Homework #4 Solutions

2. (a) In equilibrium, $C_{B_3I} = K(C_{B^-})^3 C_{I^0} \left(\frac{p}{n_i}\right)^3$

where $K = \frac{1}{(C_s)^3} \exp\left(\frac{\Delta G_{binding}}{kT}\right)$

Since we use $\left(\frac{p}{n_i}\right)$, $\Delta G_{binding}$ is defined for $n = p = n_i$
(could use any reference, e.g. $p = N_V$ for $E_f = E_V$)
If $p > n_i$, the reference hole energy is higher, so binding energy is larger.

@ 900°C, $n_i = 3.2 \times 10^{18}\ cm^{-3}$ $\quad C_{B^-} \gg n_i$, so $p \cong C_{B^-} = 6 \times 10^{19}\ cm^{-3}$
$C_{I^0} = 4.8 \times 10^{10}\ cm^{-3}$

$$C_{B_3I} = \frac{C_B^{total} - C_{B^-}}{3} = \frac{10^{20} - 6 \times 10^{19}}{3} = 1.33 \times 10^{19}\ cm^{-3}$$

$$\Delta G_{binding} = kT \ln\left(\frac{(1.33 \times 10^{19}\ cm^{-3})(5 \times 10^{22}\ cm^{-3})^3}{(6 \times 10^{19}\ cm^{-3})^3 (4.8 \times 10^{10}\ cm^{-3}) \left(\frac{6 \times 10^{19}\ cm^{-3}}{3.2 \times 10^{18}\ cm^{-3}}\right)^3}\right)$$

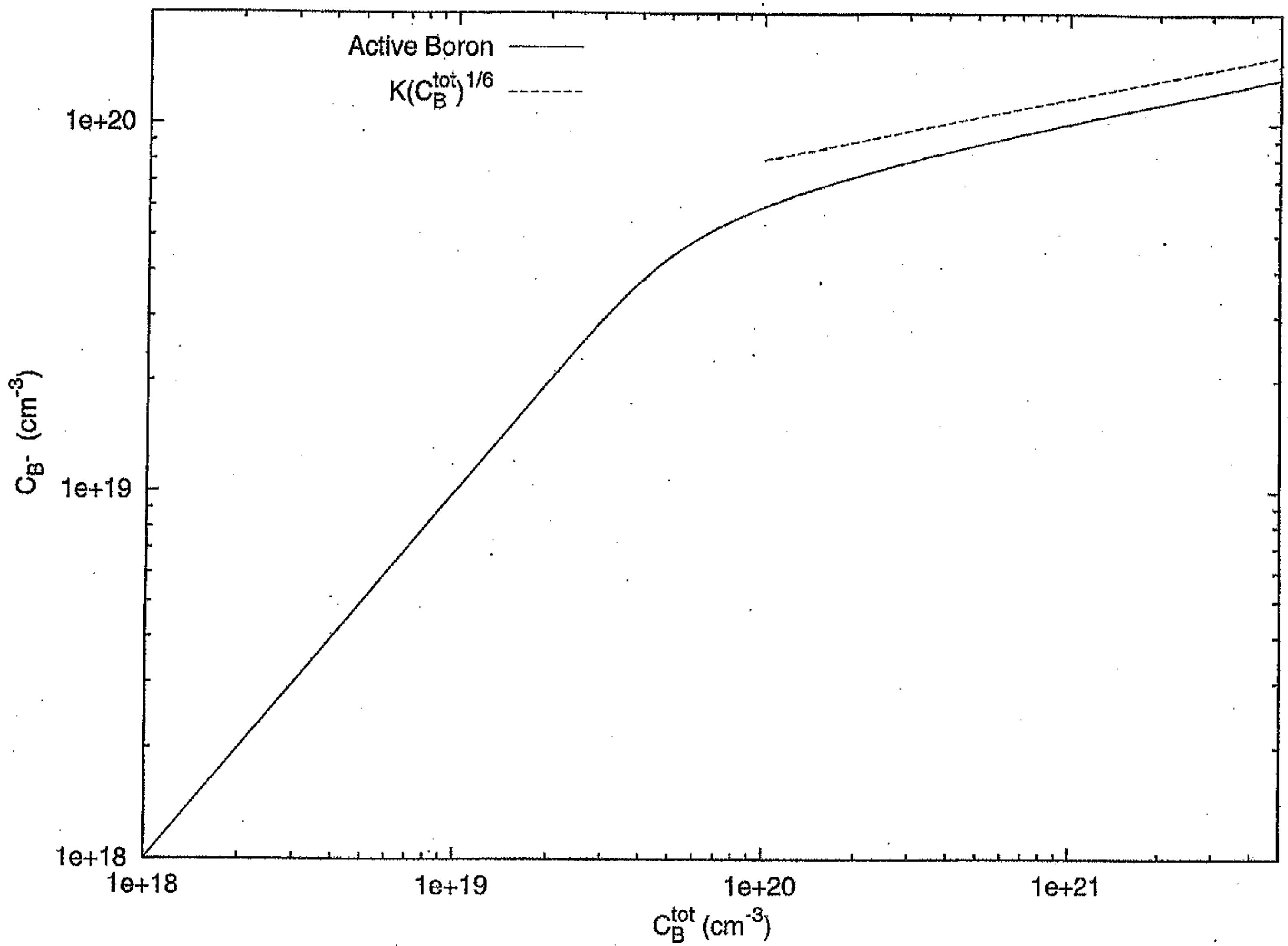
$$= 3.12\ eV \Rightarrow K = 2.0 \times 10^{-55}\ cm^9$$

