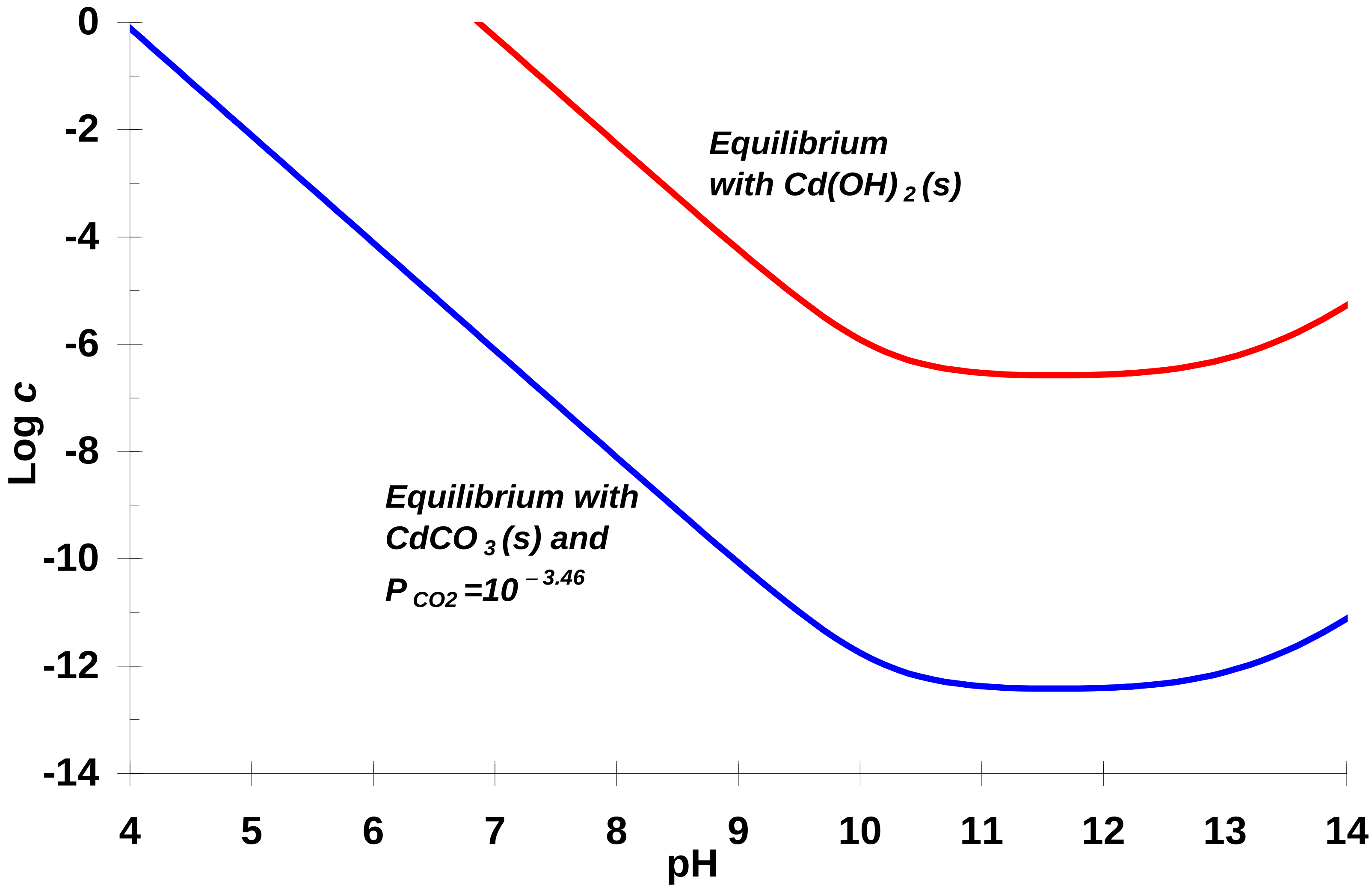
$$Cu(OH)_2(s) + CO_3^{2-} \leftrightarrow CuCO_3(s) + 2OH^-$$

$$K_{eq} = \frac{\{CuCO_3(s)\}\{OH^-\}^2}{\{Cu(OH)_2(s)\}\{CO_3^{2-}\}} = \frac{\{OH^-\}^2}{\{CO_3^{2-}\}}$$

