

① First, calculate the ionic strength of the solution

$$I = \frac{1}{2} \sum c_i z_i^2$$

$$I = \frac{1}{2} \left[[Na^+] (1)^2 + [Ca^{2+}] (2)^2 + [Mg^{2+}] (2)^2 + [K^+] (1) + [Cl^-] (-1)^2 + [SO_4^{2-}] (-2)^2 + [HCO_3^-] (-1)^2 + [CO_3^{2-}] (-2)^2 \right]$$

in an open system

$$I = \frac{1}{2} \left[(0.25 \times 10^{-3}) (1)^2 + (0.2 \times 10^{-3}) (2)^2 + (0.1 \times 10^{-3}) (2)^2 + (0.03 \times 10^{-3}) (1)^2 + (0.32 \times 10^{-3}) (-1)^2 + (0.2 \times 10^{-3}) (-2)^2 + \left(\frac{10^{-6.35} \cdot 10^{-11.7} \cdot 10^{-3.5}}{10^{-8}} \right) (-1)^2 + \left(\frac{10^{-6.35} \cdot 10^{-10.33} \cdot 10^{-1.47} \cdot 10^{-3.5}}{(10^{-8})^2} \right) (-2)^2 \right]$$

$$I = 1.54 \times 10^{-3}$$

The ionic strength will affect the value of K_{a1} & K_{a2} for the carbonate system. Solving one iteration on the values of $[HCO_3^-]$ and $[CO_3^{2-}]$ (see following spreadsheet)

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Water A

pH	8.0	pK _w	14	K _w	1E-14	*K _w	1.092E-14
		pK _{a1}	6.35	Ka ₁	4.467E-07	*Ka ₁	4.878E-07
		pK _{a2}	10.33	Ka ₂	4.677E-11	*Ka ₂	5.578E-11
		pK _h	1.47	K _h	3.388E-02		
		pP _{co2}	3.5	P _{co2}	3.162E-04		

Species in Solution	Conc (mM)	Conc (M)	Charge	z _i ² c _i	γ _L Initial	γ _L 1st Iteration
H ⁺	1.00E-08	1.00E-08	1		0.9569	0.9566
OH ⁻	1.09E-06	1.09E-06	-1		0.9569	0.9566
Ag(I)	5.00E-11	5.00E-11	1	5.00E-11	0.9569	0.9566
Na ⁺	0.00025	0.00025	1	2.50E-04	0.9569	0.9566
Ca ²⁺	0.20	0.0002	2	8.00E-04	0.8385	0.8374
Cl ⁻	0.32	0.00032	-1	3.20E-04	0.9569	0.9566
Mg ²⁺	0.10	0.0001	2	4.00E-04	0.8385	0.8374
K ⁺	0.03	0.00003	1	3.00E-05	0.9569	0.9566
SO ₄ ²⁻	0.20	0.0002	-2	8.00E-04	0.8385	0.8374

Carbonate Concentrations at Standard State

HCO ₃ ⁻	4.79E-04	-1	4.79E-04	0.9569	0.9566
CO ₃ ²⁻	2.24E-06	-2	8.95E-06	0.8385	0.8374

Ionic Strength Correction: First Iteration

HCO ₃ ⁻	5.23E-04	-1	5.23E-04	0.9566
CO ₃ ²⁻	2.92E-06	-2	1.17E-05	0.8374

Ionic Strength 1.57E-03

Ionic Strength 1.54E-03

shows that there is a slight effect of Ionic strength (see spread sheet); such that

$$I = 1.57 \times 10^{-3}$$

To make matters simple accept this value as I

Now calculate the activity coefficients w. Davies Eqn.

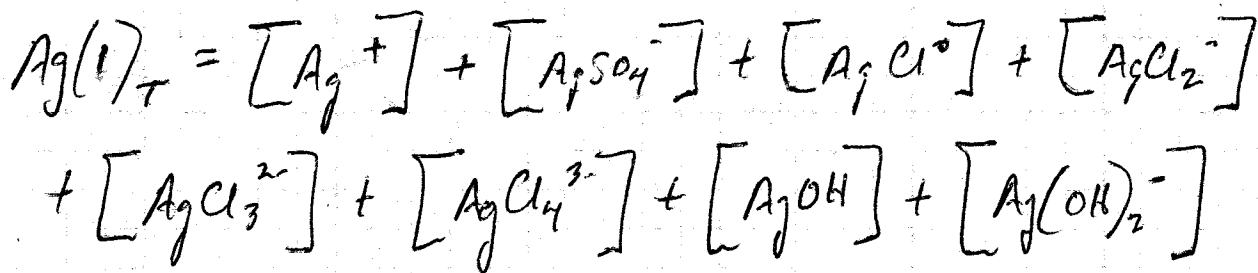
$$\log \gamma_{\pm} = -0.51 \left(\frac{z_+ z_-}{1} \right)^2 \left(\frac{(1.57 \times 10^{-3})^{1/2}}{1 + (1.57 \times 10^{-3})^{1/2}} - 0.2(1.57 \times 10^{-3}) \right)$$

