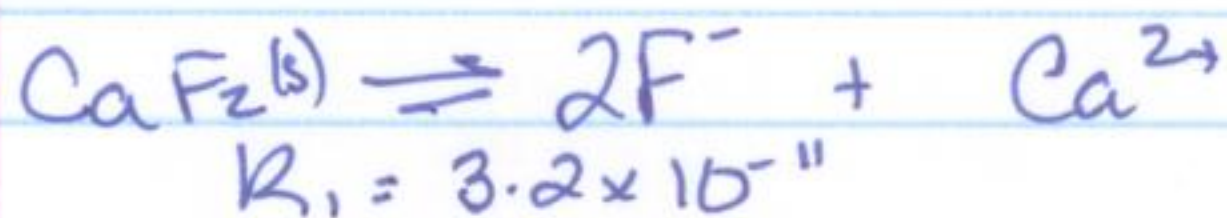
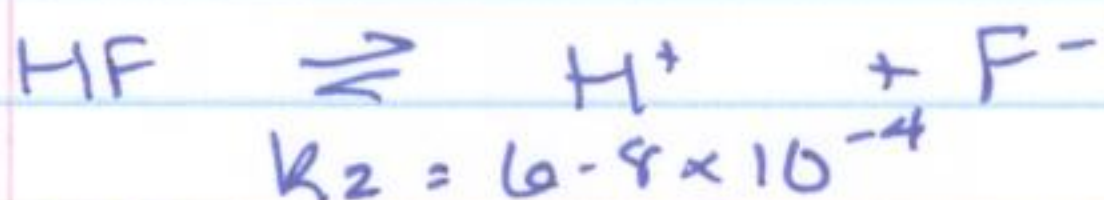


# CHM 2354 Assignment 2

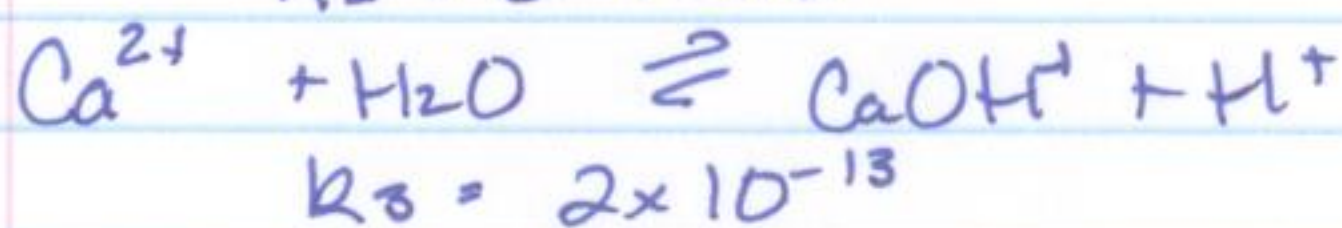
Q1.



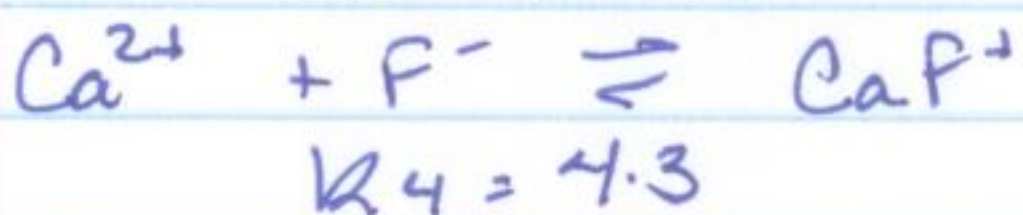
$$K_1 = [\text{F}^-]^2 [\text{Ca}^{2+}]$$



