

Practice Problem Set Ten

- A. Calculate the fraction of each Cd^{+2} containing species and the average number of ligands gained for an uncomplexed iodide concentration of 0.0550 M .
- B. If the total cadmium concentration in A is 0.100 M , find the total iodide concentration.
- C. Prepare a distribution diagram for I^- with Cd^{+2} . Label each curve with the chemical formula of the species it represents.
- D. Calculate the molarity of each silver containing species for a total Ag^+ concentration of $1.00 \times 10^{-4} \text{ M}$ in a pH 8.00 solution that contains 0.10 M total NH_3 .
- E. What is the value of $[\text{Zn}^{+2}]$ in a solution containing $1.4 \times 10^{-6} \text{ M}$ total zinc and $1.0 \times 10^{-5} \text{ M}$ total ethanediamine at pH 8.50?
- F. What is the molarity of each species present in a solution containing 0.020 M Hg^{+2} and 0.30 M ammonia at pH 8.70?
- G. What is the molarity of each species present in a solution containing 0.0132 M Pb^{+2} and 0.50 M acetic acid at pH 3.50?
- H. Plot the $-\log$ of the free metal concentration as a function of the fraction titrated for the titration of 0.0010 M Co^{+2} with 0.0020 M EDTA^{-4} in the presence of 0.30 M NH_3 and 0.10 M NH_4Cl .

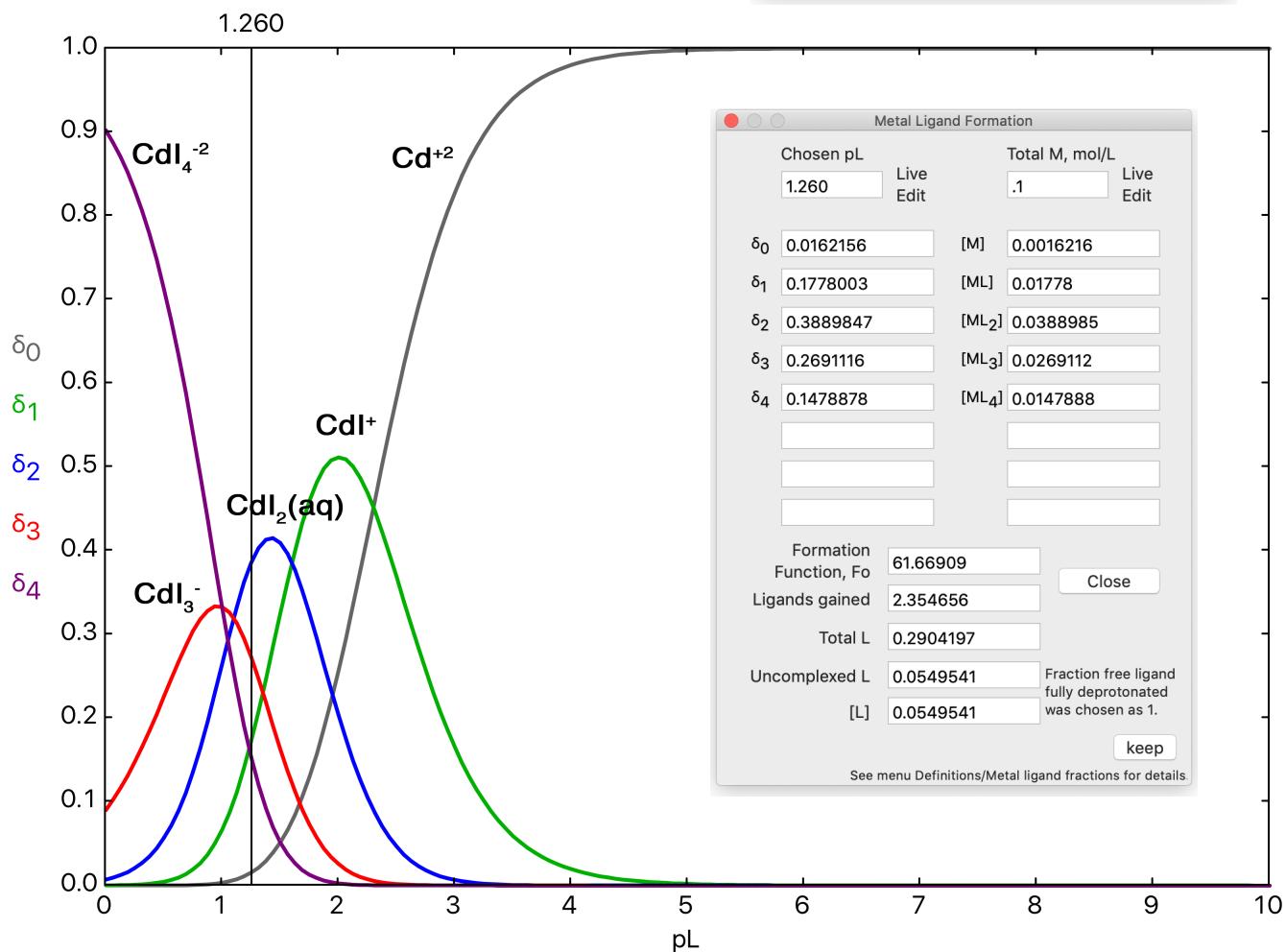
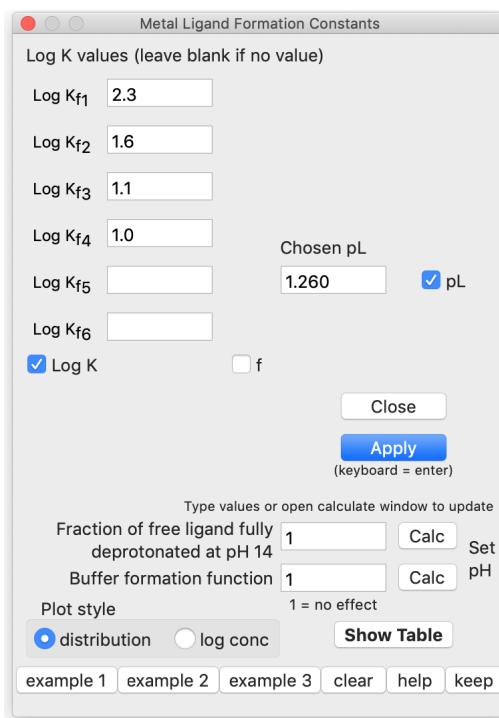
A. We are given $\frac{[L]}{\alpha_n} = 0.0550$. Since HI is a strong monoprotic acid, $\alpha_1 = 1$ (otherwise use the pH to solve for α_n) so $[I^-] = 0.0550$ and $pL = 1.260$. For Cd^{+2} and I^- , $K_f1 = 10^{2.3}$, $K_f2 = 10^{1.6}$, $K_f3 = 10^{1.1}$, $K_f4 = 10^{1.0}$.