$$\log \gamma_{\pm} = -1.927 \times 10^{-2} \quad \gamma_{\pm} = 0.9566$$

$$\log \gamma_{2+/2-} = -0.51 \left(\frac{z_+ z_-}{2} \right)^2 \left(\frac{(1.57 \times 10^{-3})^{1/2}}{1 + (1.57 \times 10^{-3})^{1/2}} - 0.2(1.57 \times 10^{-3}) \right)$$

$$\log \gamma_{2+/2-} = -7.71 \times 10^{-2} \quad \gamma_{2+/2-} = 0.8373$$

Now sum up the total $\text{Ag}(I)$



Accounting for the ionic strength corrections

$$[M_e L_n] = \gamma_{M_e} [M_e] \frac{\gamma_L^n}{\gamma_{M_e L_n}} \beta_{M_e L_n} [L]^n$$

where $M_e = \text{Ag}^{2+}$

This corrects β for ionic strength

$$\text{then } Ag(I)_T = \gamma_{Ag^+} [Ag^+] \left(1 + \sum \frac{\gamma_L^n}{\gamma_{Ag^+}} \beta_{n, AgL} [L]^n \right)$$

Where the ligands $[L]^n$ are those forming the complexes listed above, SO_4^{2-} , Cl^- , and OH^-

The values of β 's are found in Tables A.2 and A.3

to find $[Ag^+]$ use the definition of α

$$\alpha_{Ag^+} = \frac{[Ag^+]}{Ag(I)_T} = \frac{1}{\gamma_{Ag^+} \left(1 + \sum \frac{\gamma_L^n}{\gamma_{Ag^+}} \beta_{n, AgL} [L]^n \right)}$$

$$\text{then } [Ag^+] = \alpha_{Ag^+} \cdot Ag(I)_T$$

The above calculations are carried out on a spreadsheet.

For Water A

$$\alpha_{Ag^+} = 0.6567 \quad [Ag^+] = 3.2P \times 10^{-11} M$$

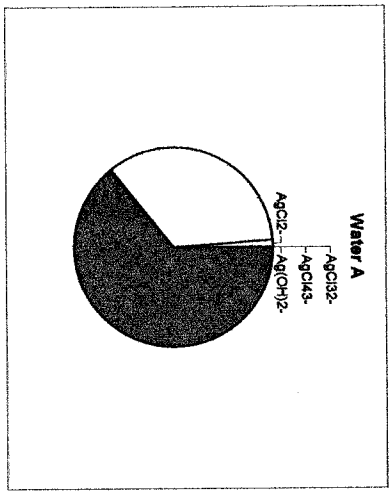
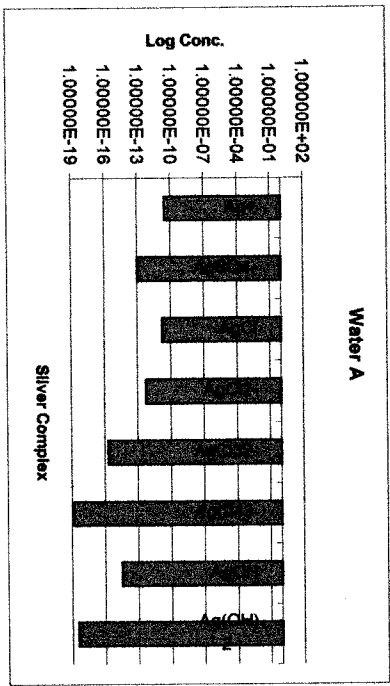
65.7% of $Ag(I)$ is Ag^+
(see following spreadsheet)