If we define $\Delta G_{binding}$ relative to hole (or electron) energy in system with $p = 6 \times 10^{19}\ cm^{-3}$, we leave off $(p/n_i)^3$ factor so

$$\Delta G_{binding} = 4.01\ eV \ \ (\text{shifted by } 3 * (E_{fi} - E_f))$$

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

$$C^{total} \cong C_{B^-} + 3C_{B_3I} = C_{B^-} + 3K(C_{B^-})^3 C_{I^0}^* \left(\frac{p}{n_i}\right)^3$$


Active Boron
$K(C_B^{tot})^{1/6}$
1e+20
1e+19
1e+18
C_{B^-} (cm^{-3})
1e+18
1e+19
1e+20
1e+21
C_B^{tot} (cm^{-3})

(b) Reactions:

	$B^- + I^0 \Leftrightarrow (BI)^0 + e^-$	[1]
	$B^- + I^+ \Leftrightarrow (BI)^0$	2
Assume fast $\longrightarrow$	$I^0 + h^+ \Leftrightarrow I^+$	3
	$I^0 + V^0 \Leftrightarrow \phi$	4
$C_{I^+} = K_2\, C_{I^0}\left(\frac{p}{n_i}\right)$	$I^+ + V^0 \Leftrightarrow \phi + h^+$	5
	$(BI)^0 + V^0 \Leftrightarrow B^- + h^+$	6
	$(BI)^0 + B^- \Leftrightarrow (B_2I)^0 + e^-$	7
	$(B_2I)^0 + V^0 \Leftrightarrow 2B^- + 2h^+$	8
	$(BI)^0 + (B_2I)^0 \Leftrightarrow (B_3I)^0 + I^0$	9
	$(B_3I)^0 + V^0 \Leftrightarrow 3B^- + 3h^+$	10
	$(BI)^0 + (BI)^0 \Leftrightarrow (B_2I)^0 + I^0$	11

(A) $$\frac{\partial C_{B^-}}{\partial t} = -R_1 - R_2 + R_6 - R_7 + 2R_8 + 3R_{10}$$

(B) $$\frac{\partial (C_{I^0} + C_{I^+})}{\partial t} = -R_1 - R_2 - R_4 - R_5 + R_9 + R_{11} - \nabla\cdot\left(F_{I^0} + F_{I^+}\right)$$

