e Laplace Transform of

$$\frac{\partial V}{\partial t} = D\frac{\partial^2 V}{\partial r^2} \xrightarrow{\mathcal{L}} p\,\bar{V}(r,p) - V(r,0) = D\frac{\partial^2 \bar{V}}{\partial r^2}$$

Use initial condition

$$p\bar{V}(r,p) - V^* = D\frac{\partial^2 \bar{V}}{\partial r^2}$$

Rearrange

$$\frac{\partial^2 \bar{V}}{\partial r^2} - \frac{p}{D}\bar{V}(r,p) = \frac{-V^*}{D}$$

$\Downarrow$ Solution to this T.D.E.

eval. of β

$$\bar{V}(r,p) = \frac{V^*}{p} + \alpha e^{-(p/D)^{1/2} r} + \beta e^{(p/D)^{1/2} r} = 0$$

as $r \to \infty$ $e^{(p/D)^{1/2} r} \to \infty$

so $\beta = 0$

Now sub. $V^* = r\,C^*$ & $\bar{V}(r,p) = r\bar{C}(r,p)$

so,

$$r\bar{C}(r,p) = \frac{rC^*}{p} + \alpha e^{-(p/D)^{1/2} r}$$

eval. of α

From boundary condition $C(r=r_0, t) = 0$ $\therefore$ $\bar{C}(r=r_0, p) = 0$ also $\bar{V}(r=r_0, p) = 0$

$$\therefore \quad 0 = \frac{r_0 C^*}{p} + \alpha e^{-(p/D)^{1/2} r_0} \Longrightarrow \alpha = \frac{-r_0 C}{p} e^{(p/D)^{1/2} r_0}$$

Now we have

$$r\bar{C}(r,p) = \frac{rC^*}{p} - \frac{r_0 C^*}{p} e^{(p/D)^{1/2} r_0} e^{-(p/D)^{1/2} r}$$

knowing that for $\frac{e^x}{e^y} = e^{x-y}$

$$r\bar{C}(r,p) = \frac{rC^*}{p} - \frac{r_0 C^*}{p} e^{-(p/D)^{1/2}(r - r_0)}$$

or (Next page)

$$\bar{C}(r,p) = \frac{C^*}{p}\left(1 - \frac{r_0}{r} e^{-(p/D)^{1/2}(r-r_0)}\right) \quad \underline{\text{eqn } A}$$

Knowing that,

$$i = nFAD\left[\frac{\partial C(r,t)}{\partial r}\right]_{r=r_0} \quad \underline{\text{eqn } B}$$

We can take $\mathcal{L}^{-1}$ of eqn A & derive however easier to take $\frac{\partial}{\partial r}$ of eqn A then $\mathcal{L}^{-1}$.

$$\frac{\partial \bar{C}(r,p)}{\partial r} = 0 - \left[\left(\frac{C^* r_0}{pr} e^{-(p/D)^{1/2}(r-r_0)}\left(-\frac{p}{D}\right)^{1/2}\right) + \left(\frac{C^* r_0}{p r^2} e^{-(p/D)^{1/2}(r-r_0)}\right)\right]$$

$\Downarrow$ Simplify

$$\frac{\partial \bar{C}(r,p)}{\partial r} = \frac{C^* r_0}{D^{1/2} p^{1/2} r} e^{-(p/D)^{1/2}(r-r_0)} + \frac{C^* r_0}{r^2 p} e^{-(p/D)^{1/2}(r-r_0)}$$

$\Downarrow \mathcal{L}^{-1}$

$$\frac{\partial C(r,t)}{\partial r} = \frac{C^* r_0}{r D^{1/2} \pi^{1/2} t^{1/2}} e^{-(r-r_0)^2} + \frac{C^* r_0}{r^2} \operatorname{erfc}\left(\frac{r-r_0}{2t^{1/2}D^{1/2}}\right)$$

To evaluate $\frac{\partial C(r,t)}{\partial r}$ at $r=0$ we know that $r = r_0$

$\therefore$ $r - r_0 = 0$ also $e^0 = 1$ $\operatorname{erf}(0) = 0$ so $\operatorname{erfc}(0) = 1 - \operatorname{erf}(0) = 1$