Water A	Metal Complexes	Charge	$\gamma_{M_{aq}}$	log β	β	$\gamma_L^0 \gamma_{M_{aq}}$	[L] ⁿ	$(\beta \gamma_L^0 \gamma_{M_{aq}})^n [L]^n$	$\gamma_{M_{aq}} [M_{aq}]$	[M _{aq}]	$\alpha_{M_{aq}}$	% Composition
	Ag ⁺	-1	0.9566	1.29	1.950E+01	0.8754	2.000E-04	3.414E-03	3.141E-11	3.284E-11	6.567E-01	65.67
	AgSO ₄ ⁻	0	1.0000	3.27	1.862E+03	0.9566	3.200E-04	5.700E-01	3.141E-11	1.072E-13	2.145E-03	0.21
	AgCl	-1	0.9566	5.27	1.862E+05	0.9566	1.024E-07	1.824E-02	3.141E-11	1.791E-11	3.581E-01	35.81
	AgCl ₂ ⁻	-2	0.8374	5.29	1.950E+05	1.0453	3.277E-11	6.679E-06	3.141E-11	5.730E-13	1.146E-02	1.15
	AgCl ₃ ²⁻	-3	0.6709	5.51	3.236E+05	1.2483	1.048E-14	4.236E-09	3.141E-11	1.330E-19	2.661E-09	0.00
	AgOH	0	1.0000	2.00	1.000E+02	0.9566	1.092E-06	1.045E-04	3.141E-11	3.281E-15	6.563E-05	0.01
	Ag(OH) ₂ ⁻	-1	0.9566	4.00	1.000E+04	0.9566	1.193E-12	1.141E-08	3.141E-11	3.584E-19	7.167E-09	0.00

$$\sum (\beta \gamma_L^0 \gamma_{M_{aq}}^n [L]^n) = 5.918E-01$$

$$1 + \sum (\beta \gamma_L^0 \gamma_{M_{aq}}^n [L]^n) = 1.592E+00$$

$$\alpha_{Ag^+} = \frac{1}{1.592E+00} = 6.284E-01$$



One could also define a modified β as

$$*\beta = \frac{\gamma_{me} \gamma_L^n}{\gamma_{meL}}$$

then $[AgL_n] = [Ag^{2+}] *\beta [L]^n$

These calculations are carried out in the following spreadsheet with similar results to the first method.

Ag(I) Speciation: 63.8% Ag^+ , 34.9% $AgCl$
1.1% $AgCl_2^-$

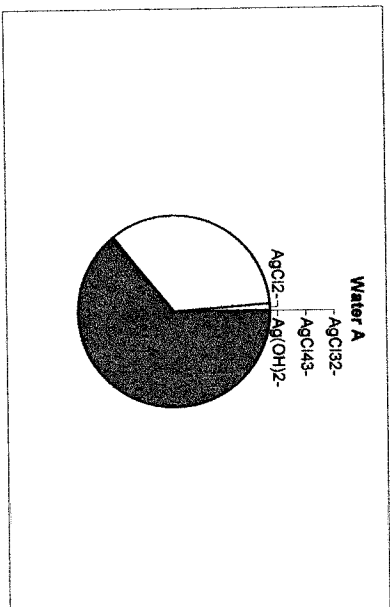
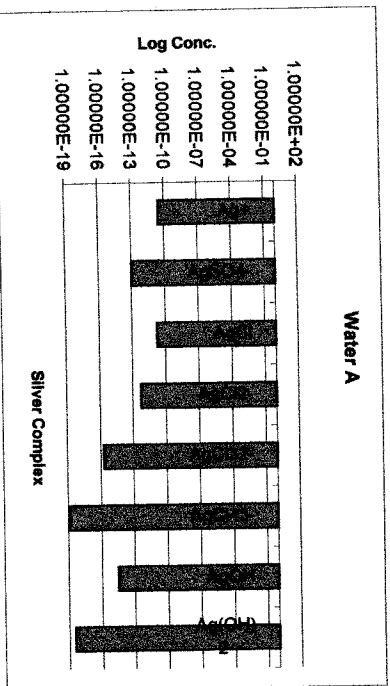
Water A Metal Complexes	Charge	γ_{metal}	log β	β	$\gamma_{metal}^n \gamma_{metal}$	* β	[L] ⁿ	* $\beta^* [L]^n$	[Me]	[MeL]	α_{MeL}	% Composition
Ag ⁺	-1	0.9566	1.29	1.950E+01	0.8374	1.633E+01	2.000E-04	3.266E-03	3.193E-11	3.193E-11	6.385E-01	63.85
AgSO ₄ ⁻	0	1.0000	3.27	1.862E+03	0.9151	1.704E+03	3.200E-04	5.453E-01	3.193E-11	1.741E-11	2.085E-03	0.21
AgCl	-1	0.9566	5.27	1.862E+05	0.9151	1.704E+05	1.024E-07	1.745E-02	3.193E-11	5.571E-13	3.482E-01	34.82
AgCl ₂ ⁻	-2	0.8374	5.29	1.950E+05	1.0000	1.950E+05	3.277E-11	6.389E-06	3.193E-11	2.040E-16	1.114E-02	1.11
AgCl ₃ ²⁻	-3	0.6709	5.51	3.236E+02	1.1941	3.884E+05	1.049E-14	4.052E-09	3.193E-11	1.294E-19	2.587E-09	0.00
AgCl ₄ ³⁻	0	1.0000	2.00	1.000E+02	0.9151	9.151E+01	1.092E-06	9.994E-05	3.193E-11	3.191E-15	6.381E-05	0.01
AgOH	0	0.9566	4.00	1.000E+04	0.9151	9.151E+03	1.193E-12	1.091E-08	3.193E-11	3.484E-19	6.969E-09	0.00
Ag(OH) ₂ ⁻	-1											

