Chemistry 2404 Forensic & Environmental Chemistry

Lecture 21. Carbonate Solubility Equilibria

Lecture 22

- Polyprotic Acids: Speciation and Complexation

Lecture 23. pE Diagrams

What is the solubility of carbonates?

The concentration of Ca^{2+} in equilibrium with calcium carbonate depends on pH. For <u>this</u> diagram, $[Ca^{2+}]_T = 0.010$ M.

Starting from an acidic solution, at what pH does $CaCO_3$ begin to precipitate,

i.e. at what pH is there enough CO_3^{2-} to precipitate $CaCO_3$ when $[Ca^{2+}] = 0.01$ M

$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.6 \times 10^{-9}$
$= 0.01\ K_{a1}K_{a2}[H_2CO_3]/[H_3O^+]^2$

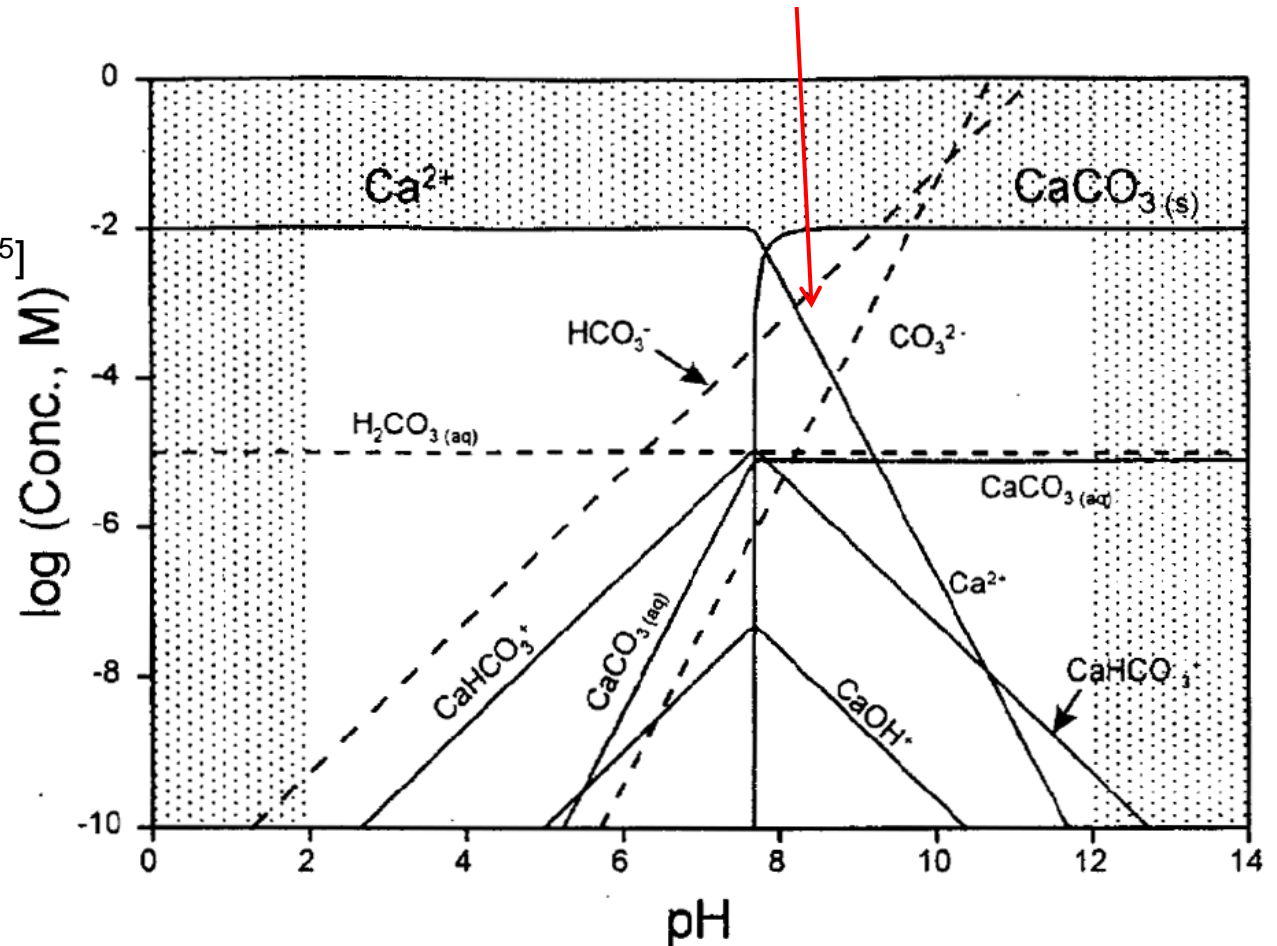$\Rightarrow [H_3O^+] = 2.45 \times 10^{-8}$
$\Rightarrow pH = 7.6$!
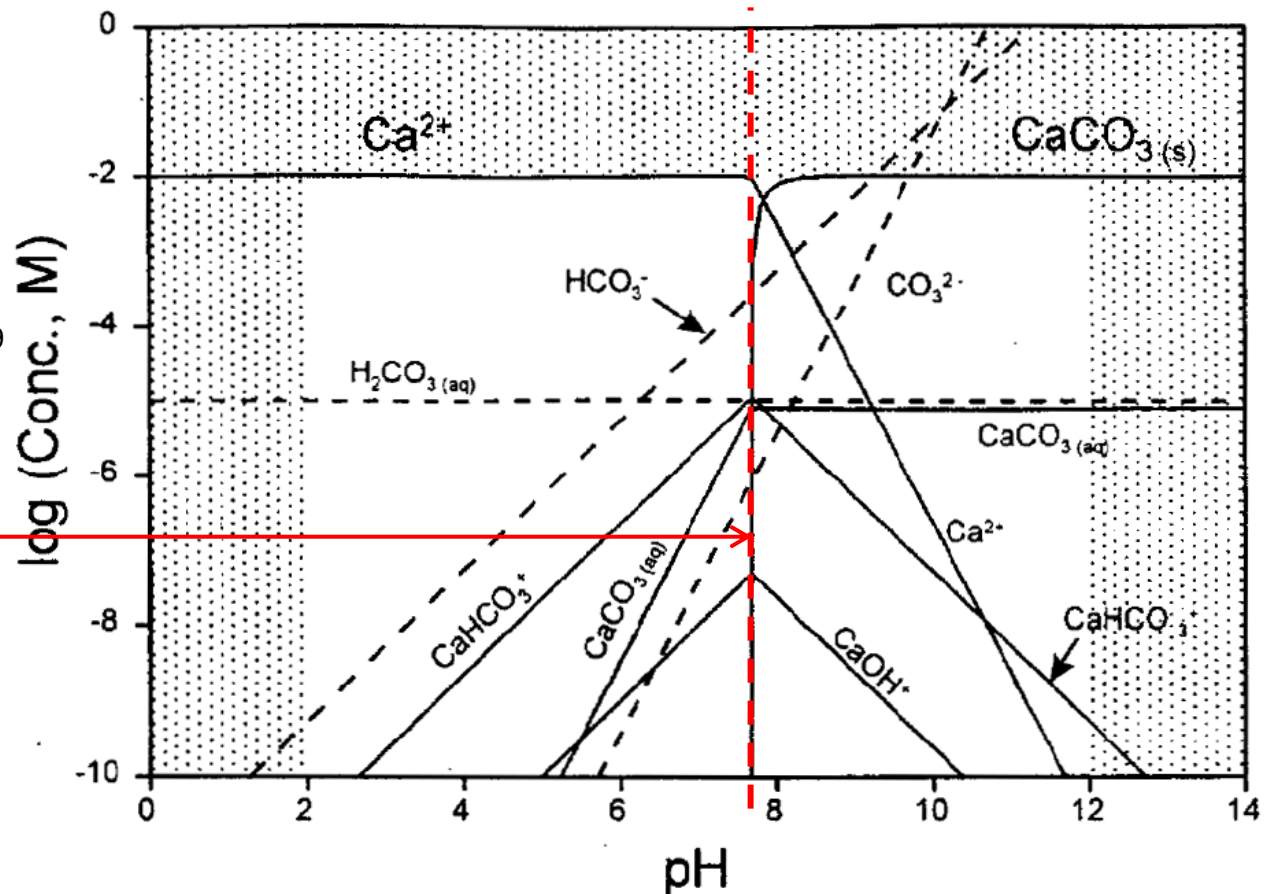
What is the solubility of carbonates?