$$K_2 = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

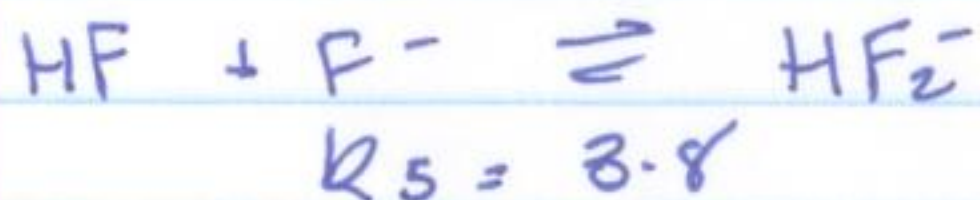


$$K_3 = \frac{[\text{CaOH}^+][\text{H}^+]}{[\text{Ca}^{2+}]}$$



2.5 marks for identify all species and equilibria

$$K_4 = \frac{[\text{CaF}^+]}{[\text{Ca}^{2+}][\text{F}^-]}$$



$$K_5 = \frac{[\text{HF}_2^-]}{[\text{F}^-][\text{HF}]}$$



Mass balance:

- all Ca species originated from  $\text{CaF}_2$
- all F species originated from  $\text{CaF}_2$

$$2(\text{Total Ca species}) = \text{Total Fluorine species}$$

$$2\{[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaF}^+]\} = [\text{F}^-] + [\text{HF}] + [\text{CaF}^+] + 2[\text{HF}_2^-]$$

3 marks for mass balance;

Simplify Mass Balance:

divided as 1 mark for 2 total Ca = total F

and 2 for actual expression

$$2[\text{Ca}^{2+}] + 2[\text{CaOH}^+] + [\text{CaF}^+] - [\text{F}^-] - [\text{HF}] - 2[\text{HF}_2^-] = 0$$

Express every concentration in mass balance as a function of any one species it doesn't matter which.

Valid assumptions at pH 2.

1 mark for

$$\frac{[\text{CaOH}^+]}{[\text{Ca}^{2+}]} = 2 \times 10^{-11}; [\text{CaOH}^+] \text{ negligible wrt } [\text{Ca}^{2+}]$$

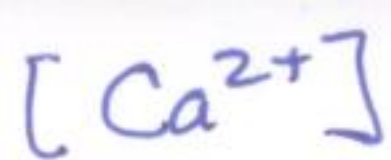
valid

Valid at pH 3

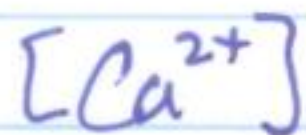
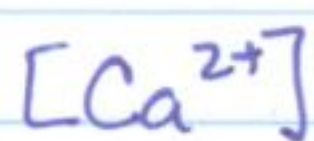
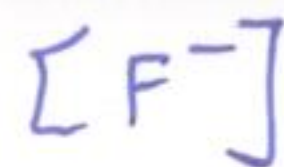
$$\frac{[\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^9; [\text{HF}] \text{ negligible wrt } \text{F}^-$$

$$\frac{[\text{HF}_2^-]}{[\text{F}^-][\text{HF}]} \text{ negligible wrt } \text{F}^-$$

assumptions

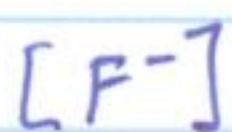


or

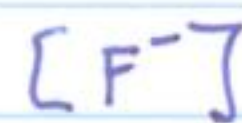


$\frac{k_1}{[F^-]^2}$

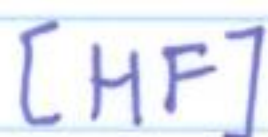
(1)



$\sqrt{\frac{k_1}{[Ca^{2+}]}}$



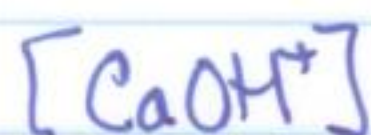
(2)



$\frac{[H^+]}{k_2} \sqrt{\frac{k_1}{[Ca^{2+}]}}$



(3)

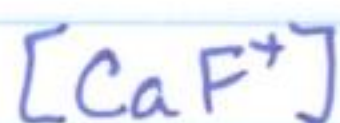


$\frac{k_3 [Ca^{2+}]}{[H^+]}$

2.5 marks for expressing everything in terms of one variable.

