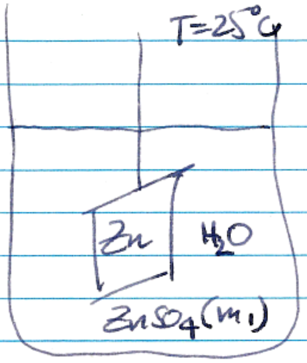
Introduction to Electrochemical Cells + Equilibrium

- what is electrochemistry – The science of chemical reactions involving electron transfer

first, let's look at the std. p.chem. treatment –

Example

$$Zn = Zn^{++} + 2e^-$$



– elemental zinc (metallic zinc) is insoluble in water

– ionized zinc is soluble

∴ if Zn loses 2 electrons to form Zn^{++}, then Zn^{++} dissolves

∴ Zn dissolution occurs only by electron transfer – to sustain rxn requires an electron sink

* electrode – electronic conductor

* electrolyte – ionic conductor

electrochemistry exists because of immiscibility

⇒ electrons can't swim /// what if they can?
→ ions can't run ///

– tendency of this rxn to occur is measured by that electrical potential at the electrode

greater tendency to dissolve will result in greater tendency for electrons to accumulate in the electrode ⇒ by measuring the electrical potential of any electrode w.r.t. a standard electrode we get a ranking of the tendencies of metals to dissolve in a given medium

⇒ electrochemical series, emf series
"electromotive force"

in water the standard electrode is hydrogen

$$\underset{\uparrow}{\tfrac{1}{2} H_2 (g, 1\,\text{atm})} = \underset{\uparrow}{H^+ (a=1)} + e^-$$

conducted on platinized platinum   1.2 mole/litre

- emf series ⇒ ≡ium potentials ⇒ reversible rxns // See insert.
- reversible work at const. T + P = $-\Delta G$

electrical work = qV

charge transferred = $\underset{\uparrow}{n}\mathcal{F}$ ← Faraday const.
96485 C/mol
N_{Av} electrons!

electrovalency of rxn

$$-w_{rev} = \Delta G = -n\mathcal{F}\mathcal{E}$$

recall in general that for a chemical rxn

$$aA + bB = cC + dD$$

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{a_C^{\,c}\, a_D^{\,d}}{a_A^{\,a}\, a_B^{\,b}}\right)$$

if such rxn can be made to occur in an e.c. all we can monitor voltage!

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln\left(\frac{a_C^{\,c}\, a_D^{\,d}}{a_A^{\,a}\, a_B^{\,b}}\right)$$ Nernst Eq^n

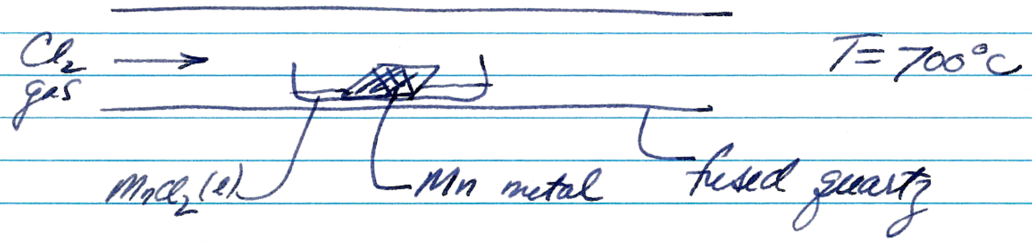
$$\mathcal{E} = \mathcal{E}^\circ - 0.0591 \log_{10}(\quad)$$ T=25°C

electrochemical cell: device for keeping two electrode rxns separated in such a way that they occur only by transport of e^- through external circuit /

now let's look at the intro to e.c. from another perspective — the overall electrical circuit.

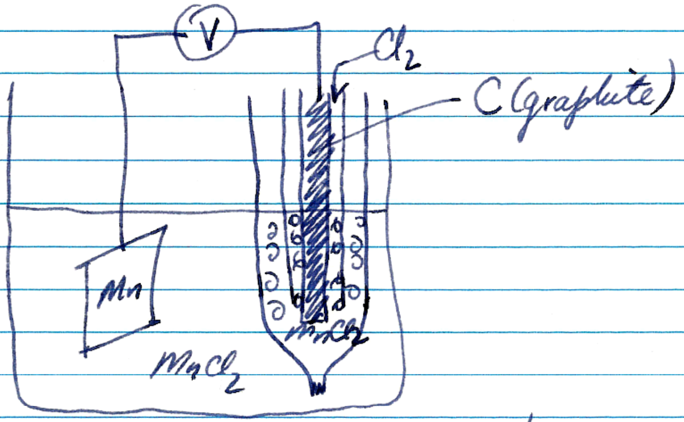
Example: chlorination of manganese at elevated T