When equilibrium is reached between $CaCO_3$ and $CO_2(g)$ the pH has increased to 8.24. The concentration of Ca^{2+} in this equilibrium is determined by

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}]K_{a1}K_{a2}[H_2CO_3]/[H_3O^+]^2 \Rightarrow [Ca^{2+}] = K_{sp}[H_3O^+]^2 /K_{a1}K_{a2}[H_2CO_3]$$

$[Ca^{2+}] = \dfrac{[4.6 \times 10^{-9}][5.3 \times 10^{-9}]^2}{[4.4 \times 10^{-7}][4.7 \times 10^{-11}][1.3 \times 10^{-5}]}$

$= 4.8 \times 10^{-4}$

Hydrolysis and Speciation

As we have noted before, there are many other situations where polyprotic acid hydrolysis is important. In the environment the pH of the aquatic systems is frequently controlled by one species, such as CO_2, in equilibrium with a solid or gas reservoir in large quantities. The speciation of other chemicals then adjusts to the ambient pH.

Even if we don't know what controls the pH in a particular system, we can still measure it.

- Hydrolysable metal ions: Al^{3+}, Fe^{3+}, Fe^{2+}, Zn^{2+}…

- Acidic gases: H_2S, CO_2, HNO_2, …

- Organic acids and chelating agents: H_4EDTA, H_3NTA, citric acid…

- Phosphates and silicates: H_3PO_4, H_4SiO_4

Xenobiotic acids: 2,4,6-TCP

The organic pollutant 2,4,6-trichlorophenol is a chemical pollutant found in organisms, but which is not normally found in or produced by nature. The phenolic proton is weakly acidic, $pK_a = 6.13$.

If a spill leads to about 1×10^{-4} M 2,4,6-TCP in groundwater, how will the speciation depend on pH?

[TCP] >> [TCP⁻]
(e.g.; [TCP]:[TCP⁻] = 100:1)
$pH = pK_a - 2$
Therefore, $\alpha[H_3L]_{max}$ ($\alpha \sim 1$)
occurs at $pH \leq 6.13 - 2 = 4.13$

Where [TCP] = [TCP⁻]
(i.e.; $\alpha[TCP] = 0.5$)
$pH = pK_a$

[TCP] << [TCP⁻]
(e.g.; [TCP]:[TCP⁻] = 1:100)
$pH = pK_a + 2$
Therefore, $\alpha[H_3L]_{min}$ ($\alpha \sim 0$)
occurs at $pH \geq 6.13 + 2 = 8.13$
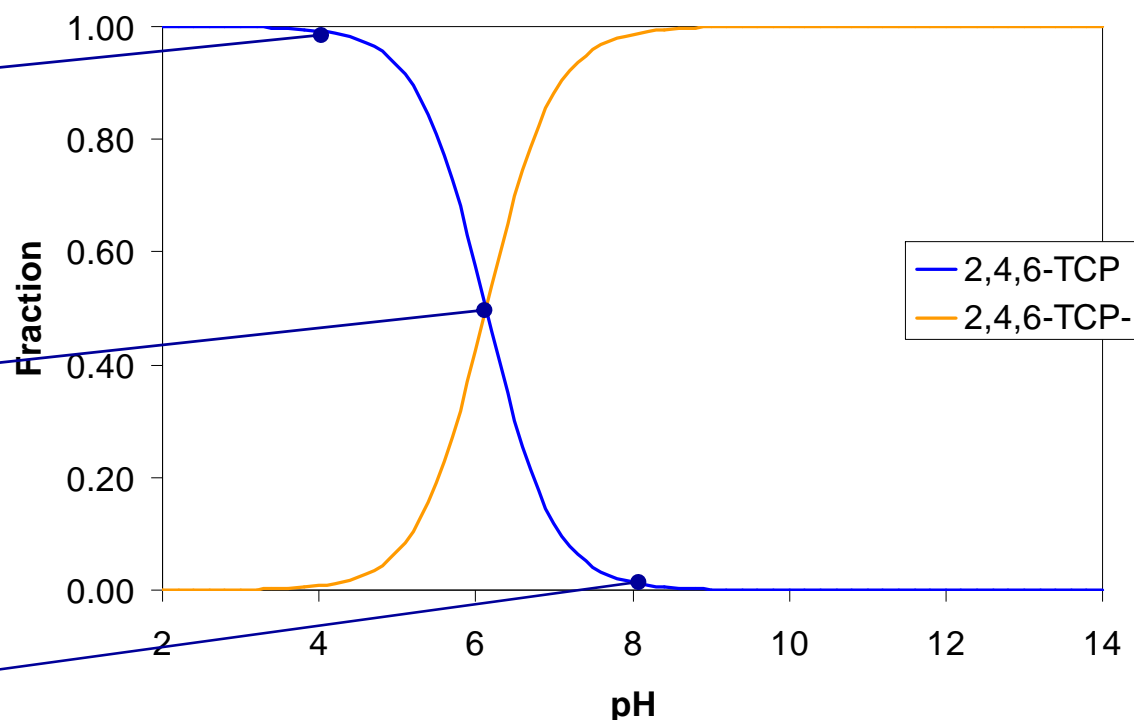
Polyprotic Chelates: H₃NTA

Chelating agents, such as EDTA and nitrilotriacetic acid (H₃NTA) used to improve the action of detergents also have the ability to leach out heavy metals (Pb, Hg, Cd) from sediments at the bottom of lakes and rivers. This is undesirable, since it is preferable that the heavy metals remain locked in the sediments rather than becoming mobilised.
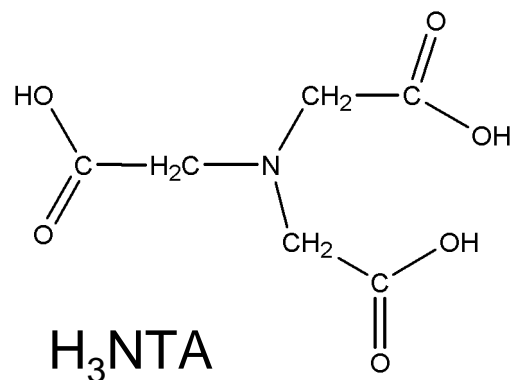
H₃NTA