Solve/delta fractions (distribution plot style) and click on **Show Table** for results.

$$\delta_0 = \frac{[Cd^{+2}]}{C_M} = 0.0162, \delta_1 = \frac{[CdI^+]}{C_M} = 0.178,$$

$$\delta_2 = \frac{[CdI_2(aq)]}{C_M} = 0.389, \delta_3 = \frac{[CdI_3^-]}{C_M} = 0.269,$$

$$\delta_4 = \frac{[CdI_4^{-2}]}{C_M} = 0.148, \text{ and } \bar{n} = 2.355$$



B. If $C_M = 0.100$ M (add to upper right in window above) then the total iodide molarity is $C_L = \bar{n} C_M + [L]/\alpha_1 = 2.355(0.100) + 0.0550 = 0.290$

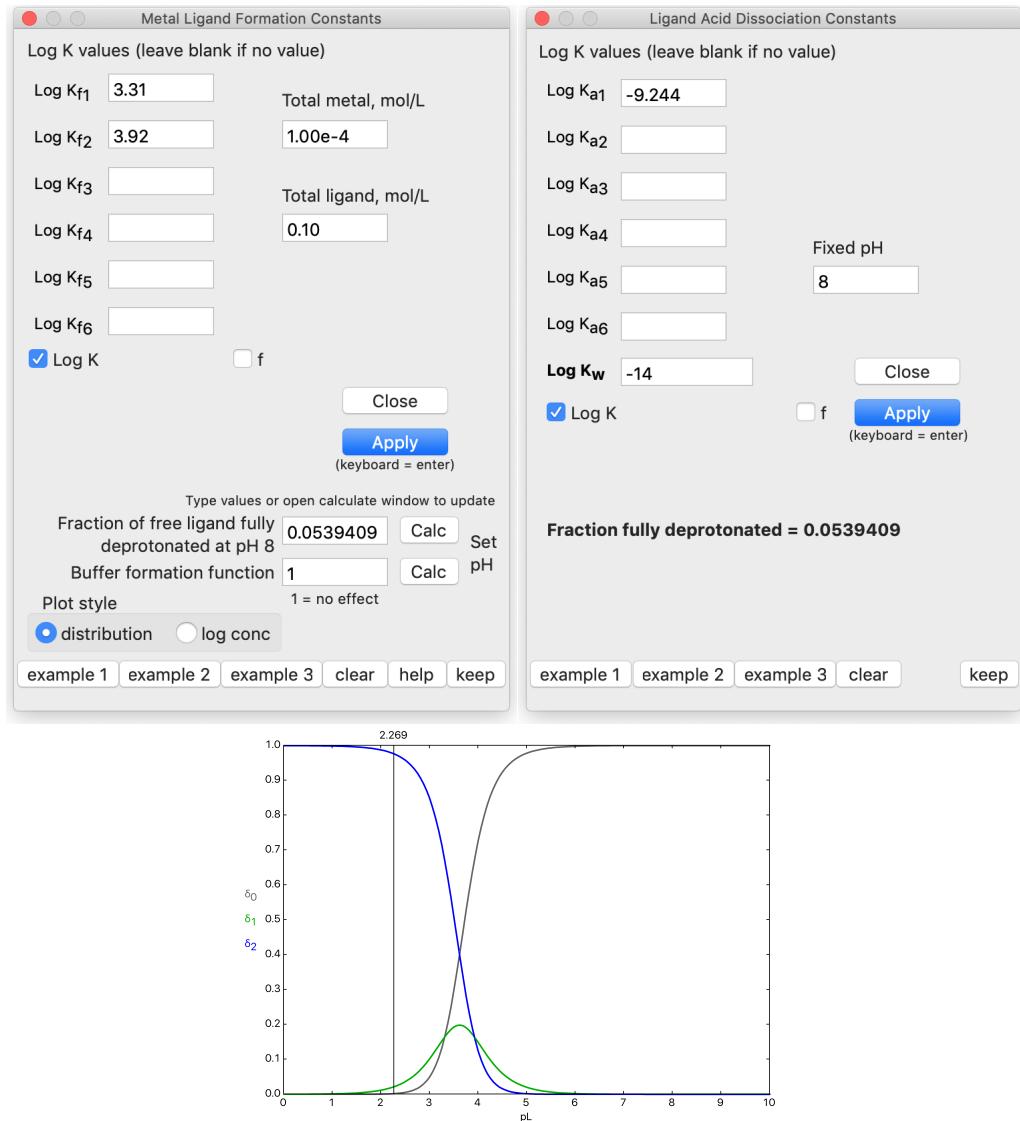
C. Plot/Distribution vs pL for metal Kf and label as shown above.