Method 1 — Thermochemical



$$Mn + Cl_2 \rightarrow MnCl_2\,(l)$$

Method 2 — Electrochemical



Cathode?
anode?

$$Mn \rightarrow Mn^{2+} + 2e^-$$

$$Cl_2 + 2e \rightarrow 2Cl^-$$

$$Mn + Cl_2 = MnCl_2\,(l)$$

driving force for this rxn (ΔG) can be related to the voltage measured (potential difference)

Comments about V measurement

Types of Cells:

Formation Cells $Mn / MnCl_2 / Cl_2, C$

$Mn + Cl_2 = MnCl_2$

what happens when everything is not at unit activity?

$Mn / MnCl_2 - NaCl / Cl_2, C$

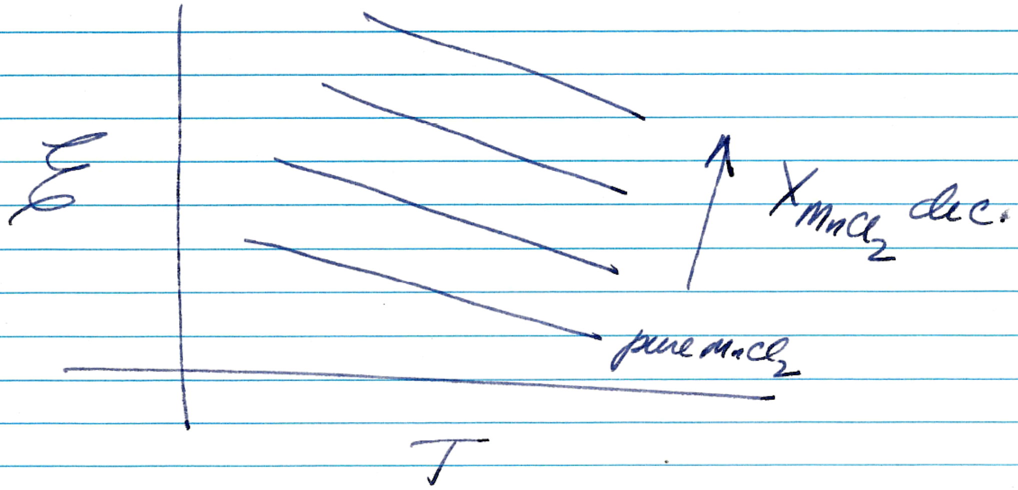
⇒ measure solution properties of multicomponent soln's

$Mn + Cl_2 = \underline{MnCl_2}$ (in sol^n)

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{2F} \ln a_{MnCl_2}$$

⇒ set up cells with various conc. of $MnCl_2$ in NaCl

measure $\mathcal{E}$ vs T $\underline{\underline{\mathcal{E} = a + bT}}$



$$\Delta\bar{G}_{MnCl_2} = RT\ln a_{MnCl_2} = -2\mathcal{F}(\mathcal{E}-\mathcal{E}^\circ)$$

$$\Delta\bar{S}_{MnCl_2} = -2\mathcal{F}\left\{\frac{\partial(\mathcal{E}-\mathcal{E}^\circ)}{\partial T}\right\}$$

$$\Delta\bar{H}_{MnCl_2} = -2\mathcal{F}\left\{\frac{\partial[(\mathcal{E}-\mathcal{E}^\circ)/T]}{\partial\, 1/T}\right\}$$

how to get properties of NaCl?

what happens if Mn is not pure?

instead of $Mn \,/\, MnCl_2 \,/\, Cl_2, C$ $\quad \mathcal{E}^\circ$

we have $Mn\text{-}X \,/\, MnCl_2 \,/\, Cl_2, C$ $\quad \mathcal{E}$

$$\mathcal{E}-\mathcal{E}^\circ = \frac{RT}{2\mathcal{F}}\ln a_{Mn}.$$

in other words, consider the cell

$$Mn \,/\, MnCl_2 \,/\, Mn\text{-}X$$

what is spontaneous chem. rxn?

$$Mn \longrightarrow Mn\text{-}X$$

$Mn \rightarrow Mn^{2+} + 2e$ at high conc.