# 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:***

$$Zn(OH)_2(am) \leftrightarrow Zn^{2+} + 2OH^- \qquad K_{s0,am} = (Zn^{2+})(OH^-)^2$$

$$Zn(OH)_2(\alpha) \leftrightarrow Zn^{2+} + 2OH^- \qquad K_{s0,\alpha} = (Zn^{2+})(OH^-)^2$$

$$Zn(OH)_2(\beta) \leftrightarrow Zn^{2+} + 2OH^- \qquad K_{s0,\beta} = (Zn^{2+})(OH^-)^2$$

$$ZnO(s) + H_2O \leftrightarrow Zn^{2+} + 2OH^- \qquad K_{s0,ZnO} = (Zn^{2+})(OH^-)^2$$

*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 $K_{si}$, no solid will be present.*

*How much solid will be present at equilibrium?*

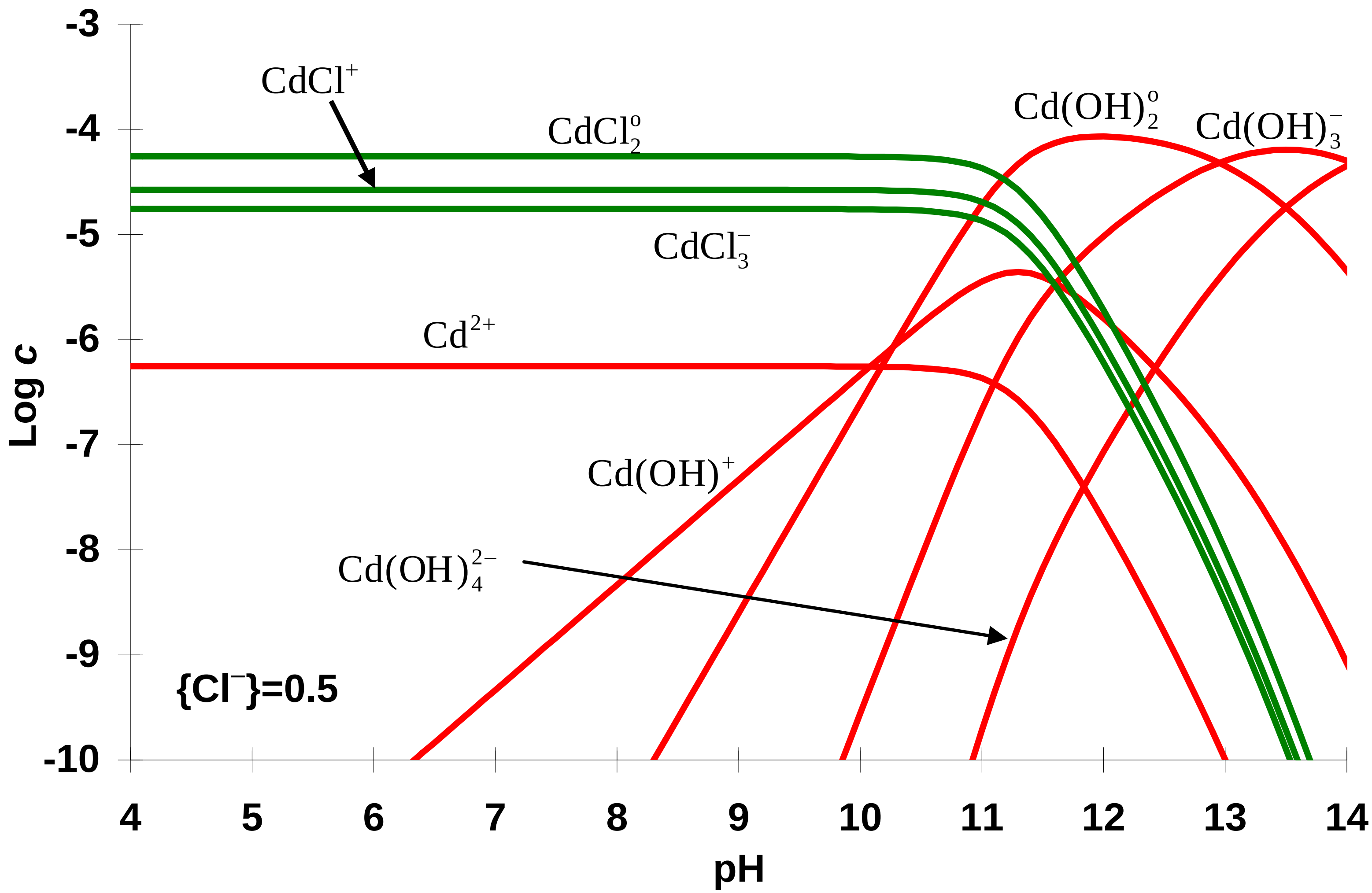
*The amount of metal that is present as a solid at equilibrium is the difference between $TOTMe_{init}$ and $TOTMe_{fin}$; the amount of solid present depends on this difference and the MW of the solid.*