$\frac{k_3 k_1}{[H^+][F^-]^2}$

(4)

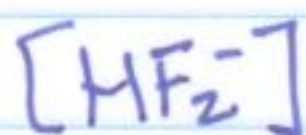


$k_4 \sqrt{k_1 [Ca^{2+}]}$

Can be any species

$\frac{k_4 k_1}{[F^-]}$

(5)



$\frac{k_5 [H^+]}{k_2} \frac{k_1}{[Ca^{2+}]}$

$\frac{k_5 [H^+][F^-]^2}{k_2}$

(6)

Substituting into mass balance

$$2[Ca^{2+}] + \frac{2k_3 [Ca^{2+}]}{[H^+]} + k_4 \sqrt{k_1 [Ca^{2+}]} - \sqrt{\frac{k_1}{[Ca^{2+}]}} - \frac{[H^+]}{k_2} \sqrt{\frac{k_1}{[Ca^{2+}]}}$$

$$- 2 \frac{k_5 k_1 [H^+]}{k_2 [Ca^{2+}]} = 0$$

1 mark for sticking it into mass balance equation correctly

From this point I used excel....

pH 2

Solver Sol<sup>n</sup>

$[Ca^{2+}] \quad 1.3 \times 10^{-3}$

$[F^-] \quad 1.6 \times 10^{-4}$

$[HF] \quad 2.4 \times 10^{-3}$

$[CaOH^+] \quad 2.5 \times 10^{-14}$

$[CaF^+] \quad 9.8 \times 10^{-7}$

$[HF_2^-] \quad 1.5 \times 10^{-6}$

Goal Seeker

$1.1 \times 10^{-3}$

$1.7 \times 10^{-4}$

$2.5 \times 10^{-3}$

$2.2 \times 10^{-14}$

$9.0 \times 10^{-7}$

$1.7 \times 10^{-6}$

pH 11 xxx13

$9.7 \times 10^{-5}$

$5.8 \times 10^{-4}$

$8.6 \times 10^{-4}$

$1.9 \times 10^{-4}$

$2.4 \times 10^{-7}$

$1.9 \times 10^{-16}$

1.5 mark for explanation of how mass balance was solved.

Anything that makes sense is fair, goal seeker, solver, trial and error, programmable

↑↑  
Not able to get as close to the "goal" of 0

2 marks for final answers; these may vary depending method used, but should be in same range as mine

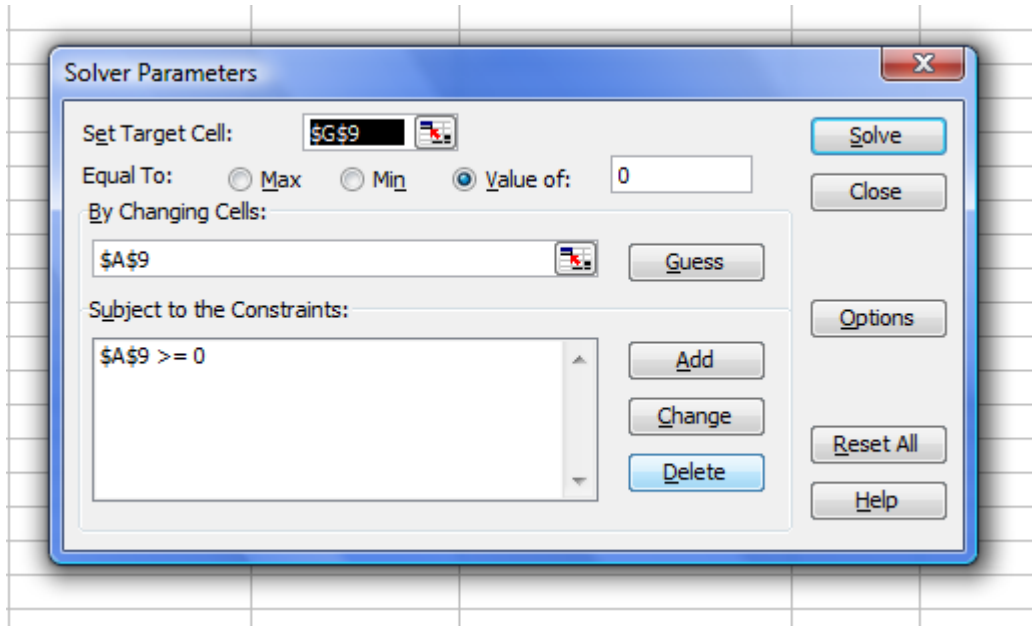
calculator as long as student did the work