$\underline{Mn^{2+} + 2e \rightarrow Mn\text{-}X}$ at low conc.

$$Mn \rightarrow Mn\text{-}X$$

$\Delta G = \Delta G^\circ + RT\ln a_{Mn}$ // requirements of Mn-X system?

for this rxn, $\Delta G^\circ = 0 \Rightarrow \mathcal{E}^\circ = 0$

$\mathcal{E} = -\frac{RT}{2\mathcal{F}} \ln a_{Mn}$ // use molten salt conc. cell to measure t.d. properties of metal alloy

$\Rightarrow$ Then Gibbs-Duhem integration give properties of the alloying element X

What about chlorine pressure?

put 2 chlorine electrodes, but different chlorine pressures.

$Cl_2(g, P = P') / MnCl_2 / Cl_2(g, P_{ref})$

suppose $P' < P_{ref}$

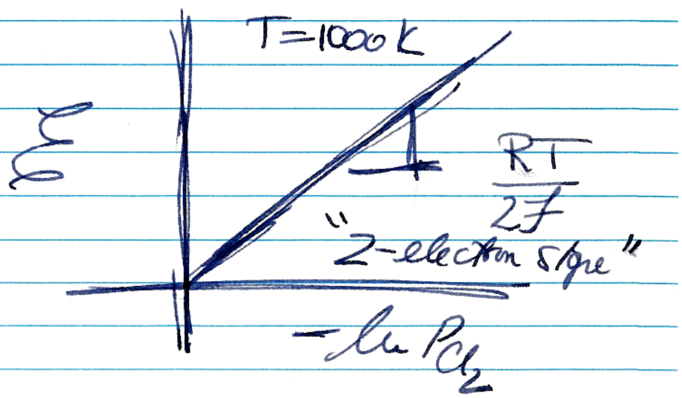
$\Rightarrow$ cell rxn is $Cl_2(P_{high}) \rightarrow Cl_2(P_{low})$

$$Cl_2(P_{ref}) + 2e^- \rightarrow 2Cl^-$$
$$2Cl^- \rightarrow Cl_2(P') + 2e^-$$
$$\overline{\qquad\qquad\qquad\qquad\qquad}$$
$$Cl_2(P_{ref}) \rightarrow Cl_2(P')$$

$\Delta G = \Delta G^\circ + RT \ln(P'/P_{ref})$

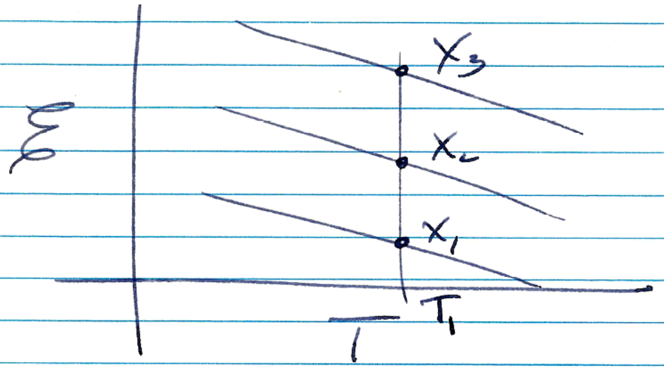
$\mathcal{E} = -\frac{RT}{2\mathcal{F}} \ln(P'/P_{ref})$

$\mathcal{E}$ (V)	P_{Cl_2} (atm)
0	1
0.099	0.1
0.198	0.01
⋮	⋮

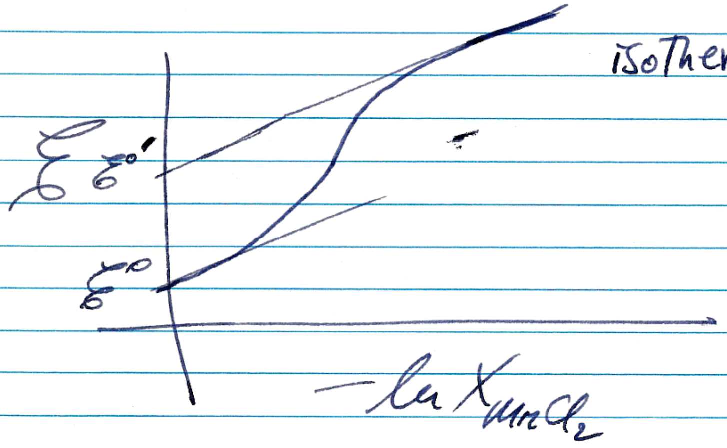


Thermodynamic Models

Mn / $MnCl_2$ – NaCl / Cl_2, C



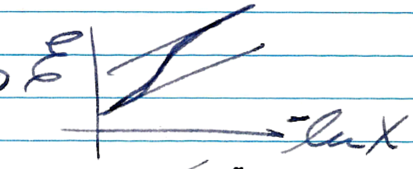
$$\mathcal{E} = \underset{\Delta\bar{H}_{MnCl_2}}{\underset{\uparrow}{a}} + \underset{-\Delta\bar{S}_{MnCl_2}}{\underset{\uparrow}{b}}T$$



