Homework #3 Solutions

1. $$J_{AX} = -d_{AX}\frac{\partial C_{AX}}{\partial x} + Z_{AX}\mu_{AX}C_{AX}\mathcal{E} \qquad [1]$$

$$\mathcal{E} = \frac{\partial}{\partial x}\left[(E_{fi} - E_f)/q\right]$$

$$= +\frac{kT}{q}\frac{\partial}{\partial x}\ln\left(\frac{p}{n_i}\right) = \frac{kT}{q}\frac{1}{p}\frac{dp}{dx}$$ Assuming M-B statistics

Einstein relation: $\mu_{AX} = \frac{q}{kT}d_{AX}$

so

$$J_{AX} = -d_{AX}\left[\frac{\partial C_{AX}}{\partial x} - Z_{AX}C_{AX}\frac{\partial}{\partial x}\ln\left(\frac{p}{n_i}\right)\right] \qquad [2]$$

in equilibrium:
$np = n_i^2$ & if $C_{A^-} \cong C_A$ $\quad p = n + C_A$ (concentration of charged defects negligible)

$$\frac{p}{n_i} = \frac{C_{A^-}}{2n_i} + \sqrt{\left(\frac{C_{A^-}}{2n_i}\right)^2 + 1}$$

$$\frac{\partial}{\partial x}\left(\ln\frac{p}{n_i}\right) = \frac{n_i}{p}\frac{\partial}{\partial x}\left(\frac{p}{n_i}\right)$$

$$= \frac{n_i}{p}\left[\frac{1}{2n_i}\frac{\partial C_{A^-}}{\partial x} + \cancel{2}\left(\frac{C_{A^-}}{2n_i}\right)\frac{1}{2n_i}\frac{\partial C_{A^-}}{\partial x}\frac{1}{\cancel{2}}\left(\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right)^{-1/2}\right]$$

$$= \left(\frac{n_i}{p}\right)\left(\frac{1}{2n_i}\right)\left(\frac{\partial C_{A^-}}{\partial x}\right)\left[1 + \frac{C_{A^-}}{2n_i}\left(\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right)^{-1/2}\right]$$

$$= \cancel{\left(\frac{n_i}{p}\right)}\left(\frac{1}{2n_i}\right)\left(\frac{\partial C_{A^-}}{\partial x}\right)\frac{\cancel{\left[\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right]^{1/2} + C_{A^-}/2n_i}}{\left(\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right)^{1/2}}\quad p/n_i$$

$$= \frac{1}{2n_i}\left(\frac{\partial C_{A^-}}{\partial x}\right)\left[\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right]^{-1/2} \qquad [3]$$

Also since in equilibrium

$$\frac{C_{A^-}C_X}{C_{A^-X}} = K(T) \Rightarrow C_{A^-X} = \frac{C_{A^-}C_X}{K(T)}$$

$$\frac{\partial C_{A^-X}}{\partial x} = \frac{C_X}{K(T)}\frac{\partial C_{A^-}}{\partial x} + \frac{C_{A^-}}{K(T)}\frac{\partial C_X}{\partial x}$$

$$= \frac{C_{A^-X}}{C_{A^-}}\frac{\partial C_{A^-}}{\partial x} + \frac{C_{A^-X}}{C_X}\frac{\partial C_X}{\partial x} \quad [4]$$

substituting [3] & [4] into [2]

$$J_{AX} = -d_{A^-X}\left[\left(\frac{\partial C_{A^-}}{\partial x}\right)\left[\frac{C_{A^-X}}{C_{A^-}} - Z_{A^-X}\frac{C_{A^-X}}{2n_i}\left(\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right)^{-1/2}\right] + \frac{C_{A^-X}}{C_X}\frac{\partial C_X}{\partial x}\right]$$

$$= -d_{A^-X}\frac{C_{A^-X}}{C_{A^-}}\left[\frac{\partial C_{A^-}}{\partial x}\left\{1 - Z_{A^-X}\frac{C_{A^-}}{2n_i}\left(\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right)^{-1/2}\right\} + \frac{C_{A^-}}{C_X}\frac{\partial C_X}{\partial x}\right] \quad [5]$$

now consider each species separately: $J_{A^-X} = J_{A^-X^0} + J_{A^-X^+} + J_{A^-X^{++}}$

$$\frac{\partial C_{X^0}}{\partial x} = 0 \quad , \quad Z_{A^-X^0} = -1$$

so
$$J_{AX^0} = \underbrace{-d_{A^-X^0}\frac{C_{A^-X^0}}{C_{A^-}}}_{D_{A^-X^0}}\left\{1 + \frac{C_{A^-}}{2n_i}\Big/\left[\left(\frac{C_{A^-}}{2n_i}\right)^2+1\right]^{1/2}\right\}\frac{\partial C_{A^-}}{\partial x}$$