*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 $TOTMe_{diss}$.*

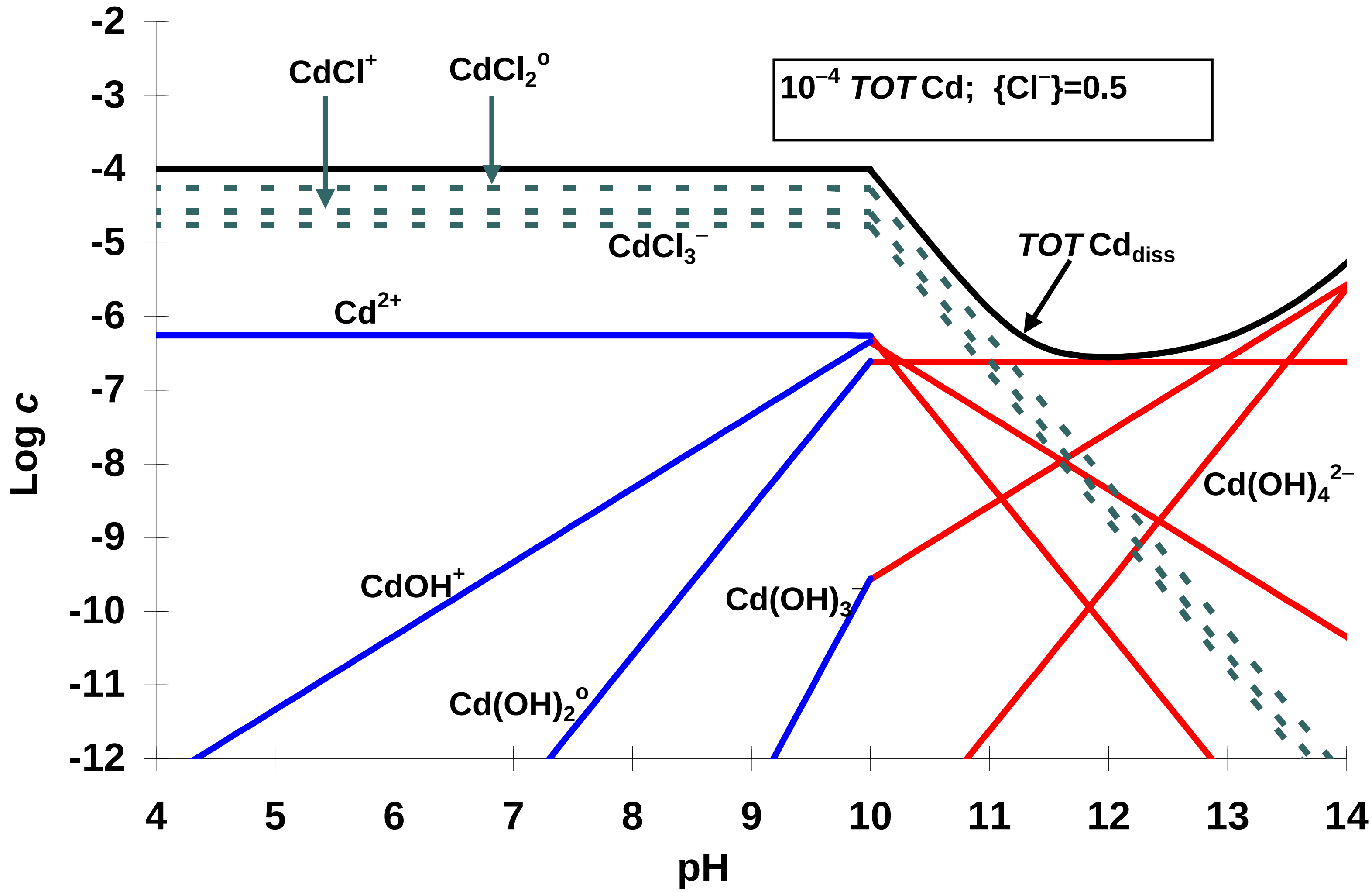
# Equilibrium with Metal Solids

*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.*

***Conventional:*** $Cd(OH)_2(s) \leftrightarrow Cd^{2+} + 2OH^-$ $\quad K_{s0}$

***Minteq:*** $Cd^{2+} + 2H_2O \leftrightarrow Cd(OH)_2(s) + 2H^+$ $\quad 1/{*K_{s0}} = K_{mineql}$

***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:***

$$\mathit{TOT}\mathrm{Me}_{solid} = \mathit{TOT}\mathrm{Me}_{input} - \mathit{TOT}\mathrm{Me}_{diss,eq}$$