1. Suppose we have the following cell at 25°

(a) First user standard condition determines which cation undergoes reaction by comparing their standard reaction potential.

(b) Calculate standard EMF

(c) Suppose the following concentration for Ca^{2+} and K^+:

$[Ca^{2+}(aq)] = 1M$

$[K^+(aq)] = 10^{-6}$ M

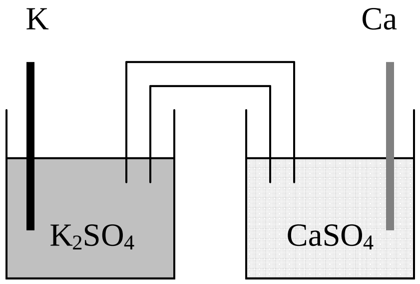
Calculate EMF.

(d) Plot the cell potential as a function of $\frac{[Ca^{2+}(aq)]^{1/2}}{[K^+(aq)]}$ concentration.

(e) What is the ratio of $\frac{[Ca^{2+}(aq)]^{1/2}}{[K^+(aq)]}$ at which the direction of reaction would change?

(f) Start with $[Ca^{2+}] = 0$ and $[K^+] = 1M$ we allow a current to flow. At equilibrium when there no potential anymore what will be the final concentration of $[Ca^{2+}]$?

(g) What will be the total amount of charge transfer?



2. Consider a z-z electrolyte

$$\rho(x) = n^0 z e_0 \left[exp \frac{(-zF\varphi(x))}{RT} - exp \frac{(zF\varphi(x))}{RT} \right]$$

(a)Derive the equation for capacity

$$C = \frac{\varepsilon\varepsilon_0}{L_D} cosh\left(\frac{zF\varphi}{2RT}\right), \qquad L_D = \frac{1}{\kappa}$$

(b) Obtain an equation for charge density σ for small potential. Can this equation describe the experimental data (the plot of the charge density as a function of potential is in the lecture note).

(a) We write both reactions in reduction forms:

$K^+ + e^- \rightarrow K$ $\qquad E_K^0 = -2.92\,V$

$Ca^{2+} + 2e^- \rightarrow Ca$ $\qquad E_{Ca}^0 = -2.76\,V$

Since $E_{Ca}^0 > E_K^0$ the reduction of Ca is more favorable, therefore Ca electrode is the cathode side.

(b) $E^0 = E_c^0 - E_a^0 = -2.76 - (-2.92) = 0.16\,V$

And the overall reaction will be:

$$K + \frac{1}{2}Ca^{2+} \rightarrow K^+ + \frac{1}{2}Ca$$

(c) using Nerst Eq.

$$E = E^0 - \frac{RT}{|\nu|F} ln\left(\frac{\left[K^+(aq)\right]}{\left[Ca^{2+}(aq)\right]^{1/2}}\right) \qquad (1)$$

where $\left[K^+(aq)\right] = 1\,M$

and $\left[Ca^{2+}(aq)\right] = 10^{-6}\,M \quad \Leftrightarrow \left[Ca^{2+}(aq)\right]^{1/2} = 10^{-3}\,M$