The effectiveness of a chelating agent depends on which species are present in the highest concentration, and the availability of the particular species that acts as a ligand.
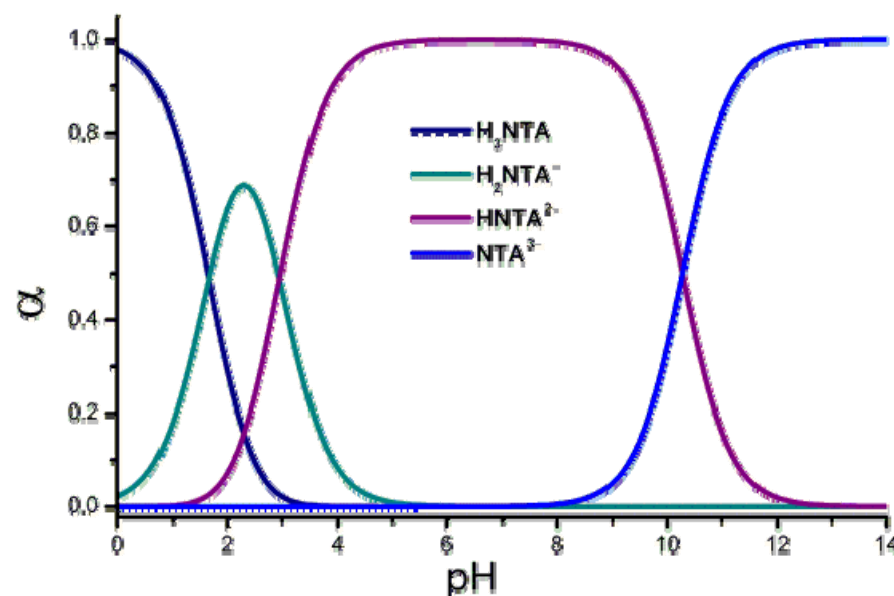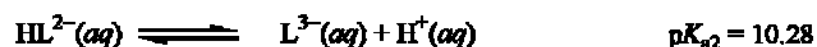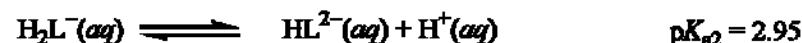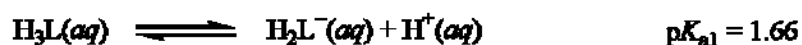

Real Data

$pK_a (1) \approx pK_a (2) \ll pK_a (3)$

H₃NTA	H₂NTA⁻ + H⁺	$pK_a(1) = 1.66$
H₂NTA⁻	HNTA²⁻ + H⁺	$pK_a(2) = 2.95$
HNTA²⁻	NTA³⁻ + H⁺	$pK_a(3) = 10.28$

Polyprotic Chelates: H_3NTA

$$\alpha_{H_3L} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

Like carbonic acid, H_3NTA, or H_3L (for "ligand") is a polyprotic acid that can undergo a series of acid hydrolysis reactions.

$$\alpha_{H_2L^-} = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$H_3L(aq) \rightleftharpoons H_2L^-(aq) + H^+(aq) \qquad pK_{a1} = 1.66$$

$$\alpha_{HL^{2-}} = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$H_2L^-(aq) \rightleftharpoons HL^{2-}(aq) + H^+(aq) \qquad pK_{a2} = 2.95$$

$$\alpha_{L^{3-}} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$HL^{2-}(aq) \rightleftharpoons L^{3-}(aq) + H^+(aq) \qquad pK_{a2} = 10.28$$

If we only have H_3L present, then we can solve for the equilibirum pH (just like CO_2).
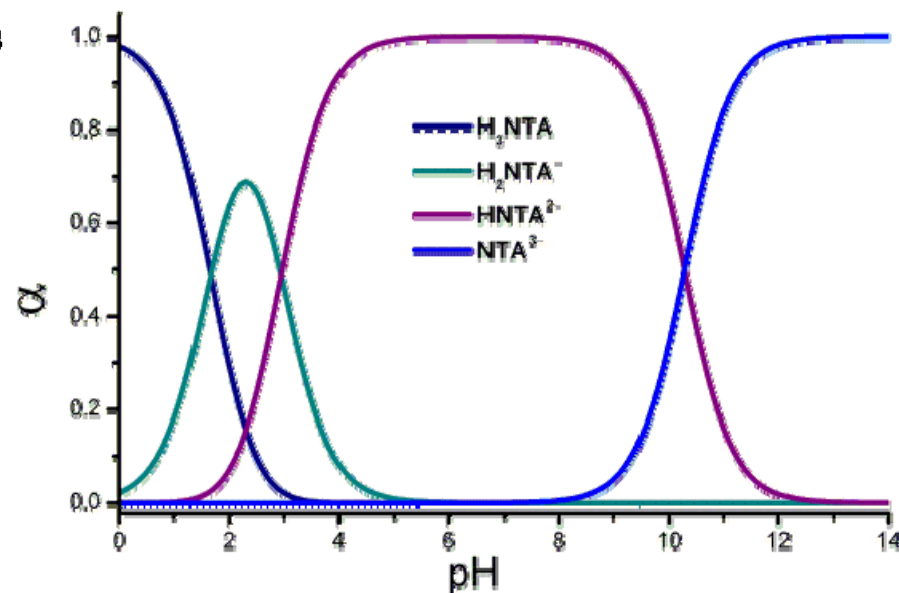Alternatively, something else may determine the pH of the systems. In that case we can plot the speciation as a function of pH once we have defined the fraction, α, of each hydrolysed form of the starting material. As usual, this depends only on the K_a's and pH.

Real Data
$pK_a (1) \approx pK_a (2) \ll pK_a (3)$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.66$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.95$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 10.28$

Deconstructing the Speciation of H_3NTA

$$H_3L(aq) \overset{K_{a1}}{\rightleftharpoons} H_2L^-(aq) + H^+(aq)$$

$$H_2L^-(aq) \overset{K_{a2}}{\rightleftharpoons} HL^{2-}(aq) + H^+(aq)$$

$$HL^{2-}(aq) \overset{K_{a3}}{\rightleftharpoons} L^{3-}(aq) + H^+(aq)$$

conjugate acid   *conjugate base*

Speciation of H_3L depends upon K_{a1} only
H_2L^- depends upon K_{a1} and K_{a2}
HL^{2-} depends upon K_{a2} and K_{a3}
L^{3-} depends upon K_{a3} only

$$H_3L(aq) \overset{K_{a1}}{\rightleftharpoons} H_2L^-(aq) + H^+(aq) \qquad K_{a1} = \frac{[H_2L^-][H^+]}{[H_3L]}$$

For each acid and its conjugate base, the Henderson-Hasselbalch equation gives the condition where their concentrations (and fractions) are equal.

$$\log K_{a1} = -\log[H_3L] + \log[H_2L^-] + \log[H^+]$$

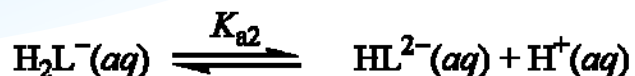$$-\log[H^+] = -\log K_{a1} + \log[H_2L^-] - \log[H_3L]$$

$$pH = pK_{a1} + \log\frac{[H_2L^-]}{[H_3L]} \qquad \textit{Henderson-Hasselbalch Equation}$$

Deconstructing the Speciation of H_3NTA: H_3L

$$H_3L(aq) \xrightleftharpoons{K_{a1}} H_2L^-(aq) + H^+(aq)$$

$pK_{a1} = 1.66$

$$pH = pK_{a1} + \log\frac{[H_2L^-]}{[H_3L]}$$

$$H_2L^-(aq) \xrightleftharpoons{K_{a2}} HL^{2-}(aq) + H^+(aq)$$

$pK_{a2} = 2.95$

$$HL^{2-}(aq) \xrightleftharpoons{K_{a3}} L^{3-}(aq) + H^+(aq)$$

$pK_{a3} = 10.28$

Where $[H_3L] \gg [H_2L^-]$
(*e.g.*; $[H_3L]:[H_2L^-] = 100:1$)
$pH = pK_{a1} - 2$
Therefore, $\alpha[H_3L]_{max}$ ($\alpha \sim 1$)
occurs at $pH = 1.66 - 2 = -0.34$

Where $[H_3L] = [H_2L^-]$
(*i.e.*; $\alpha[H_3L] = 0.5$)
$pH = pK_{a1}$, since $\log 1 = 0$

Where $[H_3L] \ll [H_2L^-]$
(*e.g.*; $[H_3L]:[H_2L^-] = 1:100$)
$pH = pK_{a1} + 2$
Therefore, $\alpha[H_3L]_{min}$ ($\alpha \sim 0$)
occurs at $pH = 1.66 + 2 = 3.66$

Legend:
- H_3NTA
- H_2NTA^-
- $HNTA^{2-}$
- NTA^{3-}

α vs pH

Real Data
$pK_a(1) \approx pK_a(2) \ll pK_a(3)$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.66$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.95$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 10.28$