D. Solve for ligand concentration.

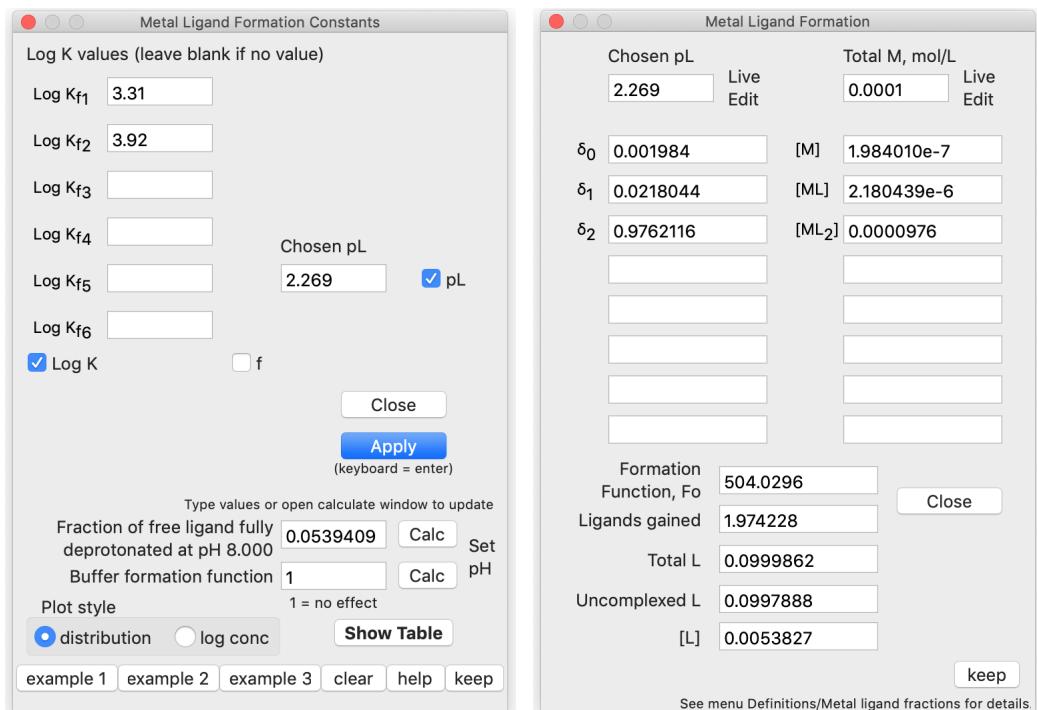
For Ag^+ and NH_3 ,
 $K_{f1} = 10^{3.31}$,
 $K_{f2} = 10^{3.92}$.

We are given
 $C_M = 1.00 \times 10^{-4} \text{ M}$,
and $C_L = 0.10 \text{ M}$.