$$E = 0.16 - 0.0258\,ln\left(\frac{1}{0.001}\right)$$

$$E = -0.018\,V$$

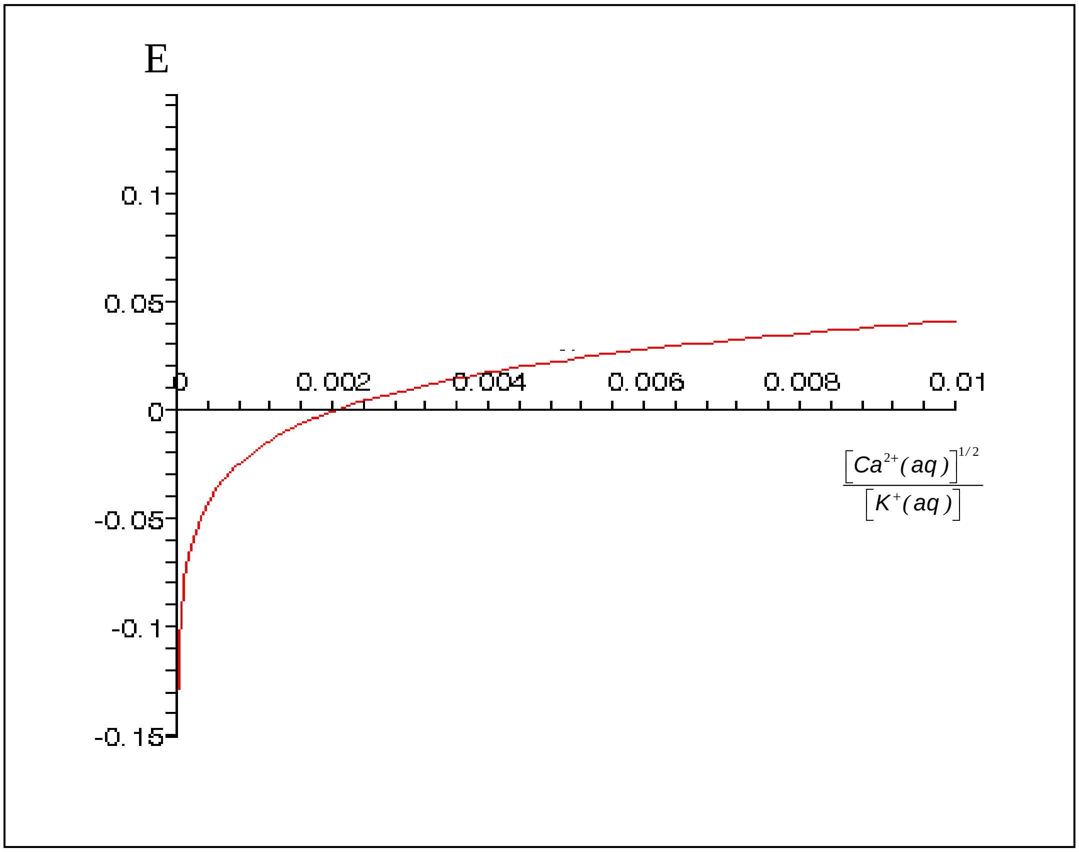
Note: The sign of the EMF potential (E=-0.018) shows that the direction of the reaction is changed due to the low concentration of $\left[Ca^{2+}(aq)\right]$ and therefore Ca will be in anode side.

(d) Using Equation (1)

$$E = E^0 - \frac{RT}{F} ln\left(\frac{\left[K^+(aq)\right]}{\left[Ca^{2+}(aq)\right]^{1/2}}\right)$$

Now we write this equation with respect to the ratio $\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^+(aq)\right]}$

$$E = E^0 + \frac{RT}{F} ln\left(\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^+(aq)\right]}\right)$$



(e) At point P: E=0 and therefore:

$$E = E^0 + \frac{RT}{F} ln\left(\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^+(aq)\right]}\right) = 0$$

$$ln\left(\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^{+}(aq)\right]}\right)=\frac{-0.16}{0.0258}=-6.201$$

$$\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^{+}(aq)\right]}=2.02x10^{-3} \qquad (2)$$

(f) The initial concentrations of K and Ca are $\left[K^{+}(aq)\right]_i=1M$ and $\left[Ca^{2+}(aq)\right]_i=0$ respectively. In this case because the ration of $\frac{\left[Ca^{2+}(aq)\right]^{1/2}}{\left[K^{+}(aq)\right]}=0$ according to the graph we have back reaction. Now if we allow the current to flow, the initial concentration of $\left[K^{+}(aq)\right]$ reduced and the concentration of $\left[Ca^{2+}(aq)\right]$ increases the EMF potential become zero. In this case the ratio of both concentrations satisfy the equation (2). Hence

$$\frac{\left[Ca^{2+}(aq)\right]_f^{1/2}}{\left[K^{+}(aq)\right]_f}=2.02x10^{-3} \qquad (3)$$