Deconstructing the Speciation of H$_3$NTA: L^{3-}

$$H_3L(aq) \xrightleftharpoons{K_{a1}} H_2L^-(aq) + H^+(aq)$$

$pK_{a1} = 1.66$

$$pH = pK_{a1} + \log\frac{[H_2L^-]}{[H_3L]}$$

$$H_2L^-(aq) \xrightleftharpoons{K_{a2}} HL^{2-}(aq) + H^+(aq)$$

$pK_{a2} = 2.95$

$$HL^{2-}(aq) \xrightleftharpoons{K_{a3}} L^{3-}(aq) + H^+(aq)$$

$pK_{a3} = 10.28$

Where $[HL^{2-}] \ll [L^{3-}]$
(*e.g.*; $[HL^{2-}]:[L^{3-}] = 1:100$)
pH = pK_{a3} + 2
So $\alpha[L^{3-}] \sim 1$
at pH = 10.28 + 2 = 12.28

Where $[HL^{2-}] = [L^{3-}]$
(*i.e.*; $\alpha[L^{3-}] = 0.5$)
pH = pK_{a3}, since log1 = 0

Where $[HL^{2-}] \gg [L^{3-}]$
(*e.g.*; $[HL^{2-}]:[L^{3-}] = 100:1$)
pH = pK_{a3} − 2
So $\alpha[L^{3-}] \sim 0$
at pH = 10.28 − 2 = 8.28
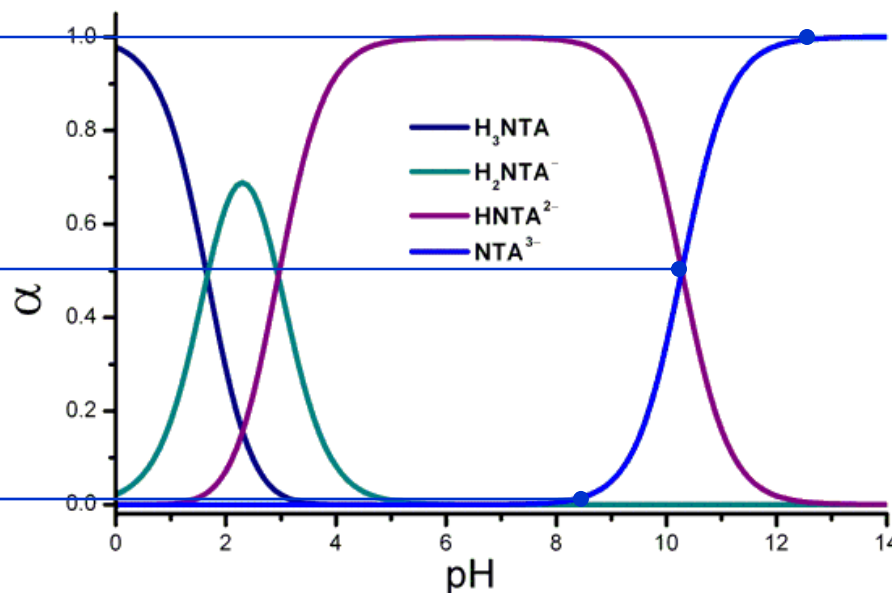
Legend:
— H$_3$NTA
— H$_2$NTA$^-$
— HNTA^{2-}
— NTA^{3-}

Real Data
$pK_a(1) \approx pK_a(2) \ll pK_a(3)$

H$_3$NTA	H$_2$NTA$^-$ + H$^+$	$pK_a(1) = 1.66$
H$_2$NTA$^-$	HNTA^{2-} + H$^+$	$pK_a(2) = 2.95$
HNTA^{2-}	NTA^{3-} + H$^+$	$pK_a(3) = 10.28$

Deconstructing the Speciation of H₃NTA: H₂L⁻

$$H_3L(aq) \xrightleftharpoons{K_{a1}} H_2L^-(aq) + H^+(aq)$$

$$H_2L^-(aq) \xrightleftharpoons{K_{a2}} HL^{2-}(aq) + H^+(aq)$$

$$HL^{2-}(aq) \xrightleftharpoons{K_{a3}} L^{3-}(aq) + H^+(aq)$$

conjugate acid   *conjugate base*

At what pH is $[H_2L^-]$ (which is a conjugate base (K_{a1}) and a conjugate acid (K_{a2})) present at a maximum?

This is the same as asking at what pH is $[HL^{2-}]=[H_3L]$?
The equilibrium condition is

$$H_3L \rightleftharpoons HL^{2-} + 2H^+$$

$$K = \frac{[HL^{2-}][H^+]^2}{[H_3L]} = K_{a1}K_{a2}$$

When $[HL^{2-}]=[H_3L]$

$$K_{a1}K_{a2} = [H^+]^2$$

$$\Rightarrow pH = \tfrac{1}{2}\left(pK_{a1} + pK_{a2}\right) = 2.3$$
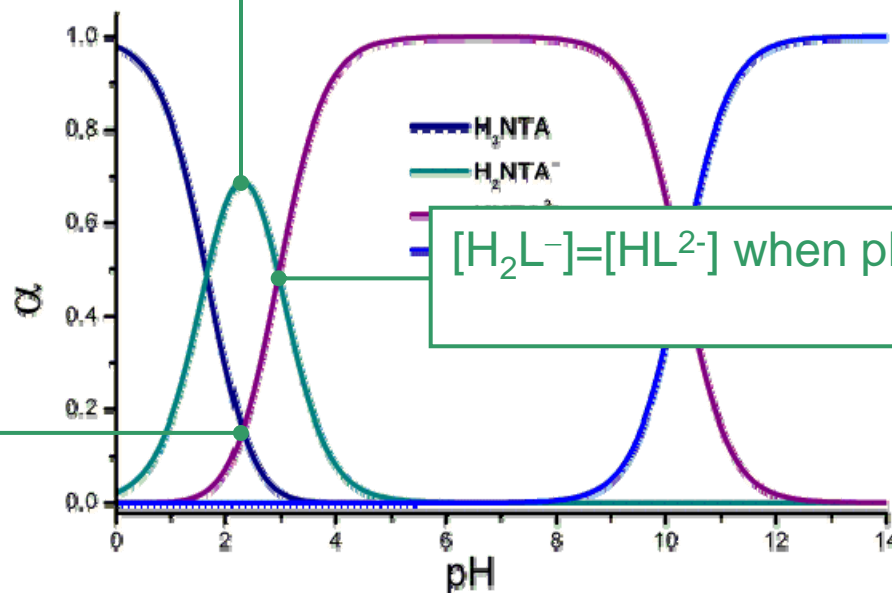
$[H_2L^-]=[HL^{2-}]$ when pH = pK_{a2} = 2.95

Real Data
$pK_a (1) \approx pK_a (2) \ll pK_a (3)$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.66$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.95$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 10.28$