$$\sum(\beta^n \gamma_L^n \gamma_{metal}^n [L]^n) = 5.661E-01$$

$$1 + \sum(\beta^n \gamma_L^n \gamma_{metal}^n [L]^n) = 1.586E+00$$

$$\alpha_{Ag^+} = 6.385E-01$$

$$[Ag^+] = 3.193E-11$$



For water B, similar calculations are done,
The ionic strength doesn't change by a significant amount when accounting for its effect on carbonate species, because other ions are in much higher concentrations.

$$I = 0.345 \text{ thus } \gamma_{\pm} = 0.7023 \text{ and } \gamma_{\pm}^2 = 0.2432$$

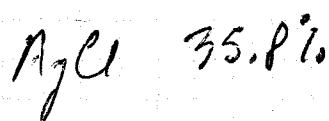
α_{Ag^+} and $[Ag^+]$ are calculated by spreadsheet, just as with water A with the following results

$$\alpha_{Ag^+} = 5.6 \times 10^{-5} \quad [Ag^+] = 2.8 \times 10^{-10}$$

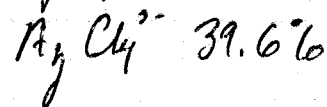
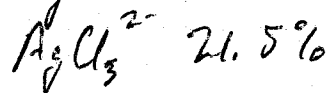
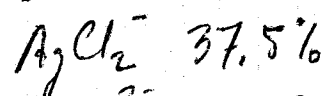
Ag^+ makes up just 0.006% of $Ag(I)$ in water B (see following spreadsheet)

(b) Other silver complexes of significance

Water A



Water B



(c) Because Ag^+ is the toxic form of $Ag(I)$, water A will have higher predicted silver toxicity

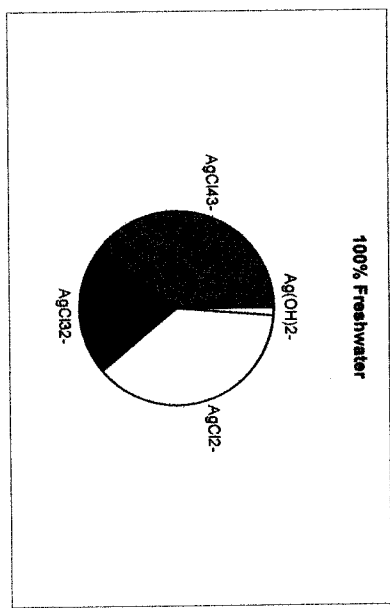
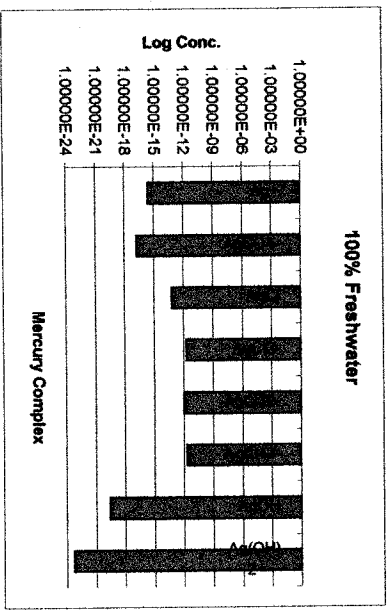
Metal Complexes	Charge	γ_{rel}	$\log \beta$	β	$\gamma_{rel} \gamma_{metal}$	$[L]^n$	$(\beta \gamma_{rel} \gamma_{metal} \cdot [L]^n)$	$\gamma_{rel} \cdot [Metal]$	$[Metal]$	α_{metal}	% Composition
Ag ⁺	-1	0.7022	1.29	1.950E+01	0.346	1.400E-02	9.454E-02	1.966E-16	2.800E-16	5.600E-05	0.006
AgSO ₄ ⁻	0	1.0000	3.27	1.862E+03	0.702	2.700E-01	3.531E+02	1.966E-16	1.859E-17	3.718E-06	0.000
AgCl	-1	0.7022	5.27	1.862E+05	0.702	7.290E-02	9.533E+03	1.966E-16	6.943E-14	1.389E-02	1.389
AgCl ₂ ⁻	-2	0.2432	5.29	1.950E+05	1.424	1.966E-02	5.466E+03	1.966E-16	1.875E-12	3.749E-01	37.493
AgCl ₃ ²⁻	-3	0.0416	5.51	3.236E+05	5.857	5.314E-03	1.007E+04	1.966E-16	1.075E-12	2.190E-01	21.498
AgCl ₄ ³⁻	0	1.0000	2.00	1.000E+02	0.702	2.028E-06	1.424E-04	1.966E-16	1.961E-12	3.982E-01	39.616
AgOH	0	0.7022	4.00	1.000E+04	0.702	4.112E-12	2.888E-08	1.966E-16	2.800E-20	5.600E-09	0.000
Ag(OH) ₂ ⁻	-1	0.7022	4.00	1.000E+04	0.702	4.112E-12	2.888E-08	1.966E-16	5.878E-24	1.136E-12	0.000