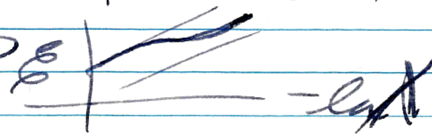
$$\mathcal{E} = \mathcal{E}^{o} - \frac{RT}{2F} \ln a_{MnCl_2}$$

$$= \mathcal{E}^{o} - \frac{RT}{2F} \ln \gamma_{MnCl_2} - \frac{RT}{2F} \ln X_{MnCl_2}$$

when $\gamma < 1$, $\ln \gamma < 0 \Rightarrow$



when $\gamma > 1$, $\ln \gamma \geq 0 \Rightarrow$



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3.53 Electrochemical Processing of Materials

Spring 2001

The Muon g-2 Experiment uses the Alternating Gradient Synchrotron (AGS) to deliver a custom muon beam into the world's largest superconducting magnet -- the "muon storage ring" -- pictured above. (Image courtesy of the U.S. Department of Energy's Brookhaven National Laboratory.)

Course Highlights

This course features problem sets with solutions and sample exams.

» Watch a video introduction featuring the course instructor.
(RM - 56K) (RM - 80K) (RM - 220K)

Course Description

This course covers a variety of topics concerning superconducting magnets, including thermodynamic and transport properties of aqueous and nonaqueous electrolytes, the electrode/electrolyte interface, and the kinetics of electrode processes. It also covers electrochemical characterization with regards to d.c. techniques (controlled potential, controlled current) and a.c. techniques (voltametry and impedance spectroscopy). Applications of the following will also be discussed: electrowinning, electrorefining, electroplating, and electrosynthesis, as well as electrochemical power sources (batteries and fuel cells).

Special Features

Faculty introduction video

GO

Assignments

Problem Set 1 (PDF)
Problem Set 1 Solution (PDF)

Model Solutions for Problem Set 2 (PDF)

Model Solutions for Problem Set 3 (PDF)

Model Solutions for Problem Set 4 (PDF)

Model Solutions for Problem Set 5 (PDF)

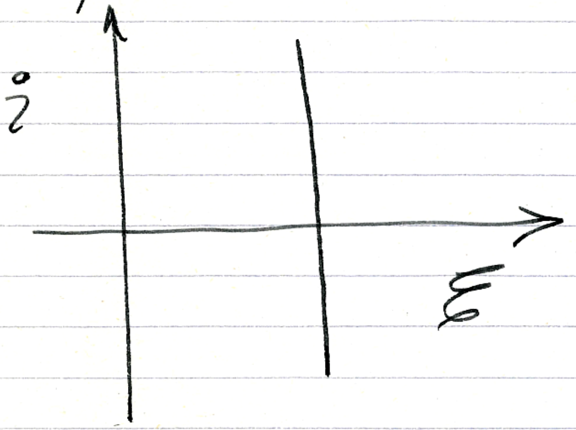
Model Solutions for Problem Set 6 (PDF)

Model Solutions for Problem Set 7 (PDF)

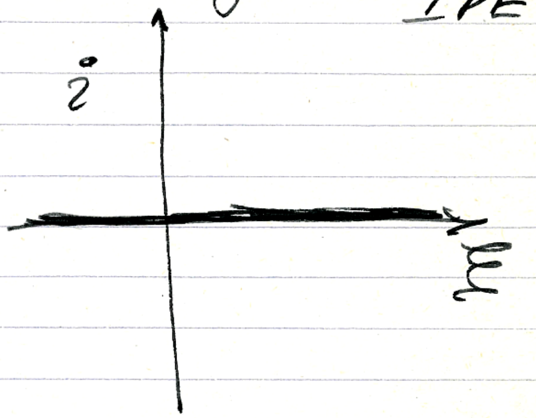
Reference Electrodes and such...