Deconstructing the Speciation of H_3NTA: HL^{2-}

$H_3L(aq) \rightleftharpoons^{K_{a1}} H_2L^-(aq) + H^+(aq)$

$H_2L^-(aq) \rightleftharpoons^{K_{a2}} HL^{2-}(aq) + H^+(aq)$

$HL^{2-}(aq) \rightleftharpoons^{K_{a3}} L^{3-}(aq) + H^+(aq)$

conjugate acid   *conjugate base*
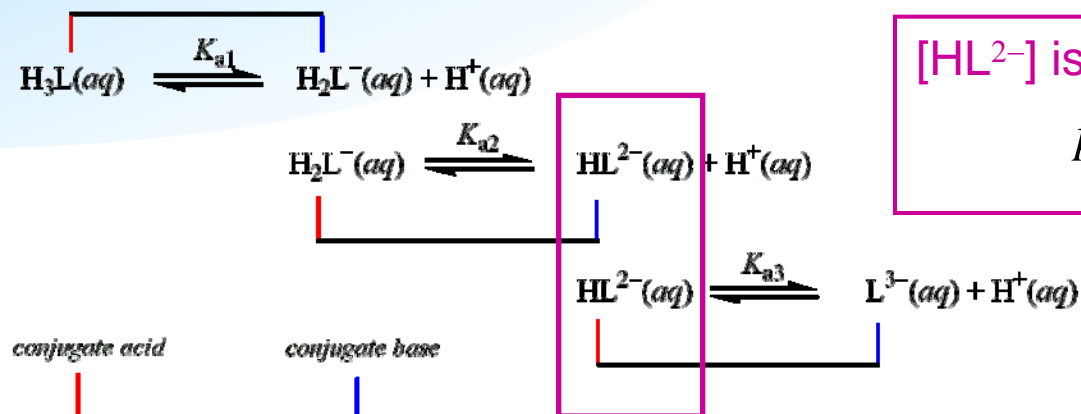
$[HL^{2-}]$ is present at a maximum at

$$pH = \tfrac{1}{2}\left(pK_{a2} + pK_{a3}\right)$$

$[H_2L^-]=[HL^{2-}]$ when pH = pK_{a2} = 2.95
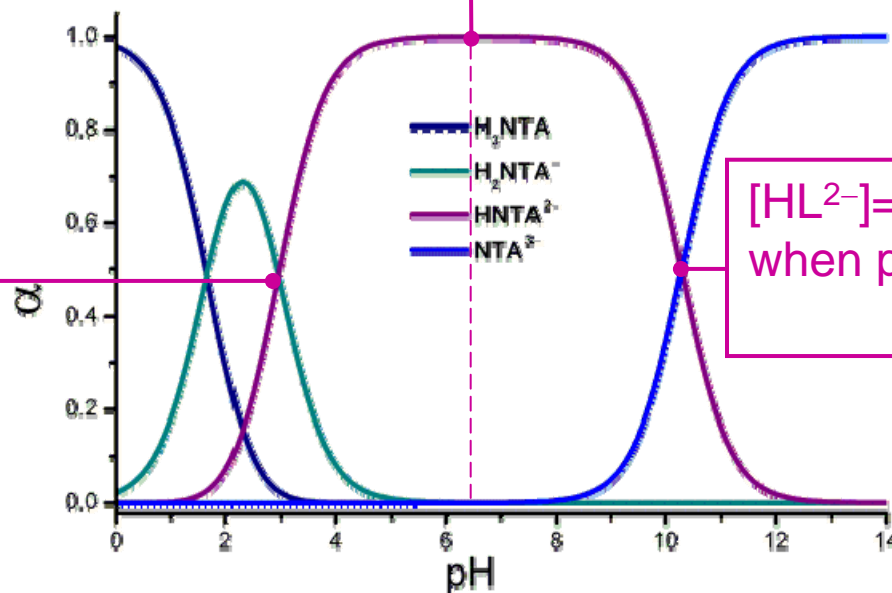
$[HL^{2-}]=[L^{3-}]$ when pH = pK_{a3} = 10.28

Legend: H_3NTA, H_2NTA^-, $HNTA^{2-}$, NTA^{3-}

Real Data
$pK_a(1) \approx pK_a(2) \ll pK_a(3)$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.66$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.95$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 10.28$

Effect of different pK_a's
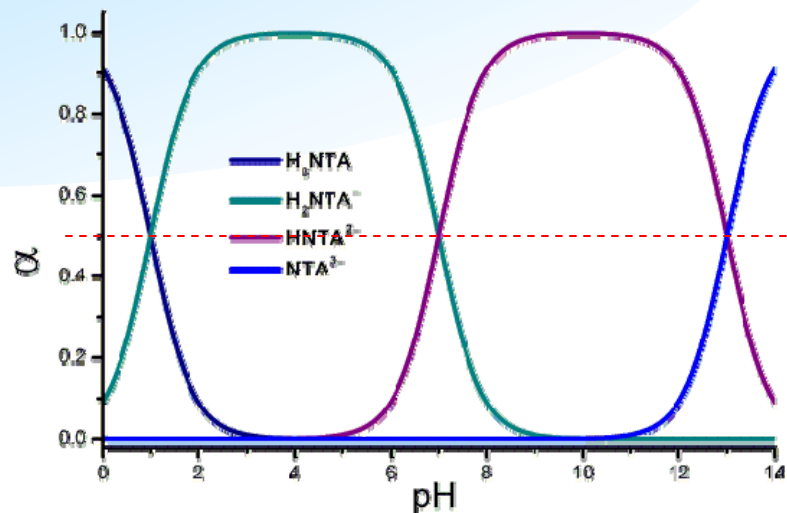
Dummy Data 2
$pK_a (1) \ll pK_a (2) \ll pK_a (3)$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.00$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 7.00$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 13.00$
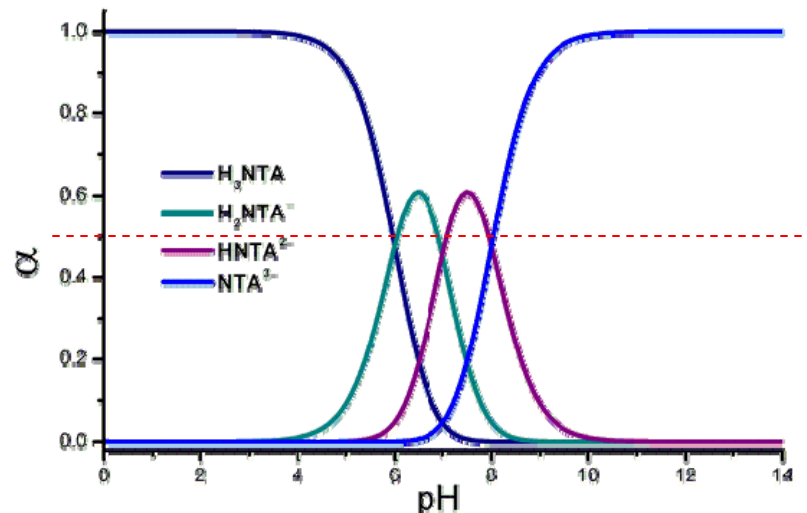
Dummy Data 3
$pK_a (1) \approx pK_a (2) \approx pK_a (3) \approx 7.0$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 6.00$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 7.00$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 8.00$
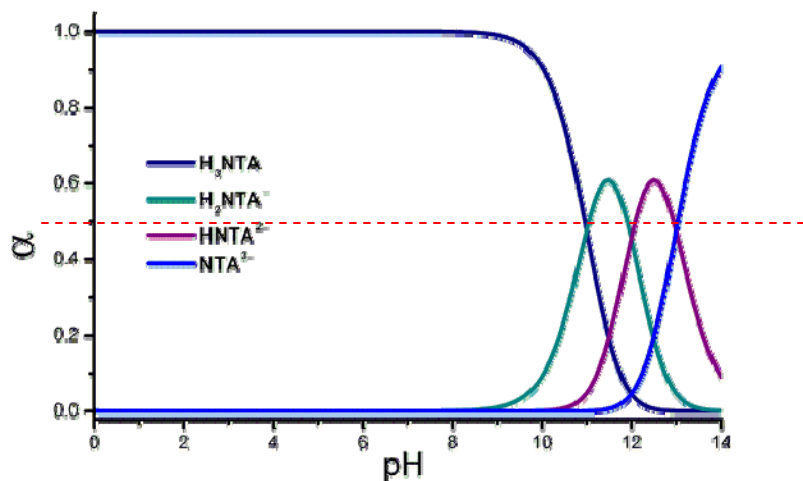
Dummy Data 4
$pK_a (1) \approx pK_a (2) \approx pK_a (3) \approx 12.0$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 11.00$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 12.00$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 13.00$
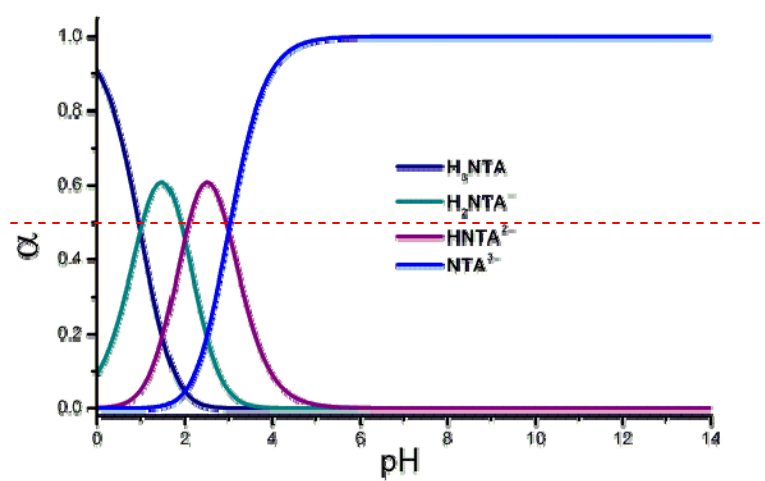
Dummy Data 5
$pK_a (1) \approx pK_a (2) \approx pK_a (3) \approx 2.0$