## CHM2354 Analytical Chemistry - Assignment 2

### Question1

k1	3.30E-11					
k2	6.80E-04					
k3	3.8					
k4	2.00E-13					
k5	4.30E+00					
H+	0.01					
Ca2+	CaOH+	CaF+	F	HF	HF2-	
	$B4 \cdot A9 / B6$	$B5 \cdot \text{SQRT}(A9 \cdot B1)$	$\text{SQRT}(B1 / A9)$	$B6 / B2 \cdot \text{SQRT}(B1 / A9)$	$B3 \cdot B6 \cdot B1 / B2 / A9$	$2 \cdot A9 + 2 \cdot B9 + C9 - D9 - E9 - 2 \cdot F9$
	0.001268	2.54E-14	8.80E-07	0.000161329	2.37E-03	1.45E-06
						3.64E-20

I used "Solver"



Solver Options ✕

Max Time:	<input type="text" value="100"/>	seconds	<input type="button" value="OK"/>
Iterations:	<input type="text" value="100"/>		<input type="button" value="Cancel"/>
Precision:	<input type="text" value="1E-18"/>		<input type="button" value="Load Model..."/>
Tolerance:	<input type="text" value="5"/>	%	<input type="button" value="Save Model..."/>
Convergence:	<input type="text" value="0.0001"/>		<input type="button" value="Help"/>

Assume Linear Model       Use Automatic Scaling  
 Assume Non-Negative       Show Iteration Results

Estimates	Derivatives	Search
<input checked="" type="radio"/> Tangent	<input checked="" type="radio"/> Forward	<input checked="" type="radio"/> Newton
<input type="radio"/> Quadratic	<input type="radio"/> Central	<input type="radio"/> Conjugate



Measured potential will be

$$\text{Reduction potential for Sn}^{4+}/\text{Sn}^{2+} - \text{Reduction potential of Hg}_2\text{Cl}_2/\text{Hg(l) saturated calomel}$$

Evaluate reduction potential for  $\text{Sn}^{4+}/\text{Sn}^{2+}$



$$E = E^0 - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

1 mark for recognizing that you can use tin couple to determine  $E_{\text{measured}}$

\* Use formal potential for tin couple in 1M HCl

$$E = 0.14 - \frac{0.059}{2} \log \frac{\frac{2 \times 10^{-4}}{26 \times 10^{-3}}}{\frac{5 \times 10^{-5}}{26 \times 10^{-3}}}$$

$$= 0.122$$

=0.5 marks for using formal potential values of 0.14 and 0.77 V in Sn and Tl Nernst equations (rather than the  $E^0$  values)

