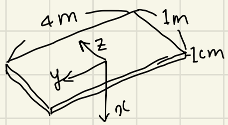
HW 3

김윤아

1.



$T = 1000\ K$

$D = 4\times10^{-7}\ cm^2\ s^{-1}$

(a) We neglect nitrogen losses from the bottom and edges of the plate.

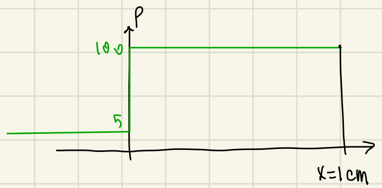
Thus, chemical potential gradient exists only in x direction.

$$\rho_n = \frac{X_n}{V_m}, \quad \frac{\partial \rho}{\partial t} = -J\cdot\nabla\rho = D\nabla^2\rho = D\cdot\frac{\partial^2 \rho}{\partial x^2}$$

$$J = -D\cdot\nabla\rho$$

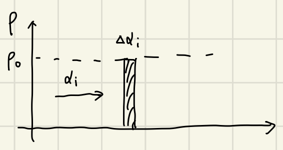
And set the surface of plate in contact with the atmosphere as $x=0$.

Then, the boundary condition can be obtained like below equations.



$$\begin{cases} \rho(0<x,\ t=0) = 100\ ppm \\ \rho(x\le 0,\ t) = 5\ ppm \\ \rho(0,\ t) = 5\ ppm \end{cases}$$

(b) For semi-finite source and i-th thin film among infinite thin film,



$$\rho_i(x,t) = \frac{\rho_0 \Delta\alpha_i}{\sqrt{4\pi D t}}\, e^{-\left(\frac{x-\alpha_i}{\sqrt{4Dt}}\right)^2}$$

In this condition, $\rho_0 = 100$ where $\alpha_i > 0$

$\rho_0 = 5$ where $\alpha_i < 0$

Then, $$\rho(x,t) = \int_0^1 \frac{100}{\sqrt{4\pi D t}}\, e^{-\left(\frac{x-\alpha}{\sqrt{4Dt}}\right)^2} d\alpha + \int_{-\infty}^{0} \frac{5}{\sqrt{4\pi D t}}\, e^{-\left(\frac{x-\alpha}{\sqrt{4Dt}}\right)^2} d\alpha$$

Set $\frac{x-\alpha}{\sqrt{4Dt}} = \eta$, $d\alpha = -2\sqrt{Dt}\, d\eta$

$$\rho(x,t) = -\frac{100}{\sqrt{\pi}}\int_{\frac{x}{\sqrt{4Dt}}}^{\frac{x-1}{\sqrt{4Dt}}} e^{-\eta^2}\, d\eta - \frac{5}{\sqrt{\pi}}\int_{+\infty}^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2}\, d\eta$$

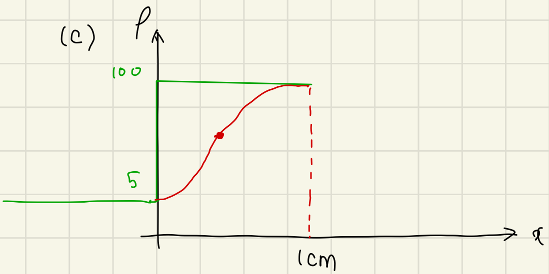
$$= -\frac{100}{\sqrt{\pi}}\left(\int_0^{\frac{x-1}{\sqrt{4Dt}}} e^{-\eta^2} d\eta - \int_0^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2} d\eta\right) - \frac{5}{\sqrt{\pi}}\left(\int_0^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2} d\eta - \overbrace{\int_0^{\infty} e^{-\eta^2} d\eta}^{\frac{\sqrt{\pi}}{2}}\right)$$

$$= 50\cdot\left(\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2} d\eta - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x-1}{\sqrt{4Dt}}} e^{-\eta^2} d\eta\right) + \frac{5}{2}\cdot\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{\sqrt{4Dt}}} e^{-\eta^2} d\eta\right)$$

$$= 50\,\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) - 50\,\mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right) - \frac{5}{2}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) + \frac{5}{2}$$

$$= \frac{95}{2}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) - 50\,\mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right) + \frac{5}{2}$$

(c)



When the average nitrogen concentration drops to 50%,

$$\rho(x,t) = \int_0^1 \rho(x,t)\,dx = 50$$

$$= \int_0^1 \frac{95}{2}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) - 50\,\mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right) + \frac{5}{2}$$

$$\int \mathrm{erf}(x)\,dx = x\,\mathrm{erf}(x) + \frac{e^{-x^2}}{\sqrt{\pi}} + C$$

$$\int \mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)dx = \frac{2\sqrt{Dt}}{\sqrt{\pi}}\, e^{-\frac{x^2}{4Dt}} + x\,\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) + C$$

$$\int \mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right)dx = \frac{2\sqrt{Dt}}{\sqrt{\pi}}\, e^{-\frac{(x-1)^2}{4Dt}} + (x+1)\,\mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right) + C$$

$$\int_0^1 \rho(x,t)\,dx = \int_0^1 \left(\frac{95}{2}\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) - 50\,\mathrm{erf}\left(\frac{x-1}{\sqrt{4Dt}}\right) + \frac{5}{2}\right)dx$$

$$= \frac{95}{2}\left[x\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) + \frac{2\sqrt{Dt}}{\sqrt{\pi}}\, e^{-\frac{x^2}{4Dt}}\right]_0^1$$