$$\Sigma(\beta \gamma_{rel} \gamma_{metal} \cdot [L]^n)$$

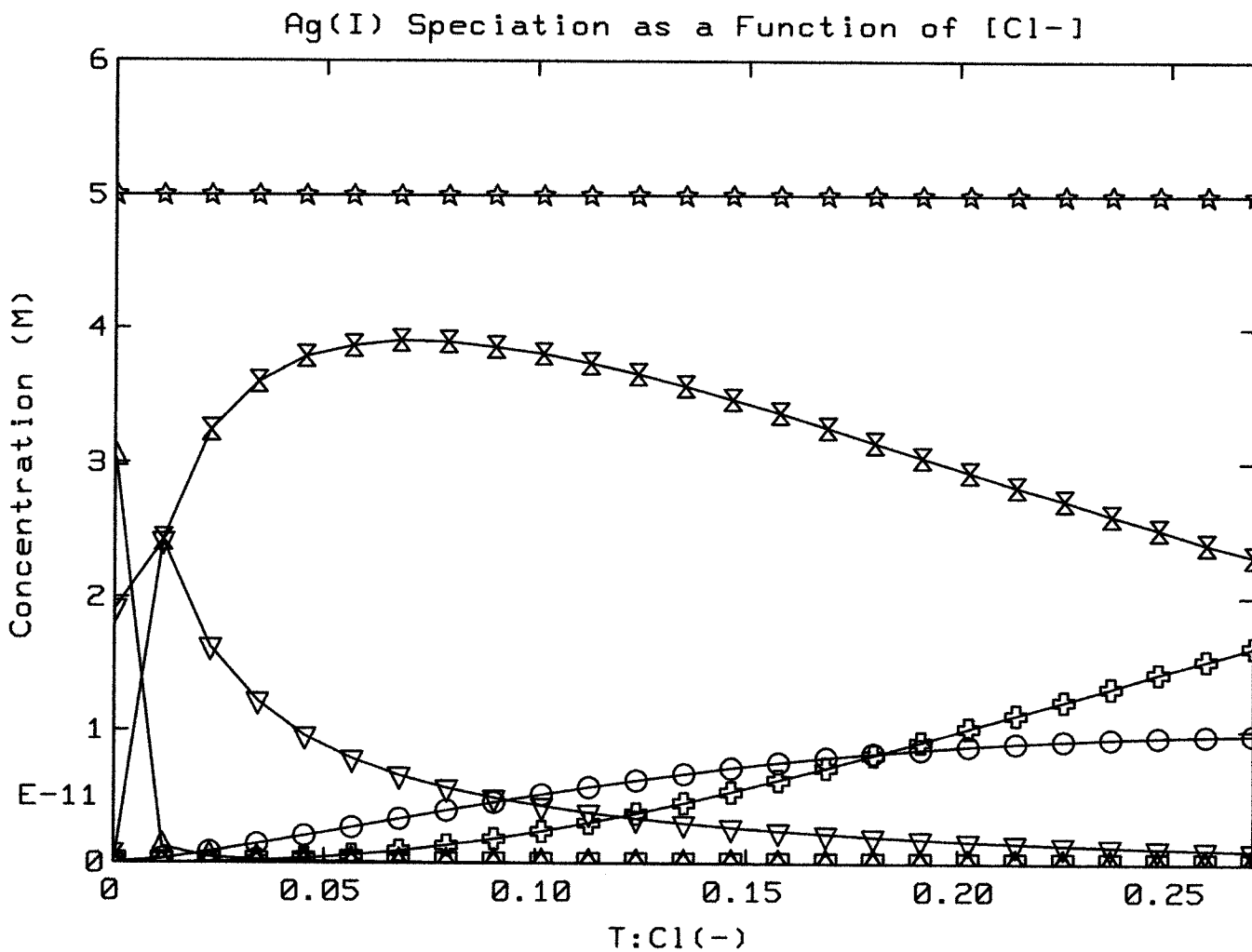
$$1 + \Sigma(\beta \gamma_{rel} \gamma_{metal} \cdot [L]^n)$$

$$\alpha_{Ag^+}$$

$$[Ag^+]$$



① MINEQL Output for Silver Complexes as a f([Cl⁻])