2 extremes of electrode behavior

reference electrode RE

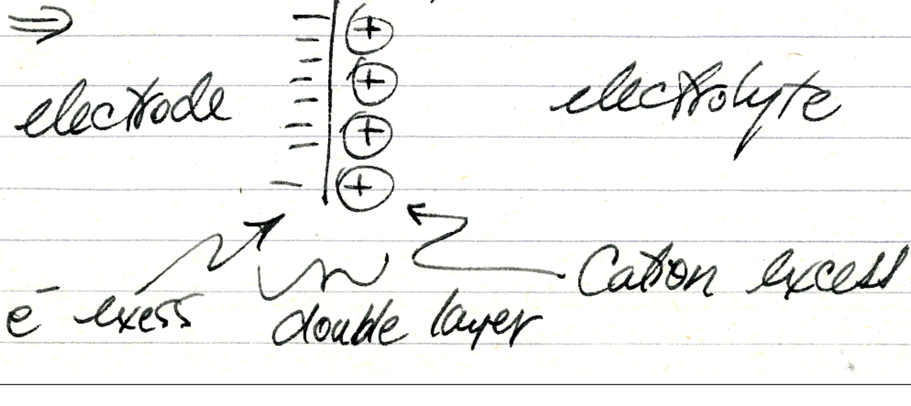


ideal polarizable electrode IPE



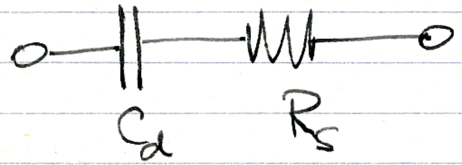
- departure of potential from =ium or Nernstian value is called POLARIZATION
- RE is nonpolarizable — draw current without change in potential
- IPE is fully polarizable — no charge transfer regardless of potential
- IPE behaves as a capacitor — why — when applied potential sets e^- population, & compensation occurs in the electrolyte e.g. if electrode becomes cathodic (e^- excess) then adjacent to electrode there will be change to place cations in greater numbers than found in the bulk electrolyte

⇒



- double layer is electrically equivalent to a CAPACITOR — we refer to the double-layer capacitance, C_d, ≈ 10 – 40 $\mu F/cm^2$

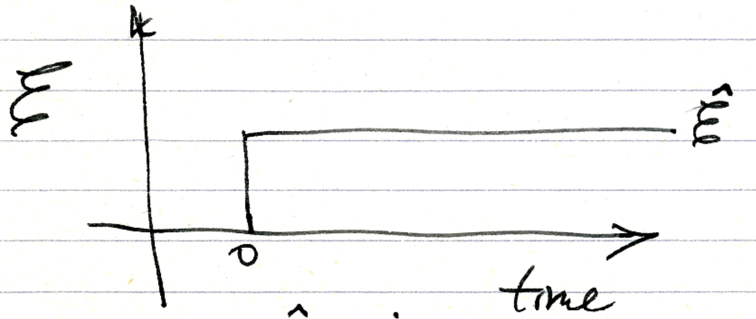
- Construct a cell consisting of IPE & RE
- RE is electrically equivalent to a short
- electrolyte is electrically equivalent to a resistor

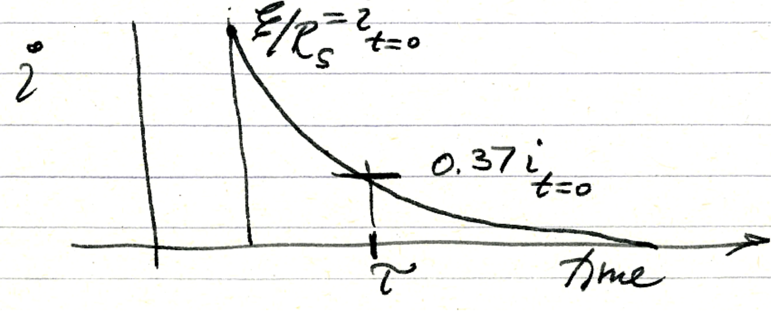


IPE | electrolyte | RE

- what happens when the applied potential is stepped from some initial value to $\hat{\mathcal{E}}$?

⇒ charging of the capacitor ≡ double layer





$\tau = R_s C_d$

$R_s \approx 1\ \Omega$

$C_d \approx 20\ \mu F$

$\therefore \tau = 20\ \mu s$

Can show that $i = \frac{\hat{\mathcal{E}}}{R_s} \exp\left(-\frac{t}{R_s C_d}\right)$

$\Rightarrow$ for potential step at IPE (no faradaic process) you still observe initially a current response!

what makes a RE work? — fast kinetics $\Rightarrow$ ~~all~~ always in $\equiv$ium $\Rightarrow$ stable potential

recall

$$\tfrac{1}{2} H_2 \overset{Pt}{=} H^+ + e^-$$

$\nearrow$ fix $P_{H_2} \Rightarrow$ fix μ_{H_2}

$\rightsquigarrow$ fix $C_{H^+} \Rightarrow$ fix μ_{H^+}

$\therefore \mu_{e^-}$ fixed $\Rightarrow \mathcal{E}_{H_2/H^+}$ fixed

how to measure $\mathcal{E}$? — measure i across standard R — draw current $\Rightarrow$ net rxn $\Rightarrow$ off equilibrium $\Rightarrow$ off std. potential