$$-50\left[(x-1)\,\mathrm{erf}\left(\frac{x-1}{2\sqrt{Dt}}\right) + \frac{2\sqrt{Dt}}{\pi}\, e^{-\frac{(x-1)^2}{4Dt}}\right]_0^1 + \frac{5}{2}$$

$$= \frac{95}{2}\left(-\frac{2\sqrt{Dt}}{\sqrt{\pi}} + \mathrm{erf}\left(+\frac{1}{2\sqrt{Dt}}\right) + \frac{2\sqrt{Dt}}{\sqrt{\pi}} \times e^{-\frac{1}{4Dt}}\right) - 50\left(-\mathrm{erf}\left(\frac{1}{2\sqrt{Dt}}\right)\right.$$

$$\left.- \frac{2\sqrt{Dt}}{\sqrt{\pi}} \times e^{-\frac{1}{4Dt}} + \frac{2\sqrt{Dt}}{\sqrt{\pi}}\right) + \frac{5}{2}$$

$$= \frac{199}{2}\left(-\frac{2\sqrt{Dt}}{\sqrt{\pi}} + \operatorname{erf}\left(\frac{1}{2\sqrt{Dt}}\right) + \frac{2\sqrt{Dt}}{\sqrt{\pi}}\, e^{-\frac{1}{4Dt}}\right) + \frac{5}{2}$$

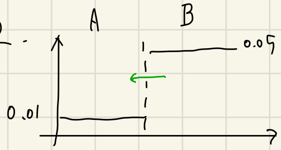
When $t=0$, $\int_0^1 \rho\, dx = 100$,

when $\int_0^1 \rho(x,t)\, dx = 50$, $t \approx 172.5$ hours

(d) $\int_0^1 \rho(x,t)\, dx = -199\frac{\sqrt{Dt}}{\sqrt{\pi}}\left(1-e^{-\frac{1}{4Dt}}\right) + \frac{199}{2}\operatorname{erf}\left(\frac{1}{2\sqrt{Dt}}\right)$

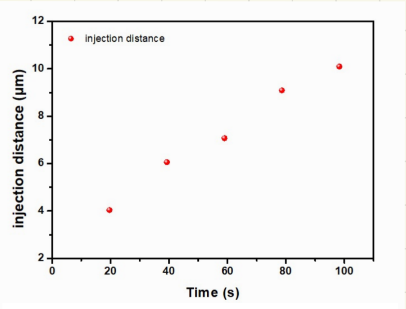
Set $\sqrt{Dt} = k$ and $\int_0^1 \rho(x,t)\,dx = -199\frac{\sqrt{k}}{\sqrt{\pi}}\left(1-e^{-\frac{1}{4k}}\right) + \frac{199}{2}\operatorname{erf}\left(\frac{1}{2\sqrt{k}}\right)$

In part (c), k is designated value and t decreases when D increases.
$(\sqrt{Dt} = k)$

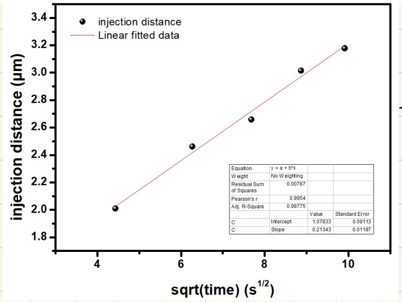
2. 

$1173\,K < T < 1473\,K$

(a) When $T = 1373\,K$

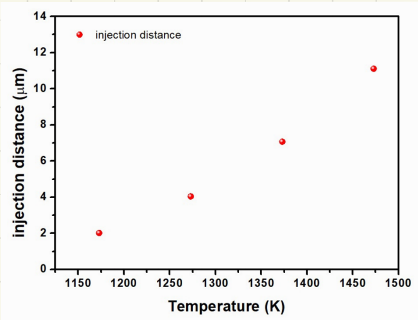


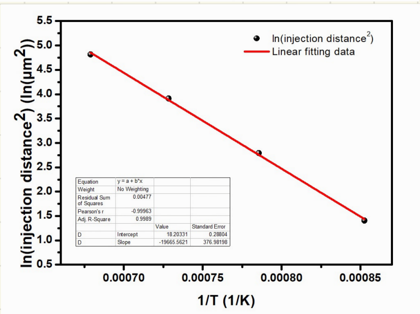
injection time (s)	$\sqrt{\text{injection time}}$ ($s^{1/2}$)	injection distance (μm)
19.657	4.434	4.04
39.314	6.270	6.06
58.972	7.680	7.07
78.629	8.867	9.09
98.286	9.914	10.1



$l \propto \sqrt{t}$

(b) When $t \approx 50\,s$





temperature (K)	(μm) injection distance
1173	2.02
1273	3.67
1373	7.07
1473	11.11

$\ln(l) \propto -\frac{1}{T}$

(c) Since $l \propto \sqrt{Dt}$, $2\ln l = \ln D + \ln t$

$D = D_0 e^{-\frac{Q}{RT}} \rightarrow \ln D = \ln D_0 - \frac{Q}{R} \cdot \frac{1}{T}$

Then, $2\ln\left(\frac{l_2}{l_1}\right) = -\left(\frac{Q}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$Q = -2R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \cdot \ln\left(\frac{l_2}{l_1}\right)$$

From (b), $T_1 = 1173\,K \rightarrow l_1 = 2.02\,\mu m$ @ $t \approx 50\,s$

$T_2 = 1273\,K \rightarrow l_2 = 3.67\,\mu m$

Then, $Q = -2R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \cdot \ln\left(\frac{l_2}{l_1}\right) \approx 148231$ J/mol