HW #4

1) FCC Fe, 0.55 wt% C, 1325 K, 0 wt% C @ 1 end

a) $\frac{\partial c}{\partial t} - \nabla(D\nabla C) - \dot{\mathcal{Z}} = 0$ assume i) $\nabla D = 0$, constant D in space
ii) $\dot{\mathcal{Z}} = 0$, no source

$\hookrightarrow \frac{\partial c}{\partial t} = D\nabla^2 C$

$\hookrightarrow C(x,t) = (C_s - C_0)\left(1 - \text{erf}\left[\frac{x}{2\sqrt{Dt}}\right]\right) + C_0$

BC) $C(0,t) = 0 = C_s$ IC) $C(x,0) = 0.55\,\text{wt\%} = C_0$

$C(\infty,t) = 0.55\,\text{wt\%} = C_0$

$$\Rightarrow \boxed{C(x,t) = C_0\,\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

b) w/ $D_{C,\text{alloy}}$ @ 1325 K = 3.3e-11 m²/s, after 10 hrs or 36,000 s

$$C = 0.25 = 0.55\,\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \Rightarrow \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{0.25}{0.55} = 0.455$$

$\text{erf}(z) = 0.455$ when $z \approx 0.4275$

$$\therefore \frac{x}{2\sqrt{Dt}} = z \Rightarrow x = 2z\sqrt{Dt} = 2(0.4275)\sqrt{(3.3e\text{-}11)(36{,}000)}$$

$$\boxed{x = 9.319e\text{-}4\ m = 0.9319\ mm}$$

HW#4 - cont

2) - pebble bed of Li_2TiO_3 spheres, $\phi = .2$ cm, $\rho = 3.43$ g/cc, M = 110 g/mol
- T produced uniformly @ rate of 5e-5 mol/day/cc
- T diffuses & gets swept away by H_2 @ 600°C
- SS: molar fraction 10^{-6} mol T/mol $LiTiO_3$
- $D = 10e^{-7}$ cm²/s

a) $\frac{\partial C}{\partial t} - \nabla(D\nabla C) - Q = 0$ assume 1) SS, $\frac{\partial C}{\partial t} = 0$
2) $\nabla D = 0$, spatially invariant D
3) spherical symmetry, $\frac{\partial C}{\partial \theta} = \frac{\partial C}{\partial \phi} = 0$

$\hookrightarrow -D\nabla^2 C = Q$

$\hookrightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) = -\frac{Q}{D}$

$\Rightarrow \frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = -\frac{Qr^2}{D} \Rightarrow r^2\frac{\partial C}{\partial r} = \frac{-Qr^3}{3D} + A_1 \Rightarrow \frac{\partial C}{\partial r} = \frac{-Qr}{3D} + \frac{A_1}{r^2}$

$C = \frac{-Qr^2}{6D} - \frac{A_1}{r} + A_2$

know $[C] = \frac{mol}{V}$, & $C_s = C_{H3} = 1e{-6}\, C_{LiTi_2O_2} = 3.118e{-8}$ mol/cc (@ surface)

for one sphere, $V = \frac{4}{3}\pi r^3 = 0.004189$ cm³, $m = \rho V = 0.01436$ g
$mol_{Li_2LiO_2} = m/M = 0.0001306$ mol, $C_{Li_2TiO_2} = 0.03118$ mol/cc

next, get Q in right units, $Q = 5e{-8} \frac{mol}{mm^3 \cdot day} \cdot \frac{1000\, mm^3}{cc} \cdot \frac{1\, day}{86{,}400\, s} = 5.787e{-10} \frac{mol}{cc \cdot s}$

next, BCs & ICs

BC) i) $C(r=1) = C_s = 3.118e{-8}$ mol/cc
ii) $C(r=0) \neq \infty$

HW#4-cont

Applying BCs

ii) $0 = 0 - \frac{A_1}{\infty} + A_2 \quad \therefore A_1 = 0 \qquad \Rightarrow C = \frac{-\mathcal{Q} r^2}{6D} + A_2$

i) $C_s = \frac{-\mathcal{Q}(1)^2}{6D} + A_2 \Rightarrow A_2 = C_s + \frac{\mathcal{Q}}{6D} = 3.118e{-8}\,\frac{mol}{cc} + 9.645e{-5}\,\frac{mol}{cc} = 9.648e{-5}$ mol/cc

$$\boxed{\Rightarrow C(r) = A_2 - \frac{\mathcal{Q} r^2}{6D} \quad w/\ A_2 = 9.6481e{-5}\ mol/cc,\ \ \mathcal{Q} = 5.787e{-10}\ mol/cc{\cdot}s}$$

b)

c) Snow loss/sphere / 1 day $= \mathcal{Q}V = 5e{-5}\,\frac{mol}{cc\cdot day} \cdot \frac{4}{3}\pi r^3 = 2.0944e{-7}\,\frac{mol}{day}$

$$\boxed{|\mathcal{Q}| = 2.0944e{-7}\,\frac{mol}{day} \quad \& \quad |\mathcal{Q}| = \mathcal{Q}V \ \text{ in SS}}$$

answers are somewhat off because of density used
↓

HW#4

3) Cu, FCC, $a = 0.36$ nm, $\nu = 1.3e13$ Hz, $Q = 1.3$ eV

a) know (4.1) $N_v = N\exp\left(\frac{-Q_v}{kT}\right) = \boxed{2.6955e21 \ \frac{\text{vacancies}}{m^3}}$

w/ $\rho = \frac{nM_{Cu}}{V_c N_A} = \frac{(4)(63.5\ g/mol)}{(a^3=(0.36e-7\ cm)^3)(6.022e23)} = 9.04\ g/cc$

& $N = \frac{N_A \rho}{M_{Cu}} = \frac{(6.022e23)(9.04)}{(63.5)} \cdot \left(1e6 \frac{cc}{m^3}\right) = 8.5734e28 \ \frac{\text{atoms}}{m^3}$

$N_v = N\exp\left(\frac{-Q_v}{kT}\right) = (8.57e28)\exp\left(\frac{-1.3\ eV}{(8.62e-5\ eV/K)((600+273)K)}\right) = 2.696e21 \ \frac{\text{vacancies}}{m^3}$

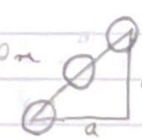
b) $D_0 = 2.5e-5\ m^2/s$, $Q = 2.1$ eV $\Gamma = \nu \exp\left(-\frac{\Delta H_m + T\Delta S_m}{kT}\right)$

know $D = \frac{1}{6}\lambda^2 \Gamma z = D_0 \exp(-Q/kT)$

$\Rightarrow \Gamma = \frac{6D_0}{\lambda^2 z}\exp(-Q/kT) = \frac{6(2.5e-5\ m^2/s)}{(2.546e-10\ m)^2(12)}\exp\left(\frac{-2.1\ eV}{(8.62e-5\ \frac{eV}{K})(600+273K)}\right) = 146.52$ Hz

↳ λ = spacing b/w planes = $a/\sqrt{2} = \frac{0.36e-9\ m}{\sqrt{2}} = 2.546e-10\ m$

$z = CN = 12$



$\Rightarrow \Gamma = \nu\exp(-Q/kT) \Rightarrow Q = \Delta H_m \Rightarrow \Delta H_m = \ln\left(\frac{\nu}{\Gamma}\right)kT = \boxed{1.897\ eV = \Delta H_m}$

Q as thermal entropy change is negligible... → $\boxed{\Delta S_m = 0}$