Since NH_3 is a weak monobase,
 α_n depends on
 $K_a = 10^{-9.244}$ and
pH 8.00. Click the first **Calc button** to find $\alpha_1 = 0.05394$ so $[L] = \alpha_1(0.10) = 0.005394$ and $pL = 2.269$ as displayed on the plot.



Solve for delta fractions with $pL = 2.269$ and click **Show Table** to find $[\text{Ag}^+] = \delta_0 C_M = 1.98 \times 10^{-7}$, $[\text{Ag}(\text{NH}_3)^+] = \delta_1 C_M = 2.18 \times 10^{-6}$, $[\text{Ag}(\text{NH}_3)_2^+] = \delta_2 C_M = 9.76 \times 10^{-5}$.



E. Solve for ligand concentration.

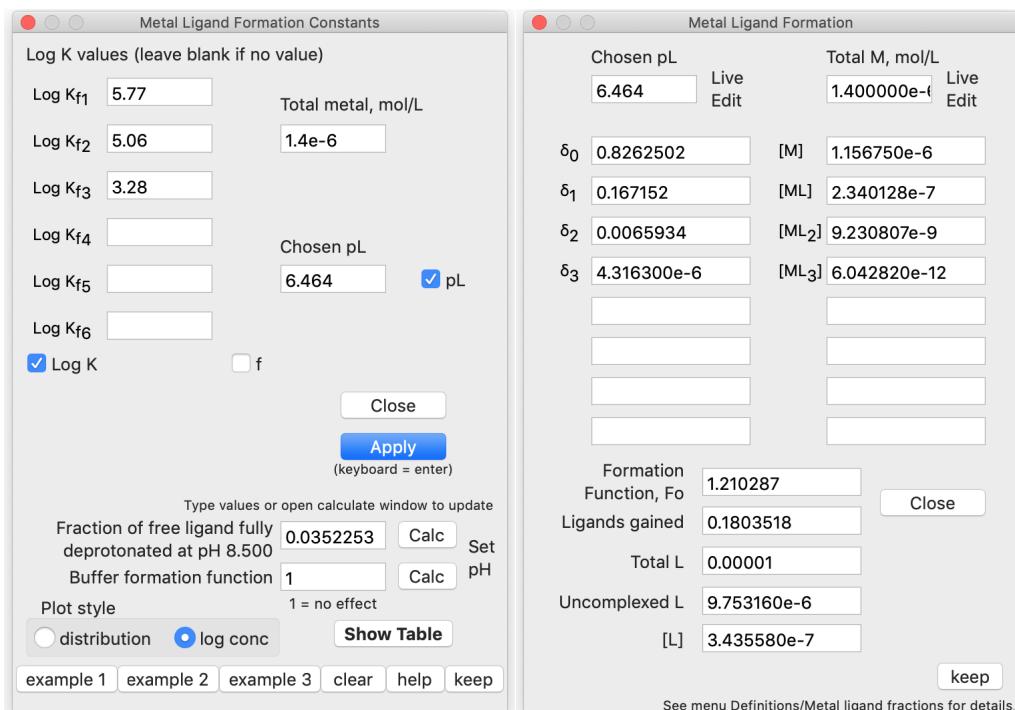
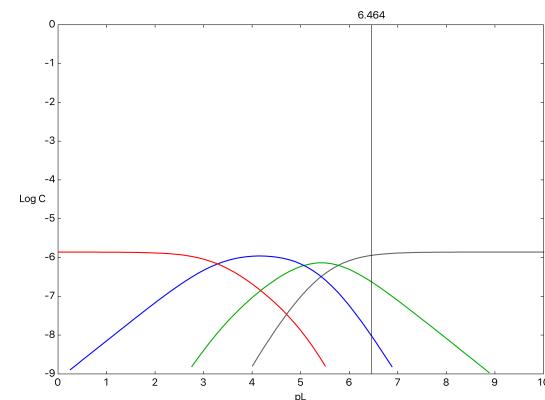
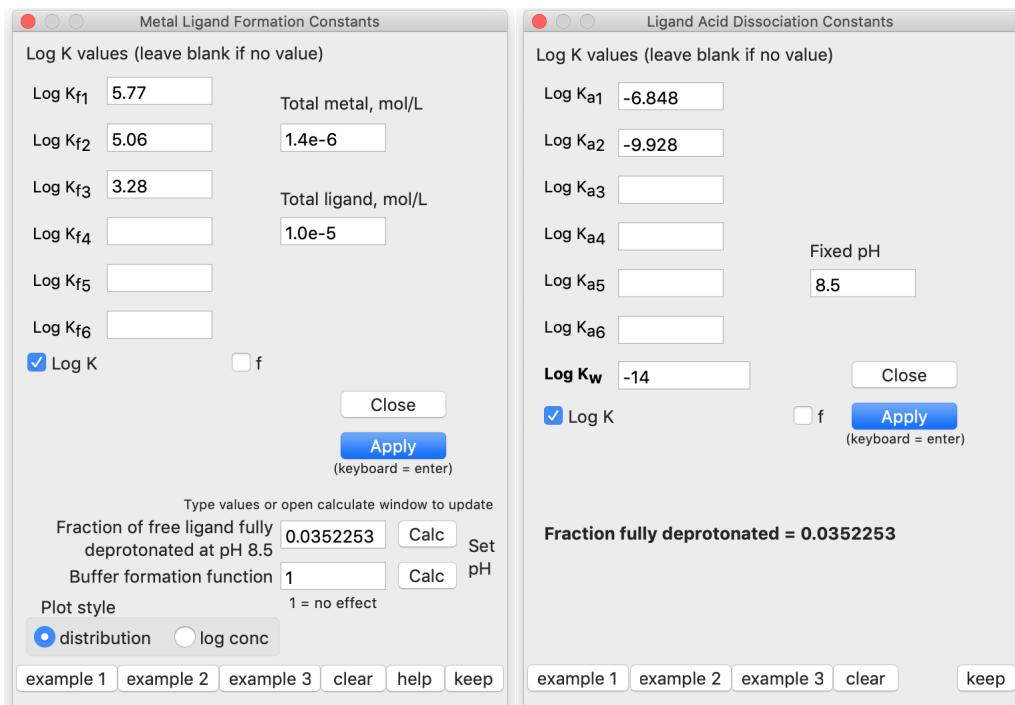
For Zn^{+2} and en,
 $K_{f1} = 10^{5.77}$,
 $K_{f2} = 10^{5.06}$,
 $K_{f3} = 10^{3.28}$.