Now we have

$$\frac{\partial C(r,t)}{\partial r} = \frac{C^*}{(D\pi t)^{1/2}} + \frac{C^*}{r} \quad \text{sub in } \underline{\text{eqn } B}$$

$$i = nFADC^*\left(\frac{1}{(D\pi t)^{1/2}} + \frac{1}{r_0}\right)$$

2] $$E_{1/2} = E^0 + \frac{RT}{nF}\ln K_d - \frac{RT}{nF}\ln\frac{D^{1/2}_{M(Hg)}}{D^{1/2}_{MXp}} - p\frac{RT}{nF}\ln C^b_X$$

RT/F = 0.0257 V n = 2

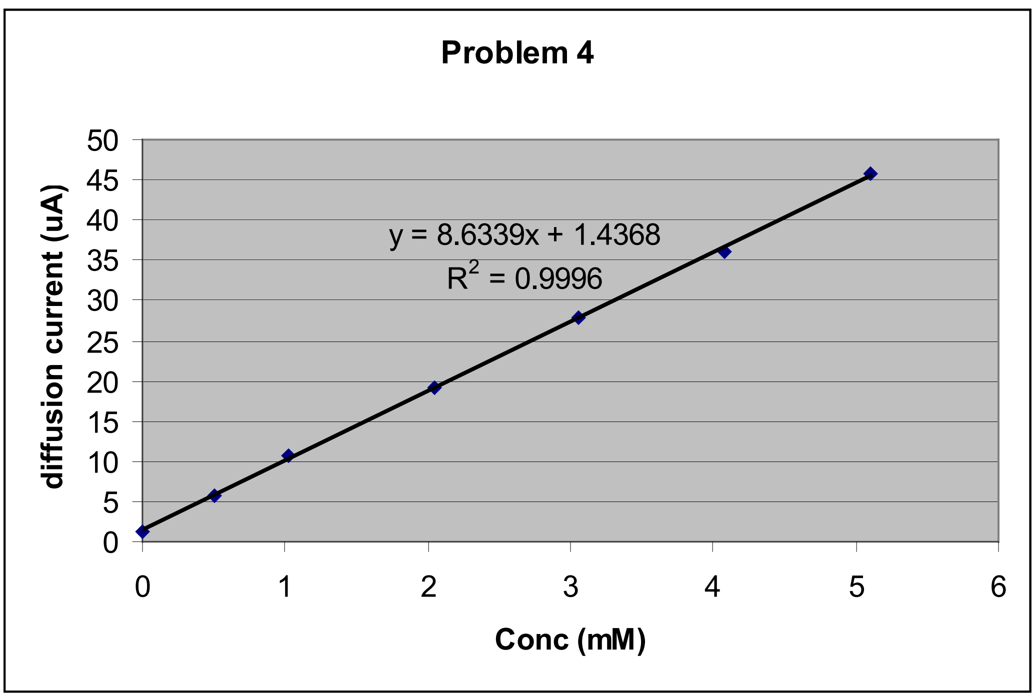
Plot $E_{1/2}$ vs. ln C_X^b using Excel or equivalent

Slope = 0.0513 V find that p = 4

Intercept = 0.566 V E^0 + RT/nF ln K_d $E^0 = 0.081$ K_d = 4.4e-20

3] 0.15 uA/c_{unk} = 0.30 uA/((Cunk10ml/11ml) + (0.5 mM(1ml/11ml))

4]



Use fitted line to find unknown concentrations.

5] slope = 8.63 = 607*2*$D^{1/2}$*$2.63^{2/3}$*$2.88^{1/6}$

D = 9.8e6 cm^2/s

6] plot log $[Pb^{2+}]$ vs. $E_{1/2}$, Nernstian relationship

$E_{½} = -0.0605 \log [Pb^{2+}] – 0.578$ $\quad -0.0605 = -0.0592\ x/n$ $\quad n = 2$ $\quad x = 2.0$

7] a) 0.000348/min b) 0.118%