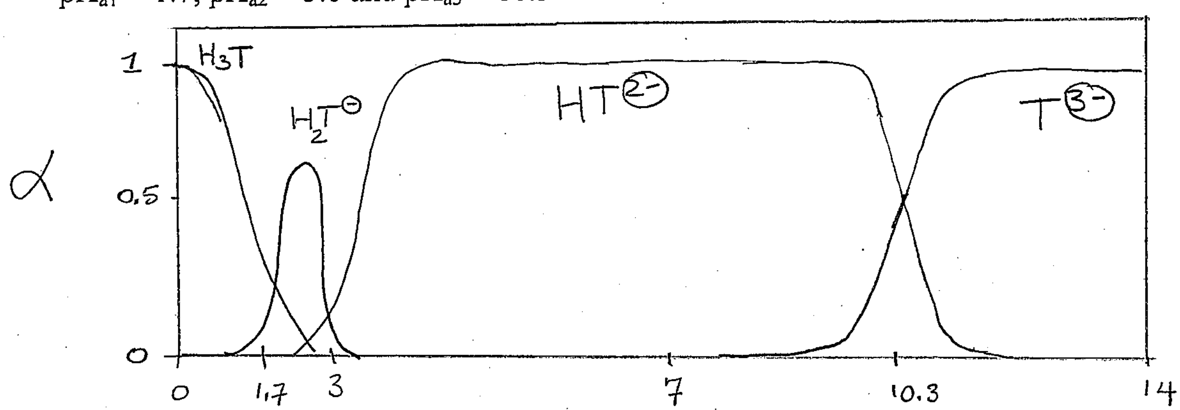
Calculate the total concentration of aqueous lead species in a water sample containing 25 mg/L of NTA at pH = 8.0 in equilibrium with solid lead (II) hydroxide and compare this to a sample without NTA present.

Note: NTA is a tetradentate ligand with four acidic protons (H_3T).
$pK_{a1} = 1.7$, $pK_{a2} = 3.0$ and $pK_{a3} = 10.3$



∴ HT^{2-} is dominant form at pH = 8.0

So we want to work w/ the following equilibrium

$$Pb(OH)_{2(s)} + HT^{2-} \rightleftharpoons Pb\text{-}T^{-} + H_2O + OH^{-}$$

which we can obtain by combing the following equilibria,

$$Pb(OH)_{2(s)} \rightleftharpoons Pb^{2+} + 2OH^{-} \qquad K_{sp} = 1.6 \times 10^{-20}$$

$$Pb^{2+} + T^{3-} \rightleftharpoons PbT^{-} \qquad K_f = 2.5 \times 10^{11}$$

$$HT^{2-} \rightleftharpoons T^{3-} + H^{+} \qquad K_{a_3} = 5.3 \times 10^{-11}$$

$$H^{+} + OH^{-} \rightleftharpoons H_2O \qquad K_w^{-1} = 1.0 \times 10^{14}$$

$$Pb(OH)_{2(s)} + HT^{2-} \rightleftharpoons PbT^{-} + H_2O + OH^{-}$$

$$K_{eq} = \frac{K_{sp} \cdot K_f \cdot K_{a_3}}{K_w}$$

$$= 2.1 \times 10^{-5}$$

We want the total lead in solution

$[Pb]_T = [Pb^{2+}] + [PbT^{\ominus}]$ in water

containing $25 \frac{mg}{L}$ NTA

Since $K_{sp}(Pb(OH)_2)$ is so low $(\sim 10^{-20})$

and $K_f(PbT^{\ominus})$ is so high $(\sim 10^{11})$

it is safe to assume that $[Pb^{2+}] << [PbT^{\ominus}]$

and $[Pb]_T \simeq [PbT^{\ominus}]$

Now, $[NTA] = \frac{25 \text{ mg}}{L} \times \frac{1 \text{ mol}}{257{,}000 \text{ mg}} = 9.7 \times 10^{-5} M$

where MW of $Na_3T = 257$ g/mol

At equilibrium, $K_{eq} = \frac{[PbT^{\ominus}][OH^{\ominus}]}{[HT^{2-}]} = 2.1 \times 10^{-5}$

and $[NTA]_T = [HT^{2-}] + [PbT^{\ominus}]$ by mass balance

(i.e. the total amt. of NTA present will be equal to the sum of the uncomplexed NTA plus the NTA complexed to lead.)

$\therefore [HT^{2-}] = 9.7 \times 10^{-5} \frac{mol}{L} - [PbT^{\ominus}]$

So $K_{eq} = \frac{[PbT^{\ominus}][OH^{\ominus}]}{(9.7 \times 10^{-5} M - [PbT^{\ominus}])} = 2.1 \times 10^{-5}$

At pH = 8.0, $[OH^{\ominus}] = 1.0 \times 10^{-6}$ M

let 'x' represent $[PbT^{\ominus}]$

so
$$\frac{(x)(1.0 \times 10^{-6} M)}{(9.7 \times 10^{-5} M - x)} = 2.1 \times 10^{-5}$$

$$1.0 \times 10^{-6}\, x = 2.1 \times 10^{-5} (9.7 \times 10^{-5} - x)$$

$$1.0 \times 10^{-6} x = 2.04 \times 10^{-9} - 2.1 \times 10^{-5} x$$

3 $2.2 \times 10^{-5}\, x = 2.04 \times 10^{-9}$

$\therefore x = 9.3 \times 10^{-5}$ M $= [PbT^{\ominus}]$

$$[Pb]_T \simeq 9.3 \times 10^{-5} \frac{mol}{L} \times \frac{207\ g}{mol} \times \frac{10^6\ \mu g}{g} = 1.9 \times 10^4 \frac{\mu g}{L}$$

which is 19,000 ppb or 19 ppm Pb in sol'n.

In the absence of NTA we use

$$Pb(OH)_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

$$K_{sp} = [Pb^{2+}][OH^-]^2$$

$$\therefore [Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.6 \times 10^{-20}}{(1.0 \times 10^{-6})^2}$$

$$= 1.6 \times 10^{-8} \frac{mol}{L}$$

$$[Pb]_T = 1.6 \times 10^{-8} \frac{mol}{L} \times \frac{207\ g}{mol} \times \frac{10^6\ \mu g}{g} = 3.3 \frac{\mu g}{L}$$

which is 3.3 ppb or 0.003 ppm Pb in sol'n