We are given

$$C_M = 1.4 \times 10^{-6} \text{ M},$$

$$C_L = 1.0 \times 10^{-5} \text{ M}.$$

Since en is a weak dibase, α_n depends on $K_{a1} = 10^{-6.848}$, $K_{a2} = 10^{-9.928}$ and pH 8.50. Click the first **Calc button** to find $\alpha_2 = .03523$ and $pL = 6.464$ at the top of the graph.



Solve for delta fractions and then Show Table to find $[Zn^{+2}] = \delta_0 C_M = 1.16 \times 10^{-6}$.

F. Solve for ligand concentration.

For Hg^{+2} and NH_3 ,
 $K_{f1} = 108.8$,
 $K_{f2} = 108.7$,
 $K_{f3} = 101.00$,
 $K_{f4} = 100.78$.

We are given
 $C_M = 0.020 \text{ M}$,
 $C_L = 0.30 \text{ M}$.

Since NH_3 is a weak monobase, α_n depends on $K_a = 10^{-9.244}$ and pH 8.70. Click the first **Calc button** to find $\alpha_1 = .2222$ and $pL = 1.256$ at the top of the graph.

Solve for delta fractions and find
 $[\text{Hg}^{+2}] = \delta_0 C_M = 1.19 \times 10^{-17}$,
 $[\text{Hg}(\text{NH}_3)^{+2}] = \delta_1 C_M = 4.14 \times 10^{-10}$,
 $[\text{Hg}(\text{NH}_3)_2^{+2}] = \delta_2 C_M = 0.0115$,
 $[\text{Hg}(\text{NH}_3)_3^{+2}] = \delta_3 C_M = 0.00638$,
 $[\text{Hg}(\text{NH}_3)_4^{+2}] = \delta_4 C_M = 0.00213$ and uncomplexed ligand = 0.2496

Solve for alpha fractions and Show Table

$$\text{to find } \alpha_0 \frac{[L]}{\alpha_1} =$$

$$[\text{NH}_4^+] = 0.194.$$

Metal Ligand Formation Constants

Log K values (leave blank if no value)

- Log K_{f1}: 8.8
- Log K_{f2}: 8.7
- Log K_{f3}: 1.00
- Log K_{f4}: 0.78
- Log K_{f5}:
- Log K_{f6}:

Total metal, mol/L: 0.020

Log K f

Ligand Acid Dissociation Constants

Log K values (leave blank if no value)

- Log K_{a1}: -9.244
- Log K_{a2}:
- Log K_{a3}:
- Log K_{a4}:
- Log K_{a5}:
- Log K_{a6}:

Fixed pH: 8.700

Log K f **Apply** (keyboard = enter)

Fraction fully deprotonated = 0.2222493

Metal Ligand Formation Constants

Log K values (leave blank if no value)

- Log K_{f1}: 8.8
- Log K_{f2}: 8.7
- Log K_{f3}: 1.00
- Log K_{f4}: 0.78
- Log K_{f5}:
- Log K_{f6}:

Total metal, mol/L: 0.020

Log K f

Metal Ligand Formation

Chosen pL: 1.256

Total M, mol/L: 0.02

δ_0 : 5.908211e-16	[M]: 1.181642e-17
δ_1 : 2.067550e-8	[ML]: 4.135100e-10
δ_2 : 0.5747196	[ML ₂]: 0.0114944
δ_3 : 0.3187543	[ML ₃]: 0.0063751
δ_4 : 0.1065261	[ML ₄]: 0.0021305