for A^-X^+ $\quad Z_{A^-X^+} = 0$

$$\frac{C_{X^+}}{C_{X^+}^{i}} = \left(\frac{p}{n_i}\right) \quad \text{so} \quad \frac{1}{C_{X^+}}\frac{\partial C_{X^+}}{\partial x} = \left(\frac{n_i}{p}\right)\frac{1}{\cancel{C^i_{X^+}}}\cancel{C^i_{X^+}}\frac{\partial}{\partial x}\left(\frac{p}{n_i}\right)$$

by [3]

also $\dfrac{C_{A^-X^+}}{C_{A^-}}\Big/\left[\dfrac{C_{A^-X^+}}{C_{A^-}}\right]_i = \dfrac{C_{X^+}}{C^i_{X^+}} = \dfrac{p}{n_i}$ by mass action

$$= \frac{1}{2n_i}\left(\frac{\partial C_{A^-}}{\partial x}\right)\Big/\sqrt{\left(\frac{C_{A^-}}{2n_i}\right)^2+1}$$

substituting in [5]

$$J_{A^-X^+} = -\underbrace{d_{A^-X^+}\left[\frac{C_{A^-X^+}}{C_{A^-}}\right]_i}_{D^i_{A^-X^+}}\left(\frac{p}{n_i}\right)\left\{1+\frac{C_{A^-}}{2n_i}\Big/\sqrt{\left(\frac{C_{A^-}}{2n_i}\right)^2+1}\right\}\left(\frac{\partial C_{A^-}}{\partial x}\right)$$

for A^-X^{++}; $Z_{A^-X^{++}} = +1$; $\dfrac{1}{C_{X^{++}}}\dfrac{\partial C_{X^{++}}}{\partial x} = \left(\dfrac{n_i}{p}\right)^2\dfrac{\partial}{\partial x}\left(\dfrac{p}{n_i}\right)^2 = \left(\dfrac{n_i}{p}\right)^2 2\left(\dfrac{p}{n_i}\right)\dfrac{\partial}{\partial x}\left(\dfrac{p}{n_i}\right)$

$\dfrac{C_{X^{++}}}{C^i_{X^{++}}} = \left(\dfrac{p}{n_i}\right)^2$ and $\qquad = \dfrac{2}{2n_i}\left(\dfrac{\partial C_{A^-}}{\partial x}\right)\Big/\sqrt{\left(\dfrac{C_{A^-}}{2n_i}\right)^2+1}$

$\dfrac{C_{A^-X^{++}}}{C_{A^-X^{++}}}\Big/\left(\left[\dfrac{C_{A^-X^{++}}}{C_{A^-X^{++}}}\right]_i\right) = \left(\dfrac{p}{n_i}\right)^2$ putting these in [5]

$$J_{A^-X^{++}} = -\underbrace{d_{A^-X^+}\left[\frac{C_{A^-X^{++}}}{C_{A^-}}\right]_i}_{D_{A^-X^{++}}}\left(\frac{p}{n_i}\right)^2\underbrace{\left\{1 - \cancel{\frac{C_{A^-}/2n_i}{\sqrt{(C_{A^-}/2n_i)^2+1}}} + \frac{\cancel{2}(C_{A^-}/2n_i)}{\sqrt{(C_{A^-}/2n_i)^2+1}}\right\}}_{h}\left(\frac{\partial C_{A^-}}{\partial x}\right)$$

$$\therefore\ J_{A^-} = J_{A^-X^0} + J_{A^-X^+} + J_{A^-X^{++}} = \underbrace{h\left(D^i_{A^-X^0} + \left(\frac{p}{n_i}\right)D^i_{A^-X^+} + \left(\frac{p}{n_i}\right)^2 D_{A^-X^{++}}\right)}_{D_A}\left(\frac{\partial C_{A^-}}{\partial x}\right)$$

as desired.

2. (a) For Gaussian $C(x,t) = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$

$D_p = D^i_{p^+X^0} + \left(\frac{n}{n_i}\right) D^i_{p^+X^-} + \left(\frac{n}{n_i}\right)^2 D^i_{p^+X^=}$

$D^i_{p^+X^0} = 3.85 \exp\left(-\frac{3.66}{kT}\right) = 7.3\times10^{-16}\ \frac{cm^2}{s}$

$D^i_{p^+X^-} = 4.44 \exp\left(-\frac{4.0}{kT}\right) = 2.9\times10^{-17}\ \frac{cm}{s}$

$D^i_{p^+X^=} = 44.2 \exp\left(-\frac{4.37}{kT}\right) = 7.5\times10^{-18}\ \frac{cm}{s}$