H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.00$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.00$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 3.00$

Complexation by Polyprotic Chelates

Real Data

$pK_a(1) \approx pK_a(2) \ll pK_a(3)$

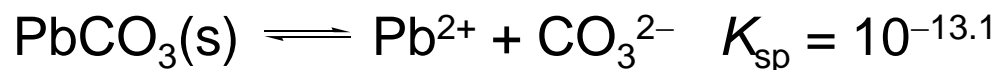|		
H_3NTA	$H_2NTA^- + H^+$	$pK_a(1) = 1.66$
H_2NTA^-	$HNTA^{2-} + H^+$	$pK_a(2) = 2.95$
$HNTA^{2-}$	$NTA^{3-} + H^+$	$pK_a(3) = 10.28$
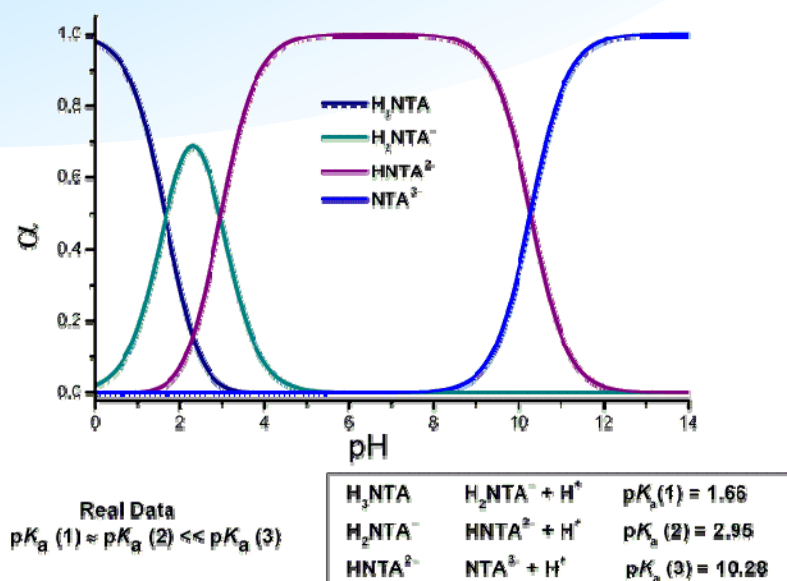
As most aquatic environments have pHs between 4-9, the major form of H_3NTA will be $HNTA^{2-}$. What happens in its complexation of lead?

Given the K_{sp} for $PbCO_3(s)$

$$PbCO_3(s) \rightleftharpoons Pb^{2+} + CO_3^{2-} \quad K_{sp} = 10^{-13.1}$$

and that NTA^{3-} forms a strong complex with Pb^{2+}:

$$Pb^{2+} + NTA^{3-} \rightleftharpoons PbNTA^- \quad K = 10^{12.6}$$

We can calculate the equilibrium constant describing the reaction between $PbCO_3(s)$ and H_3NTA at pH 7.0.

$$PbCO_3(s) + HNTA^{2-} \rightleftharpoons PbNTA^- + HCO_3^-$$
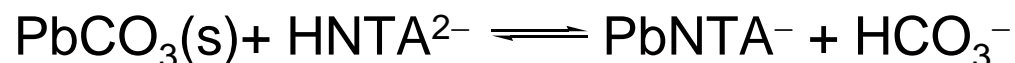
Dominant form of H_3NTA at pH 7.

We already know that HCO_3^- is dominant at pH 7.0.

Complexation by Polyprotic Chelates

$$PbCO_3 \rightleftharpoons Pb^{2+} + CO_3^{2-} \quad K_{sp} = 10^{-13.1} \quad (1)$$

$$HNTA^{2-} \rightleftharpoons NTA_3^{-} + H^{+} \quad K = 10^{-10.28} \quad (2)$$

$$Pb^{2+} + NTA^{3-} \rightleftharpoons PbNTA^{-} \quad K = 10^{12.6} \quad (3)$$

$$HCO_3^{-} \rightleftharpoons CO_3^{2-} + H^{+} \quad K_{a2} = 4.69 \times 10^{-11}$$
$$CO_3^{2-} + H^{+} \rightleftharpoons HCO_3^{-} \quad K_r = 1/K_{a2} = 2.13 \times 10^{10} = 10^{10.33} \quad (4)$$
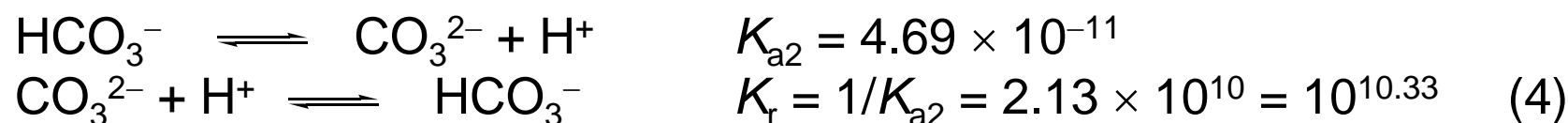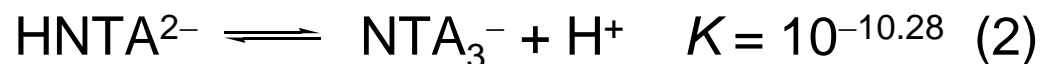
Addition of equilibrium equations 1 to 4 gives the target equation:

$$PbCO_3(s) + HNTA^{2-} \rightleftharpoons PbNTA^{-} + HCO_3^{-} \quad K = 10^{-13.1-10.28+12.6+10.33} = 10^{-0.45}$$

In H_3NTA-containing water at pH = 7, $[HCO_3^{-}] = 10^{-4}M$.

Pb^{2+} is dissolved and complexed almost stoichometrically by H_3NTA. This is easily shown by the ratio $[PbNTA]/[HNTA^{2-}] = K/[HCO_3^{-}] = 10^{-.45}/10^{-4} = 28,000$
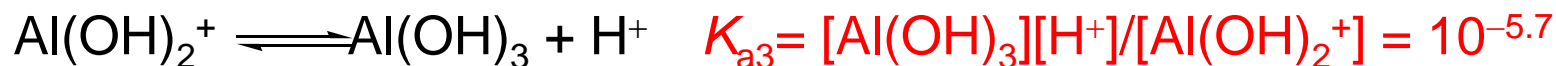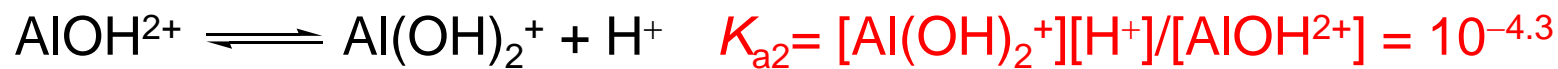
…almost all the H_3NTA is in the form of PbNTA.