Index f specifies the final concentration. The final concentration can be calculation by mass balance (for each mol of K^{+} there will be ½ mol of Ca^{2+})

$$\left[Ca^{2+}(aq)\right]_f-\left[Ca^{2+}(aq)\right]_i=\frac{1}{2}\left[K^{+}(aq)\right]_i-\left[K^{+}(aq)\right]_f$$

$$\left[Ca^{2+}(aq)\right]_f-0=\frac{1}{2}\left(1-\left[K^{+}(aq)\right]_f\right)$$

Replacing that into equation (3) we will have:

$$\frac{\left(1/2\left(1-\left[K^{+}(aq)\right]_f\right)\right)^{1/2}}{\left[K^{+}(aq)\right]_f}=2.02x10^{-3}$$

$$\left[K^{+}(aq)\right]_f = 4.08x10^{-6}$$

Now each K^{+} produces one electron and therefore the number of electron transfer per volume is given by:

$$n = N_A [K^{+}(aq)] = 6.02x10^{23} x 4.08x10^{-6} = 2.45x10^{18}$$

Each electron has e^{0}=1.602x10^{-19}C. Therefore the amount of the charge transfer becomes:

$$e = e^{0} xn = 1.602x10^{-19} x 2.45x10^{18} = 0.39\,C$$

(a) According to Poisson's equation:

$$\frac{d^2\varphi}{dx^2} = \frac{-\rho(x)}{\varepsilon\varepsilon_0}, \quad \rho(x) = n^0 ze_0 \left[exp\left(-\frac{zF\varphi(x)}{RT} \right) - exp\left(\frac{zF\varphi(x)}{RT} \right) \right]$$

replacing the charge density into Poisson's equation we have:

$$\frac{d^2\varphi}{dx^2} = \frac{-n^0 ze_0}{\varepsilon\varepsilon_0} \left[exp\left(-\frac{zF\varphi(x)}{RT} \right) - exp\left(\frac{zF\varphi(x)}{RT} \right) \right] \quad (1)$$

We define:

$$\phi = \frac{zF}{RT}\varphi \quad (2)$$

$$\Rightarrow \quad \frac{d^2\phi}{dx^2} = \frac{zF}{RT}\frac{d^2\varphi}{dx^2} \quad \Rightarrow \quad \frac{d^2\varphi}{dx^2} = \frac{RT}{zF}\frac{d^2\phi}{dx^2} \quad (3)$$

$$n^0 e_0 = N_A C^0 e_0 = FC^0 \quad (4)$$

Applying Eq. (3), (4) into (1):

$$\Rightarrow \quad \frac{d^2\phi}{dx^2}=\frac{-z^2F^2C^0}{RT\varepsilon\varepsilon_0}\left(exp(-\phi)-exp(-\phi)\right) \quad =\frac{2z^2F^2C^0}{RT\varepsilon\varepsilon_0}sinh(\phi) \qquad (5)$$

Now we define:

$$\Rightarrow \quad \kappa^2=\frac{-2z^2F^2C^0}{RT\varepsilon\varepsilon_0}$$

Therefore eq. (5) becomes:

$$\frac{d^2\phi}{dx^2}=\kappa^2\, sinh(\phi)$$

We multiply both sides into $\frac{d\varphi}{dx}$

$$\frac{d\varphi}{dx}\frac{d^2\phi}{dx^2}=\kappa^2\, sinh(\phi)\frac{d\varphi}{dx}$$

$$\frac{1}{2}\frac{d}{dx}\left(\frac{d\phi}{dx}\right)^2=\kappa^2\frac{d}{dx}cosh(\phi) \qquad (6)$$

Note: $\frac{d}{dx}cosh(x)=sinh(x),\quad \frac{d}{dx}sinh(x)=cosh(x)$

By taking an integral on both sides of (6) we get:

$$\int_{x=0}^{x=\infty} d\left(\frac{d\phi}{dx}\right)^2=2\kappa^2\int_{\varphi=\varphi_\Delta}^{\varphi=0} d\left(cosh(\phi)\right)$$