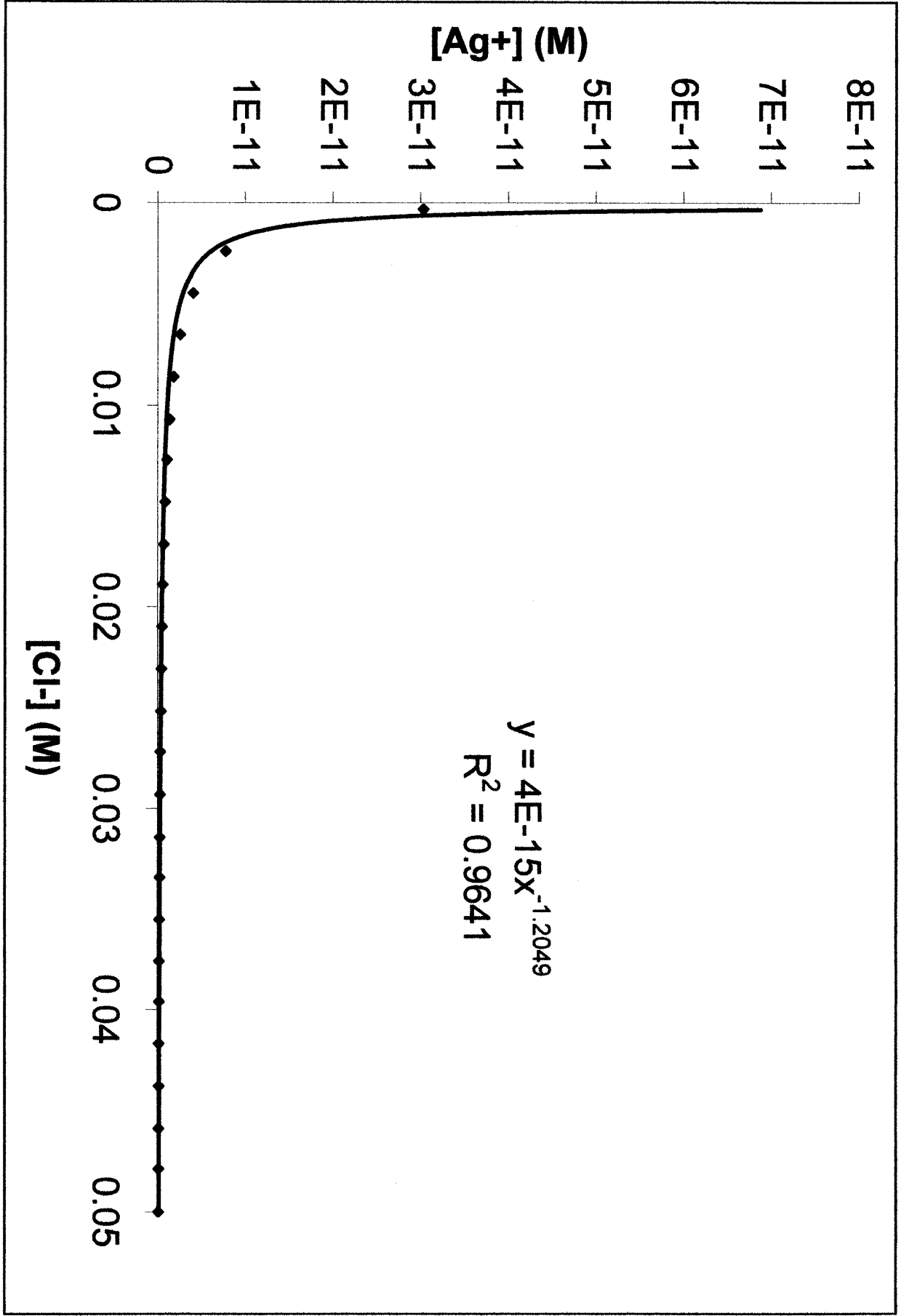
1: Ag(+) Δ 2: Ag(OH)₂⁻ \square 2: AgOH (aq) \diamond 2: AgCl₂⁻ \times 2: AgCl (aq) ∇
 2: AgCl₃⁻² \circ 2: AgCl₄⁻³ \oplus 7: TOTAL Ag(\star