Formation Function, F_o: 1.692560e+15

Ligands gained: 2.531806

Total L: 0.3001873

Uncomplexed L: 0.2495512

[L]: 0.0554626

Show Table

Acid Dissociation Constants

Log K values (leave blank if no value)

- Log K_{a1}: -9.244
- Log K_{a2}:
- Log K_{a3}:
- Log K_{a4}:
- Log K_{a5}:
- Log K_{a6}:

Total acid, mol/L: 0.2495512

Log K f **Apply** (keyboard = enter)

Acid Dissociation

Chosen pH: 8.700

Total A, mol/L: 0.2495512

a_0 : 0.7777507	[HA]: 0.1940886
a_1 : 0.2222493	[A ⁻]: 0.0554626

Dissociation Function, D_o: 1.285759

Protons lost: 0.2222493

Show Table

G. Solve for ligand concentration.

For Pb^{+2} and



$$K_f1 = 10^{2.7},$$

$$K_f2 = 10^{1.4}.$$

We are given

$$C_M = 0.0132 \text{ M},$$

$$C_L = 0.50 \text{ M}.$$

Since CH_3COO^- is a weak monobase, α_n depends on

$$K_a = 10^{-4.756}$$

and pH 3.50. Click the first **Calc button** to find $\alpha_1 =$

$$0.05255 \text{ and } pL = 1.596 \text{ at the top of the graph.}$$

Solve for delta fractions and find

$$[\text{Pb}^{+2}] = \delta_0 C_M$$

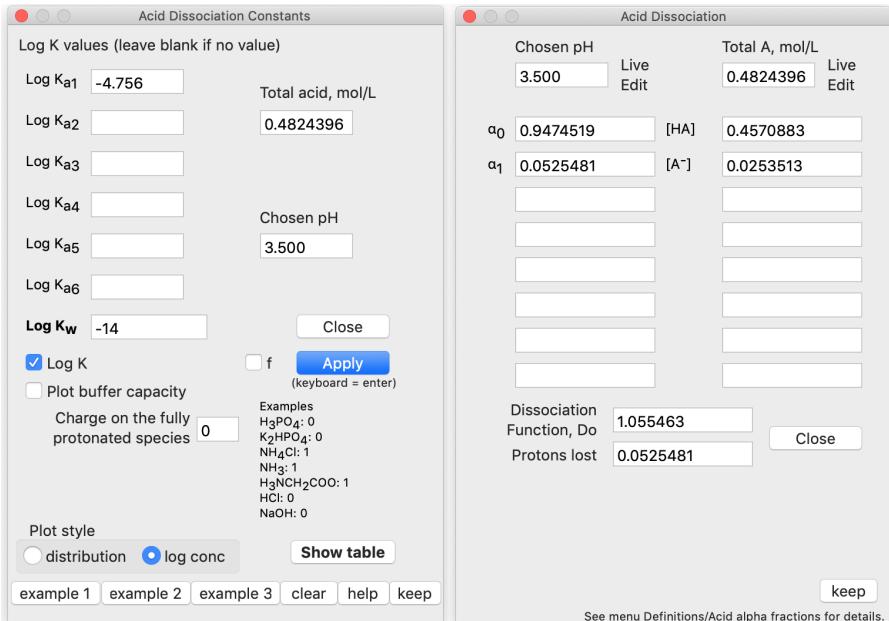
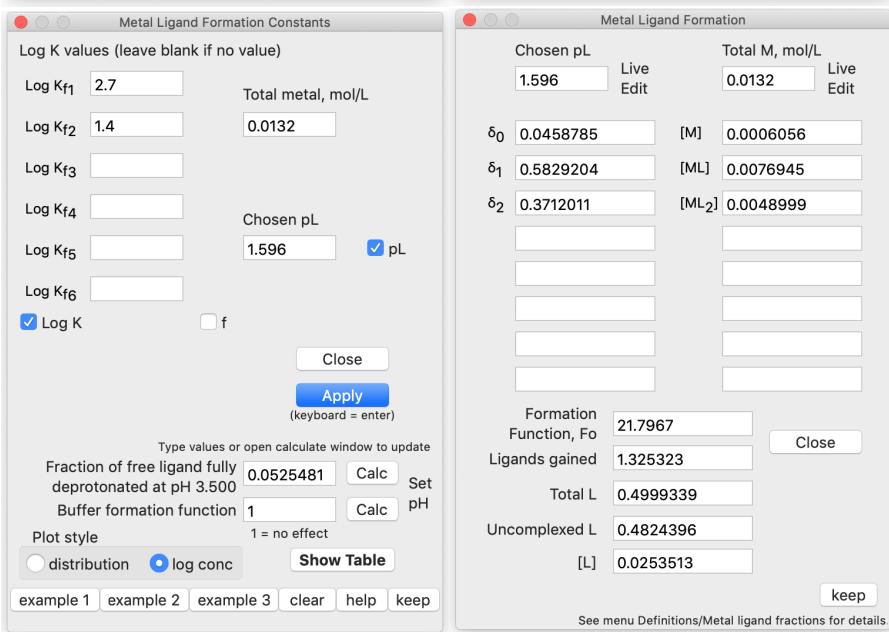
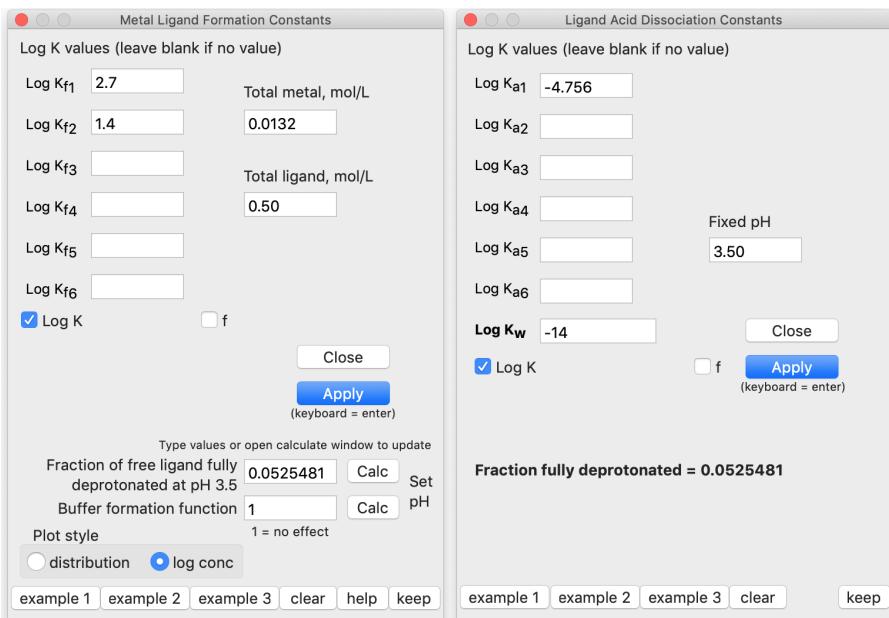
$$= 0.000606,$$