BUT IF

$$\tfrac{1}{2} H_2 \xrightleftharpoons[\hspace{6em}]{\hspace{6em}} H^+ + e^-$$

THEN

$$\tfrac{1}{2} H_2 \xrightleftharpoons[\hspace{6em}]{\hspace{6em}} H^+ + e^-$$

doesn't change $\mathcal{E}$ by much. $\uparrow$ net current examples of RE:

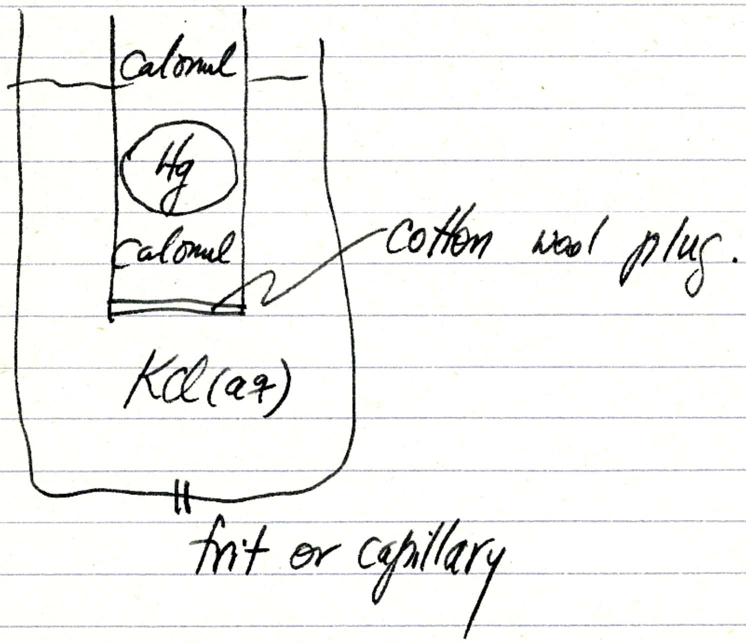
silver / silver chloride $Ag/AgCl/KCl_{(aq)}$

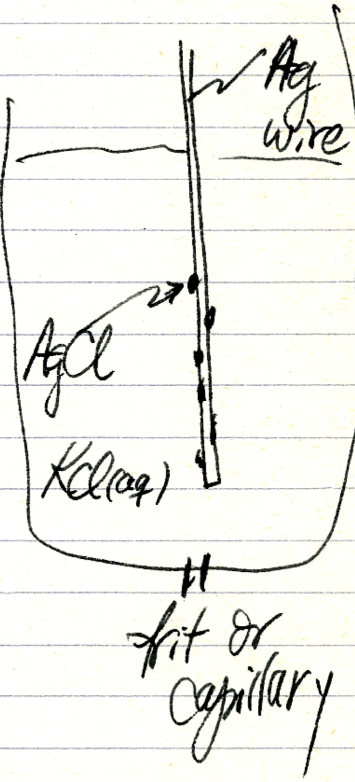
$$Ag + Cl^- = AgCl + e^-$$

Calomel – mercury / mercurous chloride

$Hg/Hg_2Cl_2/KCl\,(aq)$

$$2Hg + 2Cl^- = Hg_2Cl_2 + 2e^-$$



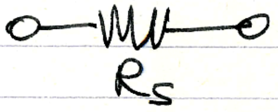


– how about RE's for molten salts?