(e) Observing the values of $[Ag^+]$ as $f([Cl^-])$ in MINEQLt, it appears that $[Ag^+]$ follows a power function of the form

$$[Ag^+] = C_1 [Cl^-]^{-C_2}$$

To perform a very basic curve fit, the data output of $[Ag^+]$ can be imported to Excel and a curve fit applied (see plot on following page). When this is done the following empirical formula results.

$$[Ag^+] = 4 \times 10^{-15} [Cl^-]^{-1.2049}$$



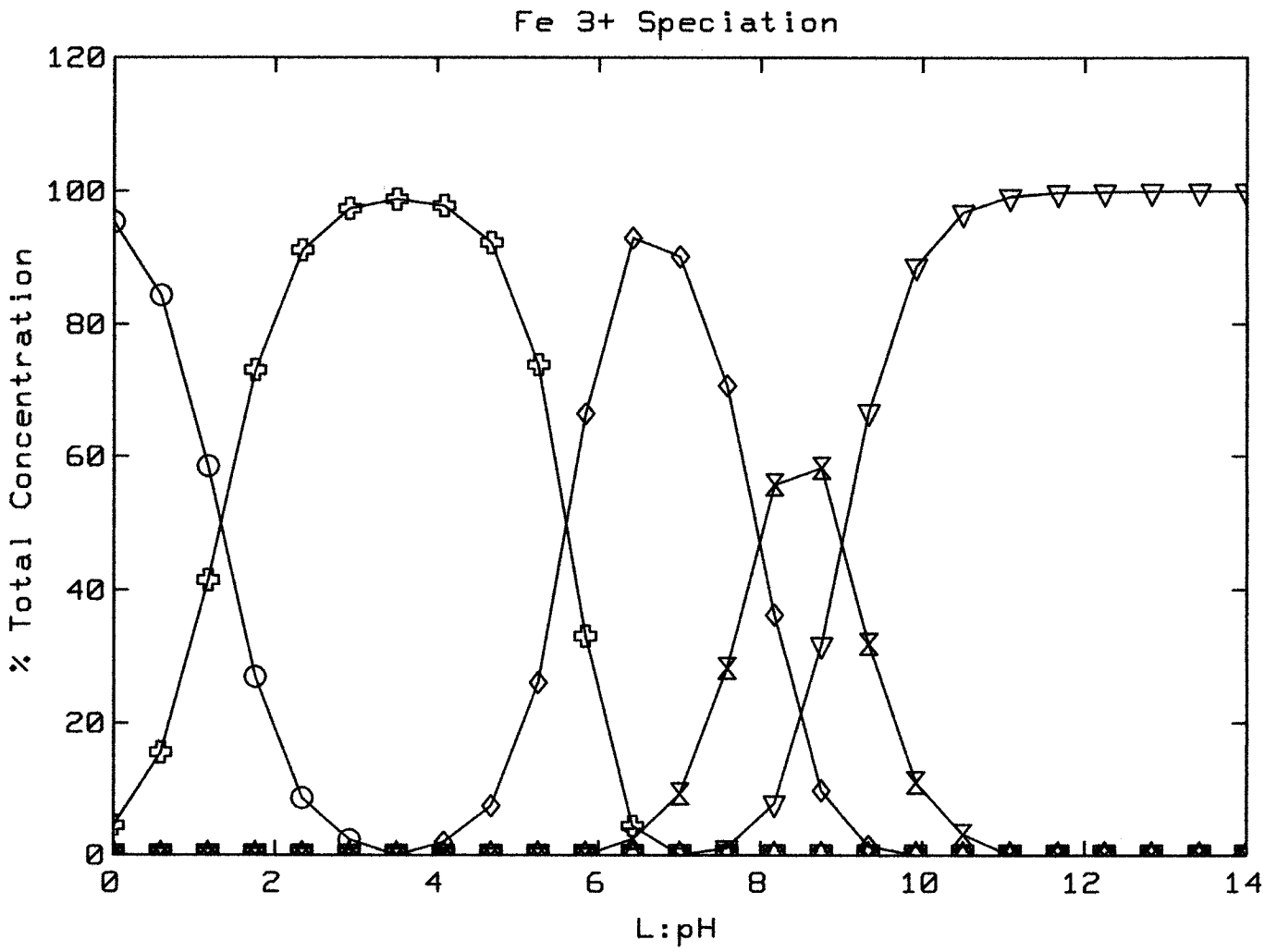
2)

(a) When $\text{Fe}(\text{OH})^{2+}$ is less than 1% of $\text{Fe}(\text{II})$ and Fe^{2+} is at high concentrations, meeting the researchers criteria, this occurs at pH approximately 3.5-4.0.