For $n = n_i$ $D = 7.7\times10^{-16}\ cm^2/s$

$Q = 2\times10^{15}\ cm^{-2}$

$C(2\times10^{-5}\ cm, t) = 10^{17}\ cm^{-3} = \frac{2\times10^{15}\ cm^{-2}}{\sqrt{\pi D t}} \exp\left(-\frac{4\times10^{-10}\ cm^2}{4Dt}\right)$

Iterate to solve
rewrite for fastest convergence $Dt = \frac{4\times10^{-10}\ cm^2}{4 \ln\left[2\times10^{-2}\ cm/\sqrt{\pi D t}\right]}$

$Dt = 1.24\times10^{-11}\ cm^2$

$t = \frac{1.24\cdot10^{-11}\ cm^2}{7.7\times10^{-16}\ cm^2/s} = 1.6\times10^{4}\ s = \underline{268\ min = 4.5\ h}$

(b) $D = D\left(\frac{Q}{\sqrt{\pi D t}}\right) = D\left(\frac{2\times10^{15}\ cm^{-2}}{\sqrt{\pi(1.24\times10^{-11}\ cm^2)}}\right) = D\left(3.2\times10^{20}\ cm^{-3}\right)$

$n_i(900°C) = 3.2\times10^{18}\ cm^{-3}$ $D = 7.3\times10^{-16}\ \frac{cm^2}{s} + \frac{3.2\times10^{20}}{3.2\times10^{18}} 2.9\times10^{-17}\ cm^2/s + \left(\frac{3.2\times10^{20}}{3.2\times10^{18}}\right)^2 7.5\times10^{-18}\ cm^2/s = 7.9\times10^{-14}$

$t = Dt/D = \frac{1.24\times10^{-11}\ cm^2}{7.9\times10^{-14}\ cm^2/s} = \underline{157\ s = 2.6\ min}$

Including electric field effects, $h \cong 2$, so $D_{eff} = 1.6\times10^{-13}\ cm^2/s$
$(n \gg n_i)$

$t = 1.3\ min$

3. $As^+ + I^0 \Leftrightarrow (AsI)^+$ (1) $(AsI)^+, (BI)^-, I^0$ diffuse

$B^- + I^0 \Leftrightarrow (BI)^-$ (2)

$(AsI)^+ + B^- \Leftrightarrow (AsB)^0 + I^0$ [3]

$As^+ + (BI)^- \Leftrightarrow (AsB)^0 + I^0$ [4]

(a)

(A) $\dfrac{\partial C_{As^+}}{\partial t} = -R_1 - R_4$

$R_1 = k_1\left(C_{As^+}C_{I^0} - \dfrac{C_{(AsI)^+}}{K_1}\right)$

$R_2 = k_2\left(C_{B^-}C_{I^0} - \dfrac{C_{(BI)^-}}{K_2}\right)$

$R_3 = k_3\left(C_{(AsI)^+}C_{B^-} - \dfrac{C_{(AsB)^0}C_{I^0}}{K_3}\right)$

$R_4 = k_4\left(C_{(BI)^-}C_{As^+} - \dfrac{C_{(AsB)^0}C_{I^0}}{K_4}\right)$

(B) $\dfrac{\partial C_{B^-}}{\partial t} = -R_2 - R_3$

(C) $\dfrac{\partial C_{I^0}}{\partial t} = -R_1 - R_2 + R_3 + R_4 - \nabla\cdot F_{I^0}$

(D) $\dfrac{\partial C_{(AsI)^+}}{\partial t} = R_1 - R_3 - \nabla\cdot F_{(AsI)^+}$

(E) $\dfrac{\partial C_{(BI)^-}}{\partial t} = R_2 - R_4 - \nabla\cdot F_{(BI)^-}$

(F) $\dfrac{\partial C_{(AsB)^0}}{\partial t} = R_3 + R_4$

R_1, R_2 fast: $C_{(AsI)^+} \cong K_1 C_{As^+}C_{I^0}$, $C_{(BI)^-} \cong K_2 C_{B^-}C_{I^0}$

Combine (A) & (D) and (B) & (E) and (C), (D) & E

(As paired & unpaired) (B paired and unpaired) (I paired & unpaired)

Note that R_1 & R_2 cancel

(A)+(D): $$\frac{\partial (C_{As^+} + C_{(AsI)^+})}{\partial t} = -\nabla \cdot F_{(AsI)^+} - R_3 - R_4$$

(B)+(E) $$\frac{\partial (C_{B^-} + C_{(BI)^-})}{\partial t} = -\nabla \cdot F_{(BI)^-} - R_3 - R_4$$

(C)+(D)+(E) $$\frac{\partial (C_{I^\circ} + C_{(AsI)^+} + C_{(BI)^-})}{\partial t} = -\nabla \cdot F_{I^\circ}$$