$$[\text{Pb}(\text{CH}_3\text{COO})^+] =$$

$$\delta_1 C_M = 0.007691,$$

$$[\text{Pb}(\text{CH}_3\text{COO})_2(\text{aq})] = \delta_2 C_M = 0.00490$$

and uncomplexed ligand = 0.4824



Solve for alpha fractions and find

$$\alpha_0 \frac{[L]}{\alpha_1}$$

$$= [\text{CH}_3\text{COOH}]$$

$$= 0.457.$$

H. *Plot pMetal titration.* The 0.30 M NH₃ and 0.10 M NH₄Cl will act as a buffer to determine the pH. Click the **second Calc button**. Based on the K_a for NH₄⁺ and the buffer concentrations the pH is 9.721. The NH₃ will also act as a ligand so enter the Co⁺² NH₃ K_f values. The buffer formation function of ammonia with Co⁺² is 2339. Click the **first Calc button**. The fraction of EDTA fully deprotonated at pH 9.721 depends on the K_a values for H₄EDTA⁺² and is 0.183.

Metal Ligand Formation Constants

Log K values (leave blank if no value)

Log K _{f1}	16.45	Initial metal, mol/L
Log K _{f2}		0.0010
Log K _{f3}		Ligand titrant, mol/L
Log K _{f4}		0.0020
Log K _{f5}		
Log K _{f6}		ϕ is fraction titrated
<input checked="" type="checkbox"/> Log K	<input type="checkbox"/> mL	<input type="checkbox"/> f
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Type values or open calculate window to update

Fraction of free ligand fully deprotonated at pH 9.721: 0.1832272 Set pH
 Buffer formation function: 2338.997 pH
 1 = no effect

Metal and Buffer Equilibria

Log K values (leave blank if no value)