(C) $$\frac{\partial C_{V^0}}{\partial t} = -R_4 - R_5 - R_6 - R_8 - R_{10} - \nabla\cdot F_{V^0}$$

(D) $$\frac{\partial C_{(BI)^0}}{\partial t} = R_1 + R_2 - R_6 - R_7 - R_9 - 2R_{11} - \nabla F_{(BI)^0}$$

(E) $$\frac{\partial C_{(B_2I)^0}}{\partial t} = R_7 - R_8 - R_9 + R_{11}$$

(F) $$\frac{\partial^2 C_{(B_3I)^0}}{\partial t} = R_9 - R_{10}$$

Note: $K_1 = K_3 K_2$

Assume $B^- + I^0 \Leftrightarrow (BI)^0 + e^-$ is fast $C_{(BI)^0} = K_1\, C_{B^-} C_{I^0}\left(\frac{p}{n_i}\right)$

Replace (A), (B) & D w/ this algebraic equation and (A)+(D), (B)+(D)

$$(A') \quad \frac{\partial (C_{B^-} + C_{(BI)^\circ})}{\partial t} = -2R_7 + 2R_8 + 3R_{10} - R_9 - 2R_{11} - \nabla \cdot F_{(BI)^\circ}$$

$$(B') \quad \frac{\partial (C_{I^\circ} + C_{I^-} + C_{(BI)^\circ})}{\partial t} = -R_4 - R_5 - R_6 - R_7 - R_{11}$$

(c) Now assume Reaction 7 is fast, $C_{(B_2I)^\circ} = K_7 \; C_{(BI)^\circ} C_{B^-} \left(\frac{f}{n_i}\right)$

$= K_{(B_2I)^\circ} C_{B^-}^2 C_{I^\circ} \left(\frac{f}{n_i}\right)^2$

Replace A', B' & E w/ $A' + 2E$ and $B' + E$

where $K_{(B_2I)^\circ} = K_1 K_7$

$$(A'') \quad \frac{\partial (C_{B^-} + \underbrace{\cancel{C_{(BI)^\circ}} + \cancel{C_{(B_2I)^\circ}}}_{\ll C_{B^-}})}{\partial t} = +3R_{10} - 3R_9 - \nabla \cdot \vec{F}_{(BI)^\circ}$$

$$(B'') \quad \frac{\partial (C_{I^\circ} + C_{I^+} + C_{(BI)^\circ} + C_{(B_2I)^\circ})}{\partial t} = -R_4 - R_5 - R_6 - R_8 - R_9 - \nabla \cdot (F_{I^\circ} + F_{I^+} + F_{(BI)^\circ})$$

Plus (C) and (F)

(d) R_9 is rate-limiting process for B_3I formation, so R_{10} can be neglected in comparison

$$R_9 = k_9^f \left[C_{(BI)^\circ} C_{(B_2I)^\circ} - C_{(B_3I)^\circ} C_{I^\circ} / K_9 \right]$$

$$= k_9^f \left[K_1 \; C_{B^-} C_{I^\circ} \left(\frac{f}{n_i}\right) K_1 K_7 \; C_{B^-}^2 C_{I^\circ} \left(\frac{f}{n_i}\right)^2 - \frac{C_{B_3I^\circ} C_{I^\circ}}{K_9} \right]$$

$$= k_9^f K_1^2 K_7 C_{I^\circ} \left[C_{B^-}^3 C_{I^\circ} \left(\frac{f}{n_i}\right)^3 - \frac{C_{(B_3I)^\circ}}{K_{(B_3I)^\circ}} \right]$$

where $K_{(B_3I)^\circ} = K_9 K_1^2 K_7$

If B_2I° and BI^- react readily to form B_3I° plus I°, then k can be estimated as $4\pi a\,(D_{B_2I^\circ} + D_{BI^-}) = 4\pi a\, D_{(BI)^-}$, with $a \sim 5\,\text{Å}$ (capture radius)

(d) $$C_{B_3I^\circ} = K_{B_3I^\circ} (C_{B^-})^3\, C_{I^\circ} \left(\frac{p}{n_i}\right)^3$$

where $K_{B_3I^\circ} = K_1^2 K_7 \; K_9$ as defined on previous page.