Note: at x=0 we have $\varphi=\varphi_\Delta$ and in x=∞, $\varphi=0$

$$\left(\frac{d\phi}{dx}\right)^2_{x=\infty}-\left(\frac{d\phi}{dx}\right)^2_{x=0}=2\kappa^2\left(cosh(\phi=0)-cosh(\phi_\Delta)\right)$$

$$\Rightarrow \quad 0-\left(\frac{d\phi}{dx}\right)^2_{x=0} = 2\kappa^2\left(1-cosh(\phi_\Delta)\right)$$

$$\Rightarrow \quad 0-\left(\frac{d\phi}{dx}\right)^2_{x=0} = 2\kappa^2\left(1-cosh(\phi_\Delta)\right)$$

Using $1-cosh(x)=2\,sinh^2\left(\frac{x}{2}\right)$

$$\Rightarrow \quad \left(\frac{d\phi}{dx}\right)^2_{x=0} = 4\kappa^2\left(sinh^2\left(\frac{\phi_\Delta}{2}\right)\right)$$

$$\Rightarrow \quad \left(\frac{d\phi}{dx}\right)_{x=0} = 2\kappa\left(sinh\left(\frac{\phi_\Delta}{2}\right)\right)$$

Applying eq.(2) we have:

$$\Rightarrow \quad \frac{zF}{RT}\left(\frac{d\varphi_\Delta}{dx}\right)_{x=0} = 2\kappa\left(sinh\left(\frac{zF}{2RT}\varphi_\Delta\right)\right)$$

$$\Rightarrow \quad \left(\frac{d\varphi_\Delta}{dx}\right)_{x=0} = 2\kappa\frac{RT}{zF}\left(sinh\left(\frac{zF}{2RT}\varphi_\Delta\right)\right) \qquad (7)$$

According to the definition of charge density σ:

$$\Rightarrow \quad \sigma = \varepsilon\varepsilon_0\left(\frac{d\varphi_\Delta}{dx}\right)_{x=0}$$

Replacing the eq.(7) into this equation we will have:

$$\Rightarrow \quad \sigma = \frac{2\varepsilon\varepsilon_0 RT}{zF}\kappa\left(sinh\left(\frac{zF}{2RT}\varphi_\Delta\right)\right)$$

And finally the definition for capacity is given by:

$$C = \left(\frac{\partial\sigma}{\partial\varphi_\Delta}\right)$$

$$C = \left(\frac{2\varepsilon\varepsilon_0 RT}{zF}\right)\left(\frac{zF}{2RT}\right)\kappa\left(cosh\left(\varphi_\Delta\right)\right)$$

$$C = \varepsilon\varepsilon_0 \kappa \left(cosh \left(\varphi_\Delta \right) \right)$$

$$C = \frac{\varepsilon\varepsilon_0}{L_D} \left(cosh \left(\varphi_\Delta \right) \right), \quad L_D = \frac{1}{\kappa}$$

(b) The equation we have for charge density:

$$\sigma = \frac{2\varepsilon\varepsilon_0 RT\kappa}{zF} sinh\left(\frac{zF\varphi}{2RT} \right)$$

For small potential:

$$sinh\left(\frac{zF\varphi}{2RT} \right) = \frac{zF\varphi}{2RT}$$

Therefore

$$\sigma = \frac{2\varepsilon\varepsilon_0 RT\kappa}{zF} \frac{zF\varphi}{2RT} = \varepsilon\varepsilon_0 \kappa\varphi$$

According to eq.4

$$\kappa = zF\sqrt{\frac{2c^0}{\varepsilon\varepsilon_0 RT}}$$

Replacing this equation into the equation for σ we will get

$$\boxed{\sigma = zF\varphi\sqrt{\frac{2\varepsilon\varepsilon_0 c^0}{RT}}}$$

This equation shows that charge density is a linear function of potential which is in agreement with experimental plot, however this equation shows that charge density is also a linear function of z which is in disagreement with the experiment. Overall this equation fails to explain the experiment