Aluminium: Metal Ion Hydrolysis and Precipitation

The mineral Gibbsite, $Al(OH)_3(s)$, is one of the solid forms of aluminium. Aluminium is a simple starting point for understanding metal ion speciation because it only exists in one oxidation state, Al(III).

The dissolved aluminium ion, Al^{3+} is in fact a *hydrated* complex ion, which is more correctly written as $[Al(OH_2)_6]^{3+}$, but we often omit the waters of hydration. However these waters are chemically important as they are *more acidic than solvent water*, and hence can undergo hydrolysis such as:-

$$Al^{3+} \rightleftharpoons AlOH^{2+} + H^+ \qquad K_{a1} = [AlOH^{2+}][H^+]/[Al^{3+}] = 10^{-5.0}$$
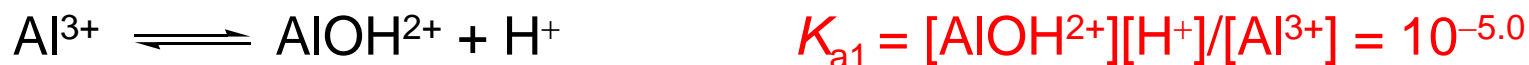
This species can undergo further hydrolysis:

$$AlOH^{2+} \rightleftharpoons Al(OH)_2^+ + H^+ \qquad K_{a2} = [Al(OH)_2^+][H^+]/[AlOH^{2+}] = 10^{-4.3}$$

$$Al(OH)_2^+ \rightleftharpoons Al(OH)_3 + H^+ \qquad K_{a3} = [Al(OH)_3][H^+]/[Al(OH)_2^+] = 10^{-5.7}$$

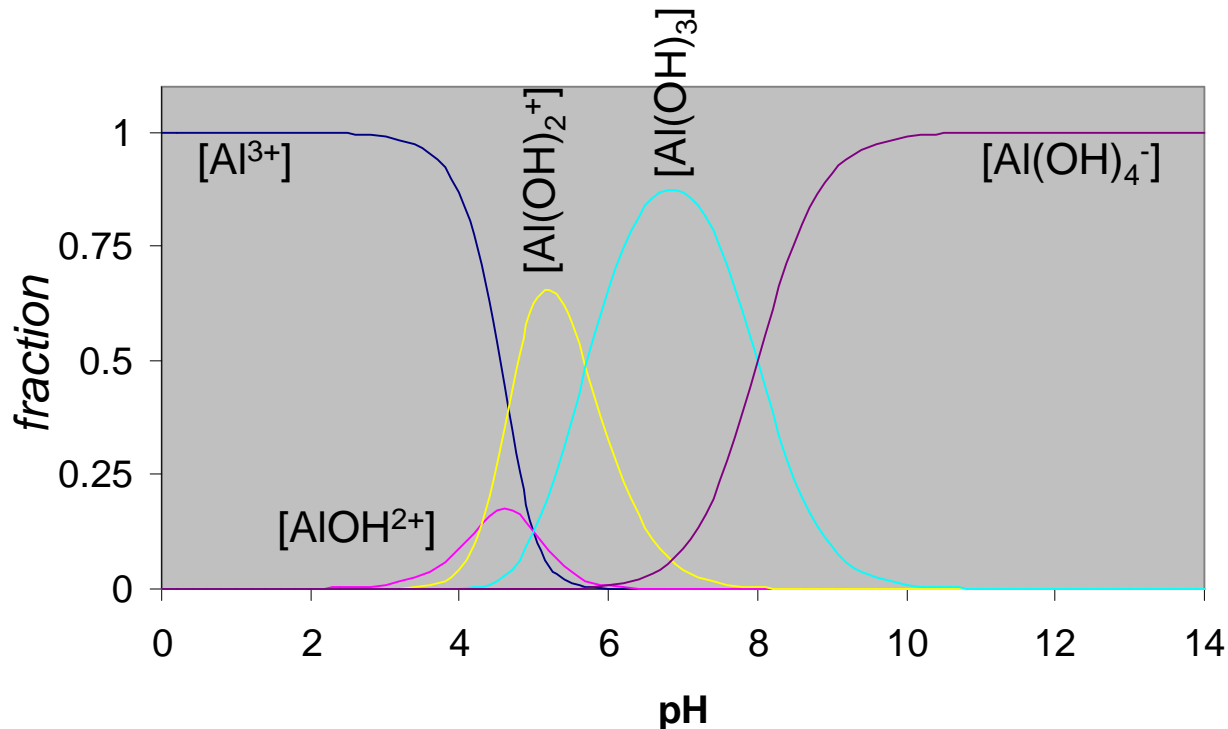$$Al(OH)_3 \rightleftharpoons Al(OH)_4^- + H^+ \qquad K_{a4} = [Al(OH)_4^-][H^+]/[Al(OH)_3] = 10^{-8}$$

Aluminium: Metal Ion Hydrolysis and Precipitation

Like any polyprotic acid we can construct a speciation diagram by defining fractions, α and solving their equilibrium conditions:
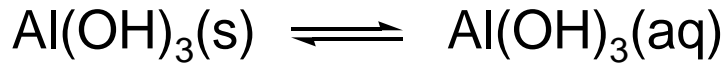
$$\alpha_{Al^{3+}} = \frac{[Al^{3+}]}{[Al^{3+}]+[Al(OH)^{2+}]+[Al(OH)_2^{+}]+[Al(OH)_3]+[Al(OH)_4^{-}]}$$

$$= \frac{1}{1+K_{a1}[H^{+}]^{-1}+K_{a1}K_{a2}[H^{+}]^{-2}+K_{a1}K_{a2}K_{a3}[H^{+}]^{-3}+K_{a1}K_{a2}K_{a3}K_{a4}[H^{+}]^{-4}}$$

…etc. (see CO_2 lectures)