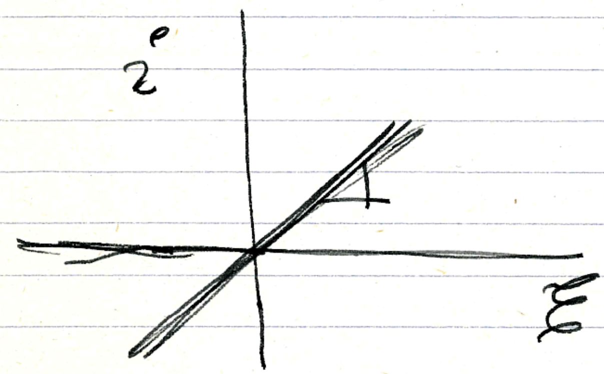
Ref. electrodes

- consider SCE / KCl (aq) / SCE

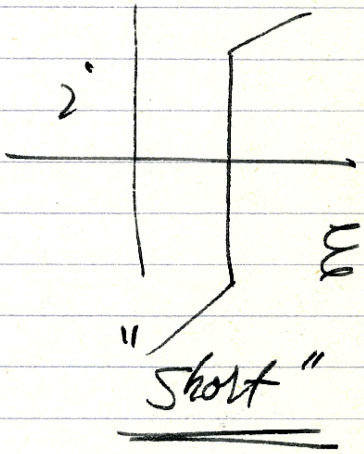
equivalent circuit? —



i-$\mathcal{E}$ characteristic? —



recall that for SCE we have



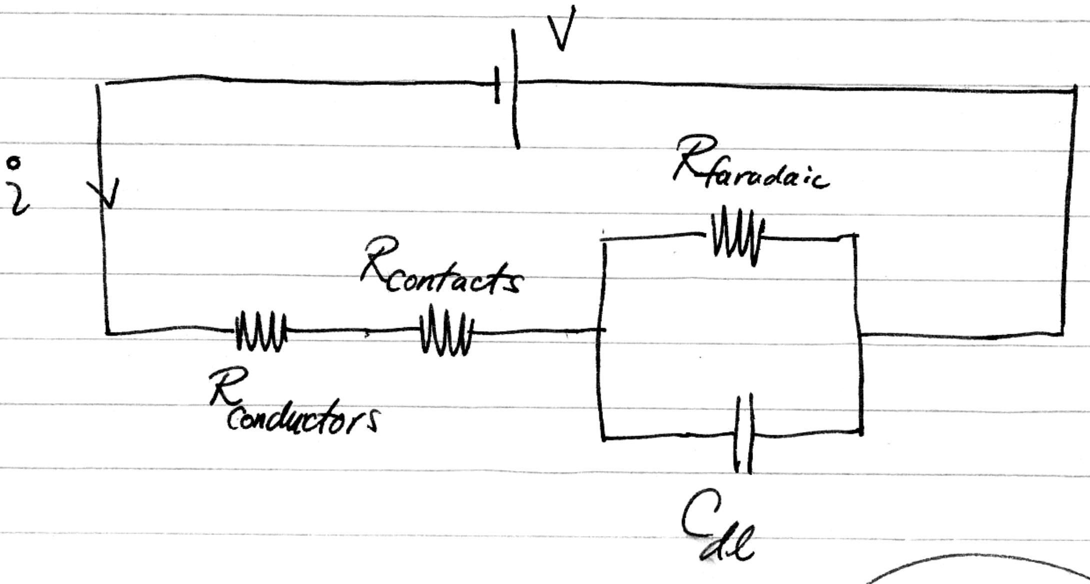
- use this for electrical conductivity measurements

Kinetics of Electrochemical Processes

- what happens when the system is perturbed from ≡ium?
  ⇒ applied potential causes current to flow
- magnitude of this current det'd by overall resistance it encounters
- sources of resistance include conductors, contacts, electrolyte solution, reactions at electrodes
- $R_{solution} \propto 1/\kappa_{el}$

$\kappa_{el} \propto$ no. carriers; carrier mobilities

- $R_{electrode\ reactions} \propto 1/\text{rate of rxn}$



$$i = \frac{V}{R_{system}}$$, more properly $$\boxed{i = \frac{V}{Z_{system}}}$$

≡in e.c. rxns, rate = $f(\mathcal{E})$

— need a model to rationalize $i = f(\mathcal{E}, C_i\text{'s})$

$$O + ne \longrightarrow R$$

e.g. $Fe^{3+} + e \longrightarrow Fe^{2+}$

— when we write $\longrightarrow$, This is <u>net</u> rxn; actually system is all the while reacting <u>IN BOTH DIRECTIONS</u> $\rightleftarrows$

$v_f = k_f C_O$; $v_b = k_b C_R$

$v_{net} = v_f - v_b$

at ≡ium, $v_{net} = 0$ and $C_O = C_O^{eq}$ and $C_R = C_R^{eq}$

$\therefore v_{net} = 0 = k_f C_O^{eq} - k_b C_R^{eq}$

define $v_0 = k_f C_O^{eq} = k_b C_R^{eq}$

$O + ne \xrightleftharpoons{v_0} R$ $v_0 \equiv$ "idle speed"

units of v are $\left[\frac{mol}{cm^2 s}\right]$: $v \equiv \frac{1}{A}\frac{dN}{dt}$

N is mole number

- Faraday's Law expresses cell productivity in terms of charge passed through external circuit