(b) When equilibrium with ferrihydrite is considered, the oversaturated conditions occurs when the solid is observed, in the pH range of approximately 4.5 - 12.5

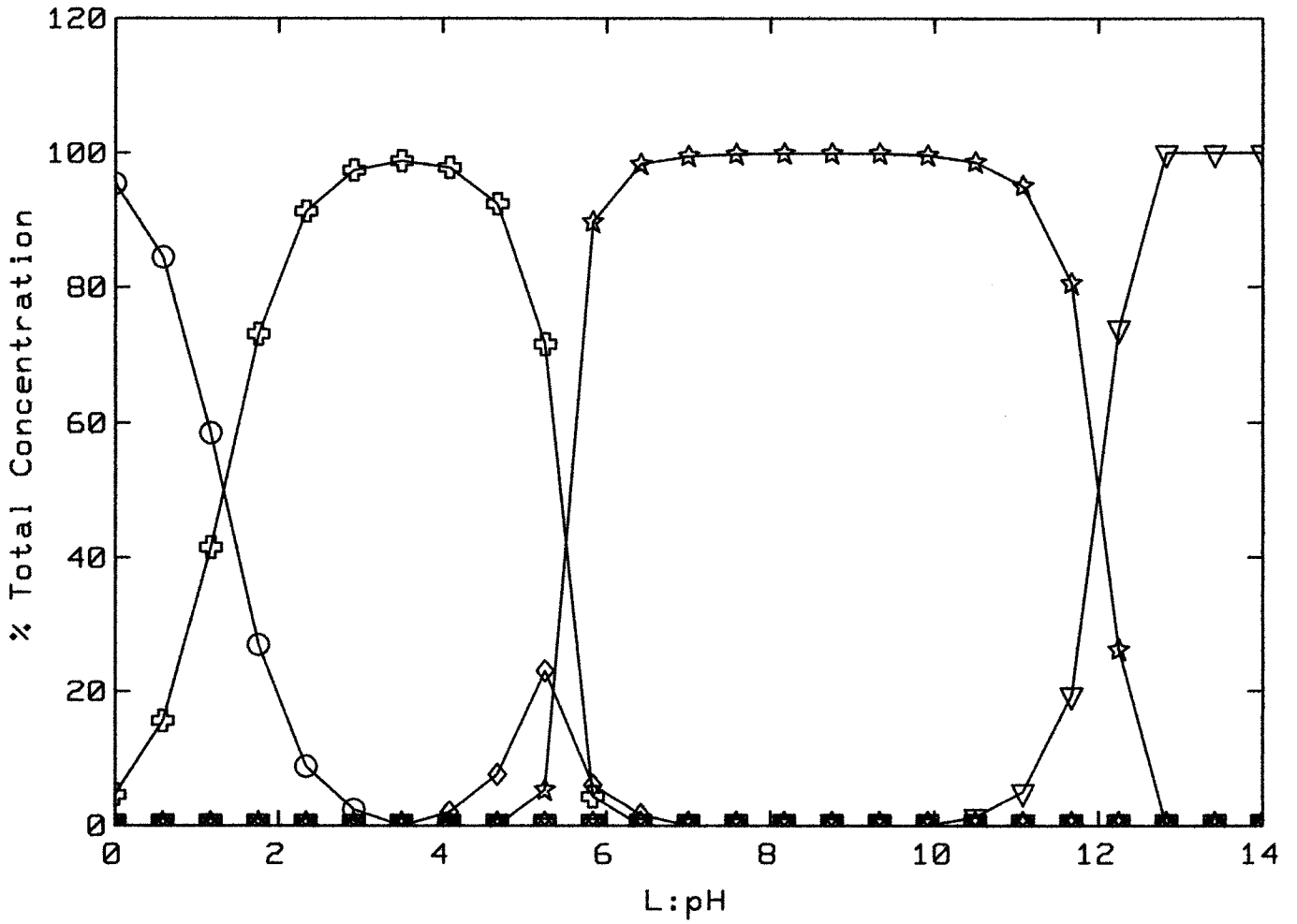
Both of these conditions are plotted on the following pages.

2a



1: Fe(3+) Δ 2: FeOH₂⁺ \square 2: Fe(OH)₂⁺ \diamond 2: Fe(OH)₃ (\times 2: Fe(OH)₄⁻ ∇
 2: FeHCitra \circ 2: Fe[Citrat] \oplus

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1: Fe(3+) Δ 2: FeOH₂⁺ \square 2: Fe(OH)₂⁺ \diamond 2: Fe(OH)₃ \times 2: Fe(OH)₄⁻ ∇
 2: FeHCitra \circ 2: FeCitrat \oplus 5: FERRIHYDR \star