Solubility of Gibbsite

An interesting feature is that the *concentration* of the $Al(OH)_3$(aq) species is independent of pH, because it is described by the equilibrium:
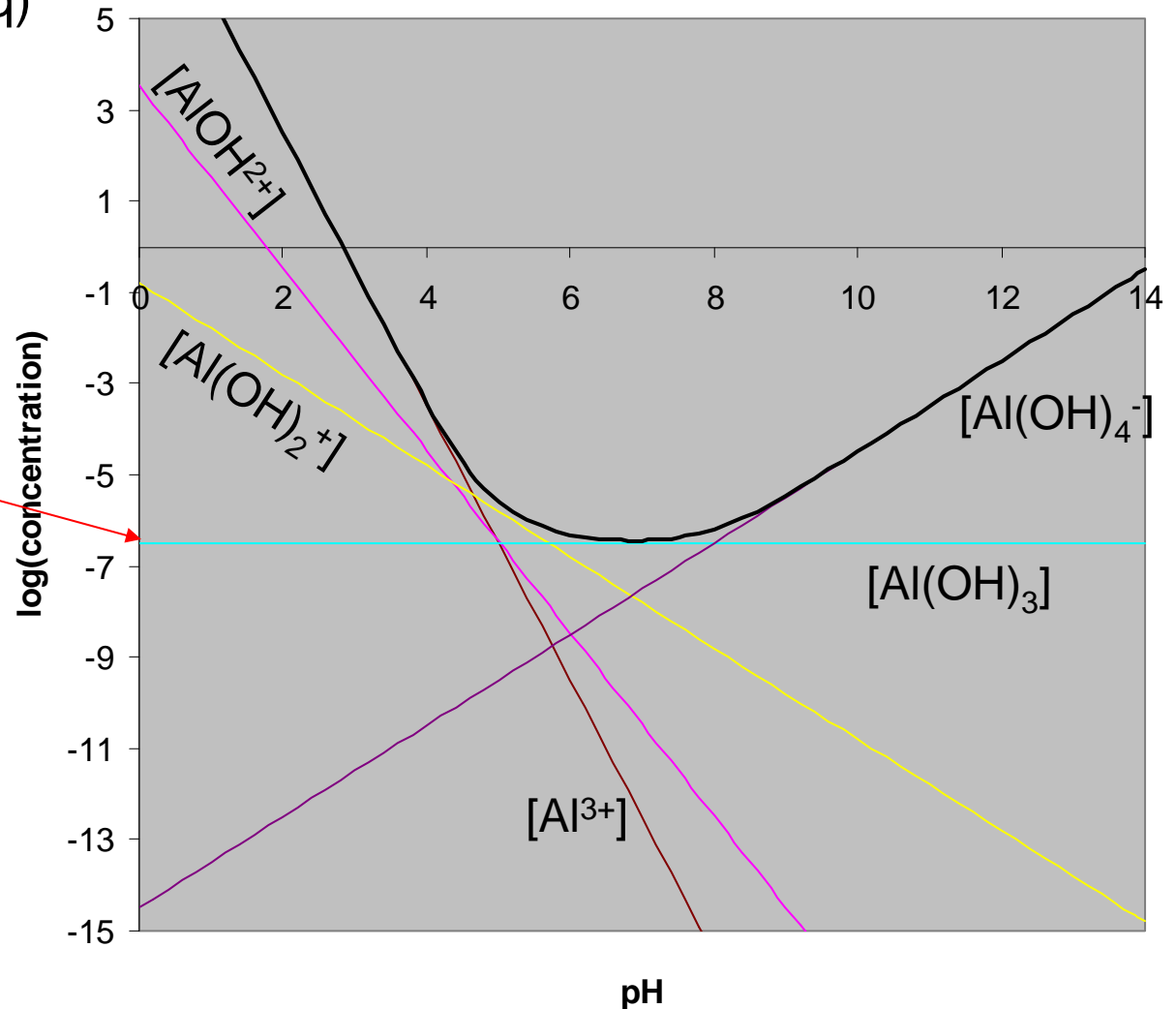
$$Al(OH)_3(s) \rightleftharpoons Al(OH)_3(aq)$$

$$K = 10^{-6.5}$$

Just like CO_2(g) fixes the H_2CO_3 concentration, solid Gibbsite fixes [$Al(OH)_3$(aq)] at $10^{-6.5}$M. As long as solid Gibbsite is present the speciation diagram is defined as shown.

Because this is such a low concentration, small amounts of Gibbsite control aluminium solubility in the environment.

log(concentration) vs pH

[AlOH^{2+}]

[Al(OH)$_2$$^+$]

[Al(OH)$_4$$^-$]

[Al(OH)$_3$]

[Al^{3+}]

Solubility of Gibbsite

The total solubility of aluminium is the sum of concentrations of all the different dissolved species.

$$[Al]_T = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4^-]$$

This is shown by the heavy black line in the speciation diagram.

On a logarithmic scale it basically follows the line of the most concentrated or dominant species, because eveything else is present at such low concentration.

[AlOH²⁺]

[Al(OH)₂⁺]

[Al(OH)₄⁻]

[Al(OH)₃]

[Al³⁺]

log(concentration)

pH
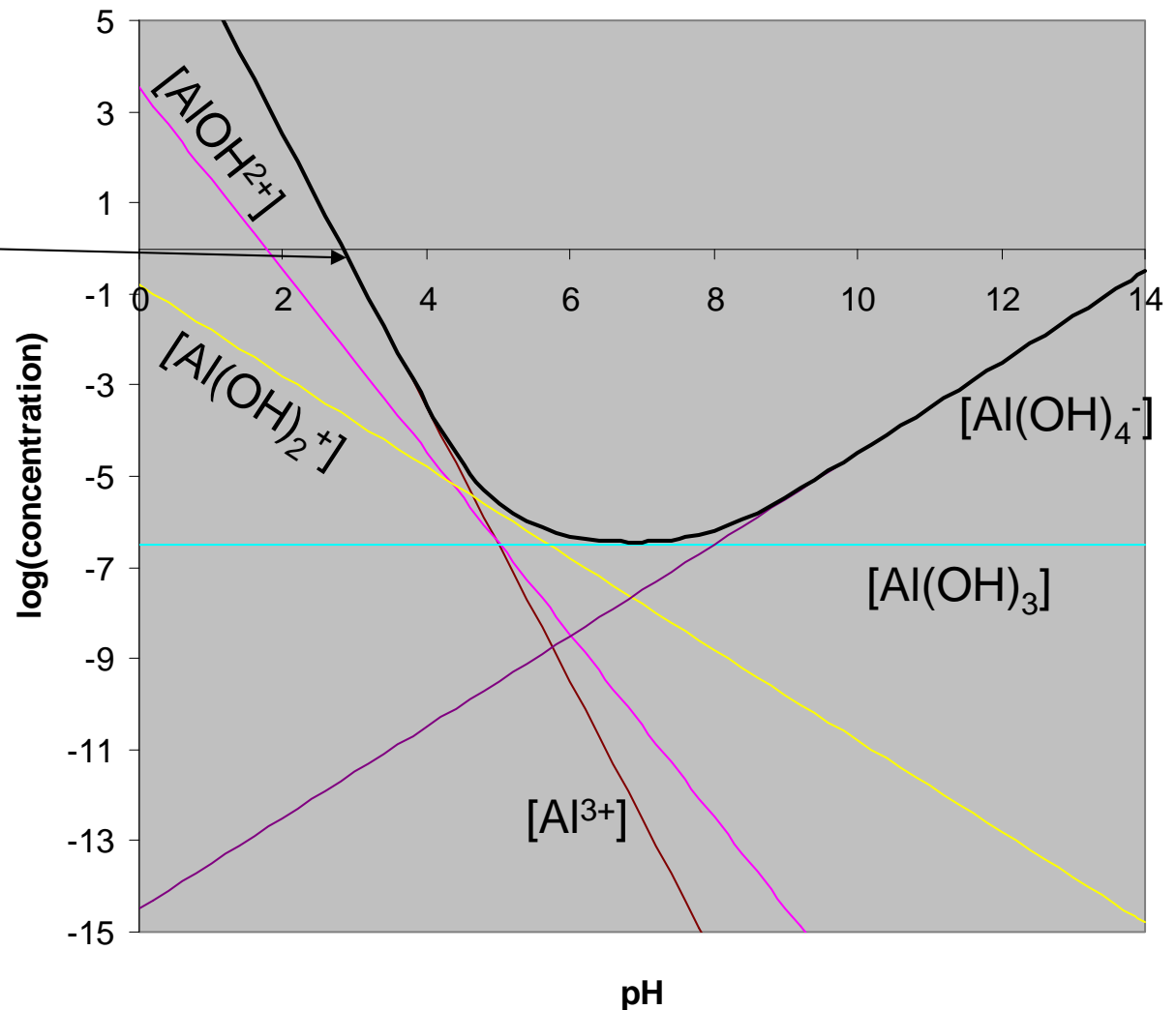
Summary

You should now be able to

- Set up the equilibrium and balance equations for complex aquatic equilibrium systems.
- Numerically solve a suitably well-defined system of equilibrium equations.
- Read a speciation diagram and a speciation/distribution diagram to identify the dominant species at a given pH.
- Decide on reasonable assumptions and approximations to simplify complex equilibrium systems, and solve them.

Next Lecture

Metal Ion Hydrolysis and Speciation

Practice/Review problems

1. Sketch the speciation diagram (using fractions) for the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), $pK_a = 2.73$.

2. Sketch the same diagram as log[concentration] versus pH at a total concentration of 1.0 mM.

3. What fraction of 2,4-D would be present in its acid form in a raindrop?

4. What would be the dominant reaction of a chelate H_3L with solid lead carbonate whose speciation was as shown for "Dummy Data 5" in this lecture? What is the expression for the equilibrium constant?