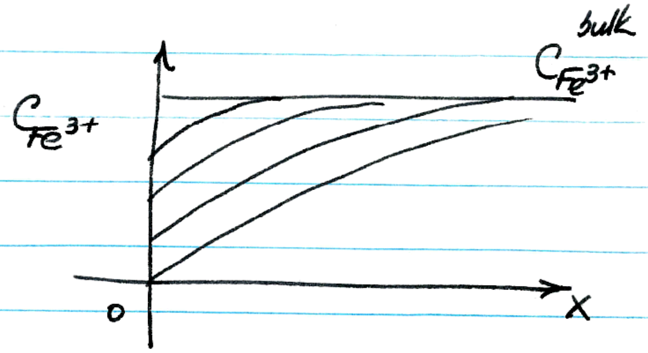
$N = Q/n\mathcal{F}$

n - electron transfer no.
$\mathcal{F}$ - Faraday constant 96485 C/mol

$$v = \frac{1}{A}\frac{d}{dt}\left(\frac{Q}{n\mathcal{F}}\right) = \frac{1}{A}\cdot\frac{1}{n\mathcal{F}}\cdot\frac{dQ}{dt} = \frac{i}{n\mathcal{F}A}$$

e.g. $Fe^{3+} + e \rightarrow Fe^{2+}$

$$v_f = k_f\, C_{Fe^{3+}}(0,t) = \frac{i_{cathodic}}{n\mathcal{F}A}$$



$$v_b = k_b\, C_{Fe^{2+}}(0,t) = \frac{i_{anodic}}{n\mathcal{F}A}$$

- can show that $k = k(\mathcal{E})$; in fact,

$$k_f = k_f^{\circ}\, e^{-(\alpha n\mathcal{F}\mathcal{E}/RT)} \;;\; k_b = k_b^{\circ}\, e^{(1-\alpha)n\mathcal{F}\mathcal{E}/RT}$$

↑ rate constant at $\mathcal{E}=0$ on potential scale in use ↑

- α is transfer coefficient — measure of asymmetry of activation barrier

- return to ≡ium for solution in which $C_O = C_R$
- equilibrium potential given by Nernst eq$^{\underline{n}}$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{a_R}{a_O}$$

$$a_R = \gamma_R C_R \ ; \ a_O = \gamma_O C_O$$

$$\mathcal{E} = \underbrace{\mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{\gamma_R}{\gamma_O}} - \frac{RT}{n\mathcal{F}} \ln \frac{C_R}{C_O}$$

$\mathcal{E}^{\circ\prime}$ ≡ formal potential

- in dilute sol$^{\underline{n}}$s, $\gamma_i \neq \gamma_i(C_i)$

- when $C_O = C_R$ at ≡ium, then $\mathcal{E} = \mathcal{E}^{\circ\prime}$;

also $v_{net} = 0 = v_f - v_b = k_f C_O^{bulk} - k_b C_R^{bulk}$

$$\therefore k_f = k_b = k_f^\circ e^{-\alpha n f \mathcal{E}^{\circ\prime}} = k_b^\circ e^{(1-\alpha) n f \mathcal{E}^{\circ\prime}} \underline{\underline{= k^\circ}}$$

k° ≡ standard rate constant
($f = \mathcal{F}/RT$ for convenience)

k° is value of k_f + k_b at $\mathcal{E} = \mathcal{E}^{\circ\prime}$

$$k_f = k^\circ e^{-\alpha n f(\mathcal{E} - \mathcal{E}^{\circ\prime})} \ ; \ k_b = k^\circ e^{(1-\alpha) n f(\mathcal{E} - \mathcal{E}^{\circ\prime})}$$

$\Rightarrow v_{net} = v_f - v_b \quad \therefore \; i = i_c - i_a$

$$\boxed{i = nFAk^\circ \left[C_O(0,t)\, e^{-\alpha n f (E - E^{\circ\prime})} - C_R(0,t)\, e^{(1-\alpha) n f (E - E^{\circ\prime})} \right]}$$

i–E characteristic of the electrode

at ≡ium, $i_{net} = i = 0 \Rightarrow i_c = i_a$

define exchange current, i_0, as $i_c = i_a$ at ≡ium

$i_0 = nFAk^\circ C_O^{(1-\alpha)} C_R^{\alpha}$

rather than deal w/ $E^{\circ\prime}$, let's use E^{eq} instead

$\eta = E - E^{eq}$, (overpotential)

$$\boxed{i = i_0 \left[\frac{C_O(0,t)}{C_O^{bulk}}\, e^{-\alpha n f \eta} - \frac{C_R(0,t)}{C_R^{bulk}}\, e^{(1-\alpha) n f \eta} \right]}$$

i–η characteristic of the electrode