Log K _a	-9.244	Buffer base form, mol/L
Log K _{f1}	1.99	0.30
Log K _{f2}	1.51	Buffer acid form, mol/L
Log K _{f3}	0.93	0.10
Log K _{f4}	0.64	Buffer pH = 9.721
Log K _{f5}	0.06	This buffer controls solution pH.
Log K _{f6}	-0.74	<input type="button" value="Close"/>
<input checked="" type="checkbox"/> Log K	<input type="checkbox"/> f	<input style="background-color: #0070C0; color: white; font-weight: bold; padding: 2px 10px; border-radius: 5px; border: none; width: 100%;" type="button" value="Apply"/>
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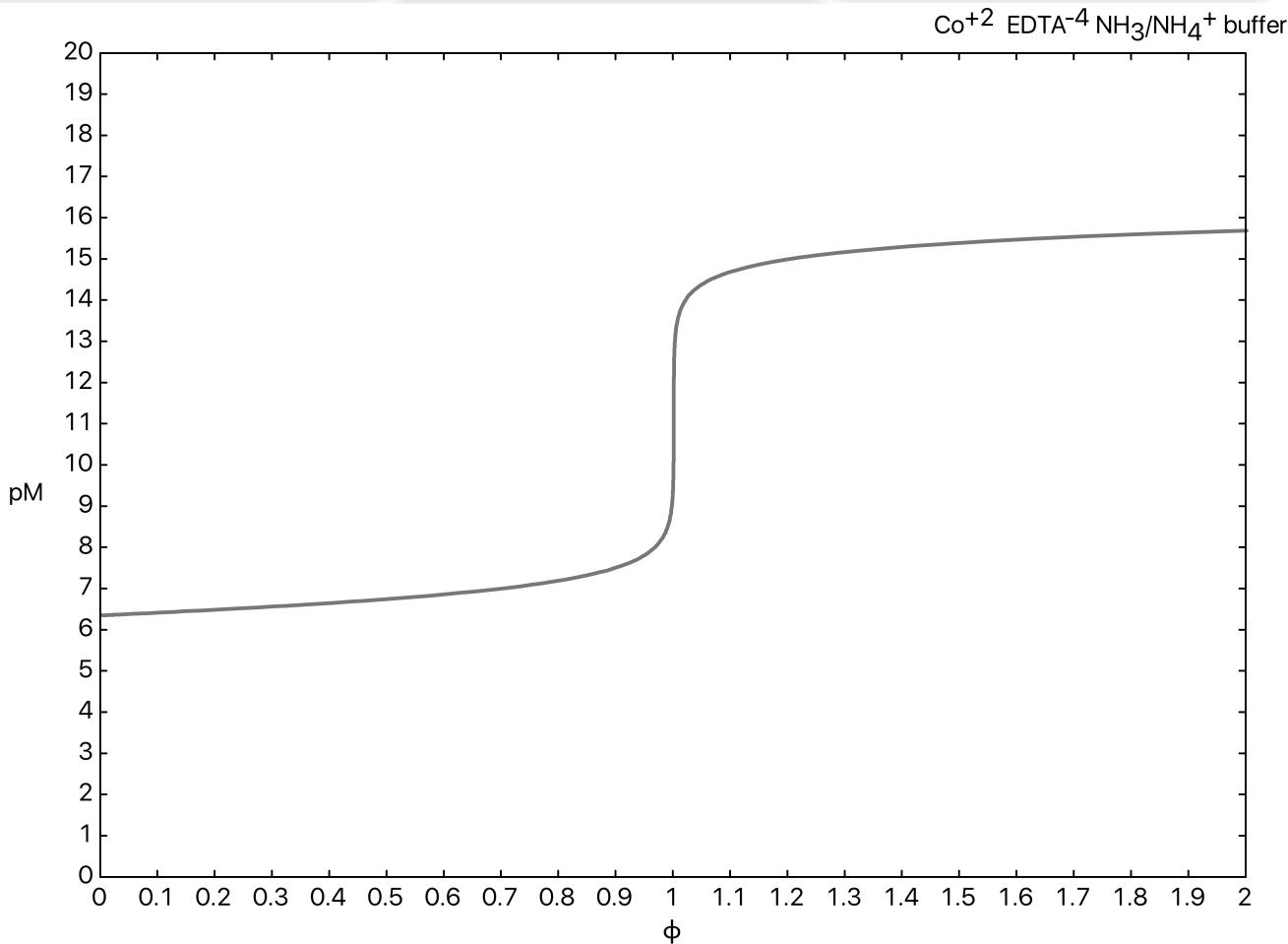
Buffer formation function = 2338.997

Ligand Acid Dissociation Constants

Log K values (leave blank if no value)

Log K _{a1}	0.00	
Log K _{a2}	-1.5	
Log K _{a3}	-2.00	
Log K _{a4}	-2.69	Fixed pH
Log K _{a5}	-6.13	9.721
Log K _{a6}	-10.37	Solution pH controlled by buffer.
Log K _w	-0.74	<input type="button" value="Close"/>
<input checked="" type="checkbox"/> Log K	<input type="checkbox"/> f	<input style="background-color: #0070C0; color: white; font-weight: bold; padding: 2px 10px; border-radius: 5px; border: none; width: 100%;" type="button" value="Apply"/>
(keyboard = enter)		

Fraction fully deprotonated = 0.1832272



Note: it is a helpful to use Option/Title to label your graphs.