(F) $$\frac{\partial C_{(AsB)^\circ}}{\partial t} = R_3 + R_4$$

(b) $$R_3 + R_4 = k_3\left(C_{(AsI)^+} C_{B^-} - \frac{C_{(AsB)^\circ} C_{I^\circ}}{K_3}\right) + k_4\left(C_{(BI)^-} C_{As^+} - \frac{C_{(AsB)^\circ} C_{I^\circ}}{K_4}\right)$$

$$k_3 \cong 4\pi a\, d_{(AsI)^+}, \quad k_4 = 4\pi a\, d_{(BI)^-}$$

$$R_3 + R_4 = 4\pi a\, d_{(AsI)^+}\left(K_1 C_{As^+} C_{I^\circ} C_{B^-} - \frac{C_{(AsB)^\circ} C_{I^\circ}}{K_3}\right)$$
$$+ 4\pi a\, d_{(BI)^-}\left(K_2 C_{B^-} C_{I^\circ} C_{As^+} - \frac{C_{(AsB)^\circ} C_{I^\circ}}{K_4}\right)$$
$$= 4\pi a \left(d_{(AsI)^+} K_1 + d_{(BI)^-} K_2\right)\left[C_{As^+} C_{B^-} - \frac{C_{(AsB)^\circ}}{K_5}\right] C_{I^\circ}$$

where $K_5 = \frac{K_3}{K_1} = \frac{K_4}{K_2}$, which must be equal as they represent different paths to same products ($As^+ + B^- + I^\circ \rightleftarrows (AsB)^\circ + I^\circ$).

Note that $D_{As} = d_{(AsI)^+} \frac{C_{(AsI)^+}}{C_{As}} = d_{(AsI)^+} K_1 C_{I^\circ}$ (and likewise for D_B), so
(if $C_{AsI} \ll C_{As}$)

$$R_3 + R_4 = 4\pi a \left(D^*_{As} + D^*_{B}\right)\left[C_{As^+} C_{B^-} - C_{(AsB)^\circ}/K_5\right]\left(\frac{C_I}{C_I^*}\right)$$

(c) Assumptions

$$\begin{cases} C_{I^\circ} = C_I^* \\ C_{(AsI)^+} \ll C_{As^+} \\ C_{(BI)^-} \ll C_{B^-} \\ R_3, R_4 \text{ fast} \Rightarrow C_{(AsB)^\circ} = K_5 C_{As^+} C_{B^-} \\ C_{As^+} \gg C_{(AsB)^\circ}, C_{B^-} \Rightarrow C_{As^+} \text{ controls } n, \mathcal{E} \end{cases}$$

Simplify system

(A)+(D)+(F) $$\frac{\partial (C_{As^+} + C_{(AsI)^+} + C_{(AsB)^\circ})}{\partial t} \simeq \frac{\partial C_{As^+}}{\partial t} = -\nabla \cdot F_{(AsI)^+}$$

(B)+(E)+(F) $$\frac{\partial (C_{B^-} + C_{(BI)^-} + C_{(AsB)^\circ})}{\partial t} \simeq \frac{\partial (C_{B^-} + C_{(AsB)^\circ})}{\partial t} = -\nabla \cdot F_{(BI)^-}$$

$$C_{B^-} + C_{(AsB)^\circ} = C_{B^-}(1 + K_5 C_{As^+}) = C_B^{total}$$

$$C_{B^-} = C_B^{total} / (1 + K_5 C_{As^+})$$

$\mathcal{E}$ depends on ∇C_{As^+}
assume C_{As^+} constant, so $\mathcal{E} = 0$ (or $\ll n_i$)
(otherwise $D_B^{eff} = f(\nabla C_{As^+})$)

$$F_{(BI)^-} = -d_{(BI)^-} \nabla C_{(BI)^-} - \mu_{(BI)^-} C_{(BI)^-} \mathcal{E}$$

$$= -d_{(BI)^-} \nabla (K_2 C_{B^-} C_{I^\circ}^*) = -d_{(BI)^-} K_2 C_{I^\circ}^* \nabla C_{B^-}$$

$$= -d_{(BI)^-} K_2 C_{I^\circ}^* \nabla \left(\frac{C_B^{total}}{1 + K_5 C_{As^+}} \right) = -\frac{d_{(BI)^-} K_2 C_{I^\circ}^*}{1 + K_5 C_{As^+}} \nabla C_B^{total}$$

Thus $$D_B^{eff} = \frac{d_{(BI)^-} K_2 C_{I^\circ}^*}{(1 + K_5 C_{As^+})} = \frac{D_B^*}{(1 + K_5 C_{As^+})}$$ (note that − sign in HW#3(c) is error)