$$E_{\text{measured}} = E_{\text{Sn}^{4+}/\text{Sn}^{2+}} - E_{\text{calomel}}$$

$$= 0.122 - 0.244$$

$$= -0.122 \text{ V}$$

1 mark for answer

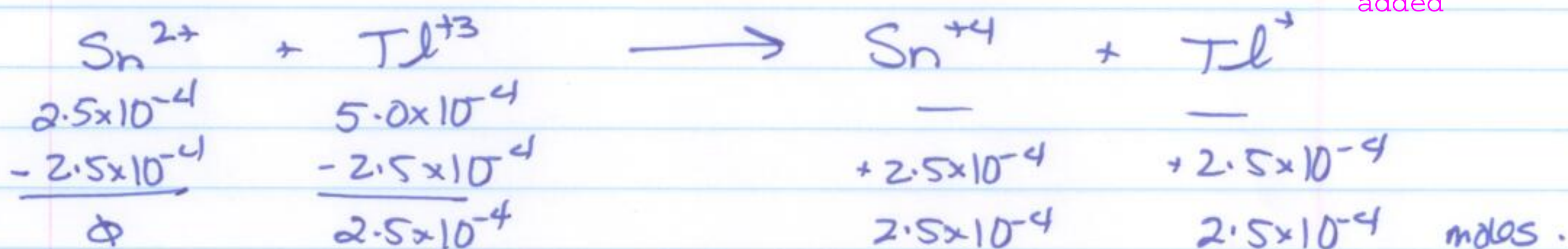
0.5 mark for

determining conc

iii) After  $10 \text{ ml} \times 0.05 \text{ M Tl}^{+3} = 5.0 \times 10^{-4}$

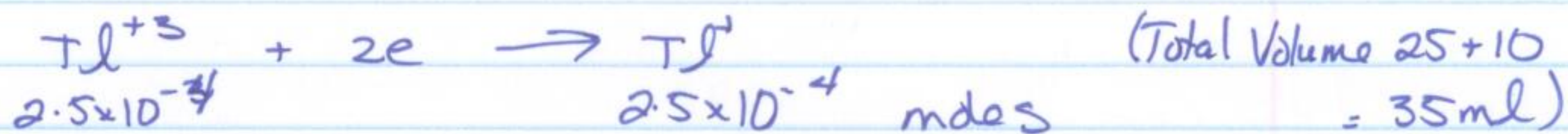
after 10 ml

added



This time use  $\text{Tl}^{+3}/\text{Tl}^{+}$  couple to determine measured potential

1 mark for using Tl couple



Evaluate  $E_{\text{Tl}^{+3}/\text{Tl}^+}$

$$E = E^{\circ} - \frac{0.059}{2} \log \frac{[\text{Tl}^+]}{[\text{Tl}^{+3}]}$$

(again use Formal potential in 1M HCl)

$$= 0.77 - \frac{0.059}{2} \log \frac{2.5 \times 10^{-4}}{\frac{35 \times 10^{-3}}{2.5 \times 10^{-4}}}$$
$$= 0.77 - \frac{0.059}{2} \log \frac{2.5 \times 10^{-4}}{35 \times 10^{-3}}$$

$$= 0.77$$

1 mark for answer

$$\begin{aligned} \text{Measured pot} &= E_{\text{Tl}^{+3}/\text{Tl}^+} - E_{\text{calomel}} \\ &= 0.77 - 0.244 \\ &= 0.526 \text{ V} \end{aligned}$$

ii.) At equivalence pt

$\text{Sn}^{2+}$  moles =  $\text{Tl}^{+3}$  moles at equivalence and rxn is essentially to completion

1 mark for equation conc

$$\text{Sn}^{4+} \text{ moles} = \text{Tl}^+ \text{ moles.}$$

$$E_{\text{eq}} = E_{\text{Sn}^{4+}/\text{Sn}^{2+}} = E_{\text{Sn}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \quad (1)$$

1 mark for Nernsts

$$= E_{\text{Tl}^{+3}/\text{Tl}^+} = E_{\text{Tl}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Tl}^+]}{[\text{Tl}^{+3}]} \quad (2)$$

Add (1) + (2)

$$2E_{\text{eq}} = E_{\text{Sn}}^{\circ} + E_{\text{Tl}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} + \frac{0.059}{2} \log \frac{[\text{Tl}^+]}{[\text{Tl}^{+3}]}$$

$$= E_{\text{Sn}}^{\circ} + E_{\text{Tl}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}][\text{Tl}^+]}{[\text{Sn}^{4+}][\text{Tl}^{+3}]}$$

2 mark for

combinations

$$= E_{\text{Sn}}^{\circ} + E_{\text{Tl}}^{\circ} - \frac{0.059}{2} \log 1 = E_{\text{Sn}}^{\circ} + E_{\text{Tl}}^{\circ}$$

$$2E_g = 0.14 + 0.77 = 0.91$$

$$E_g = 0.455$$

1 mark for final answer

$$E_{\text{measured}} = 0.211V$$

Summary

after addition of

1ml of  $Tl^{+3}$   
-0.122V

5ml of  $Tl^{+3}$   
0.211V

10ml of  $Tl^{+3}$   
0.526V