Combine to eliminate $R_{(B_3I)^\circ} = R_9$

$A''' = A'' + 3F$ $$\frac{\partial\,(C_{B^-} + C_{(BI)^\circ} + 2C_{(B_2I)^\circ} + 3C_{(B_3I)^\circ})}{\partial t} = -\nabla \cdot F_{(BI)^\circ} \quad (\text{total } B)$$

$B''' = B'' + F$ $$\frac{\partial\,(C_{I^\circ} + C_{I^+} + C_{(BI)^\circ} + C_{(B_2I)^\circ} + C_{(B_3I)^\circ})}{\partial t} = -\nabla\cdot(F_{I^\circ} + F_{I^+} + F_{(BI)^\circ}) - R_{I/V} \quad (\text{total } I)$$

C $$\frac{\partial C_{V^\circ}}{\partial t} = -\nabla \cdot J_{V^\circ} - R_{I/V} \quad (\text{total } V)$$

plus $C_{(BI)^\circ} = K_1 \left(\frac{p}{n_i}\right) C_{B^-} C_{I^\circ}$, $C_{(B_2I)^\circ} = \underbrace{K_1^2 K_7}_{K_{(B_2I)^\circ}} C_{B^-}^2 C_{I^\circ} \left(\frac{p}{n_i}\right)^2$

where $R_{I/V} = R_4 + R_5 + R_6 + R_8 + R_{10}$

3. $\Delta H^P = -0.9\,eV$, $\Delta S^P = 10^{-4}\,eV/K$, $\sigma_p = 5\times10^7\,eV/cm$

$\Omega = \Omega_{Si} = 2\times10^{-23}\,cm^3 = 1/C_s$

(a) $C_A^{ss} = C_s \exp\left(-\frac{\Delta S^P}{k}\right)\exp\left(\frac{\Delta H^P}{kT}\right)$

$= 2.14\times10^{18}\,cm^{-3}$

(b) $\Delta G_n = n\,\Delta G_n^\infty + P_n\sigma_p \qquad \Delta G_n^\infty = -kT\ln\left(\frac{C_A}{C_A^{ss}}\right)$

For a disk, $P_n = 2\pi r$, $V_n = \pi r^2 h = n\Omega$

($h = 0.27\,nm$ = thickness)

$r = \sqrt{\frac{n\Omega}{\pi h}}$, so $P_n = 2\sqrt{\frac{n\pi\Omega}{h}}$

critical size defined by $\left.\frac{d\Delta G_n}{dn}\right|_{n_c} = 0$

$$\left.\frac{d\Delta G_n}{dn}\right|_{n_c} = -kT\ln\left(\frac{C_A}{C_A^{ss}}\right) + \cancel{2}\sqrt{\frac{\pi\Omega}{h}}\,\frac{1}{\cancel{2}}\,n_c^{-1/2}\sigma_p = 0$$

$$n_c = \frac{\pi\Omega\sigma_p^2}{h\left(kT\ln\left(C_A/C_A^{ss}\right)\right)^2}$$

(c) $\Delta G_{n_c} = -n_c kT\ln\left(\frac{C_A}{C_A^{ss}}\right) + 2\sigma_p\sqrt{\frac{n_c\pi\Omega}{h}}$

For $C_A/C_A^{ss} = 100$, $n_c = 26.9\,(27)$, $\Delta G_{n_c} = 12.5\,eV$

$= 10^4$, $n_c = 6.73\,(7)$, $\Delta G_{n_c} = 6.25\,eV$

$= 10$ $\quad n_c = 107.6\,(108)$ $\Delta G_{n_c} = -25.0\,eV$