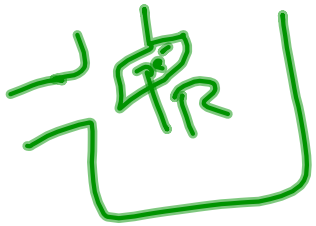
New molecule : R



$R \rightarrow O + ne^-$

This exp leads one to call measured E° an oxidation potential. It is NOT!

Reduction Potential = − Oxidation Pot.

NHE // $O + ne^- \rightarrow R$ / Pt

measure right vs. left

NHE // $O + ne \rightarrow R$ / Pt

measure left vs. right.

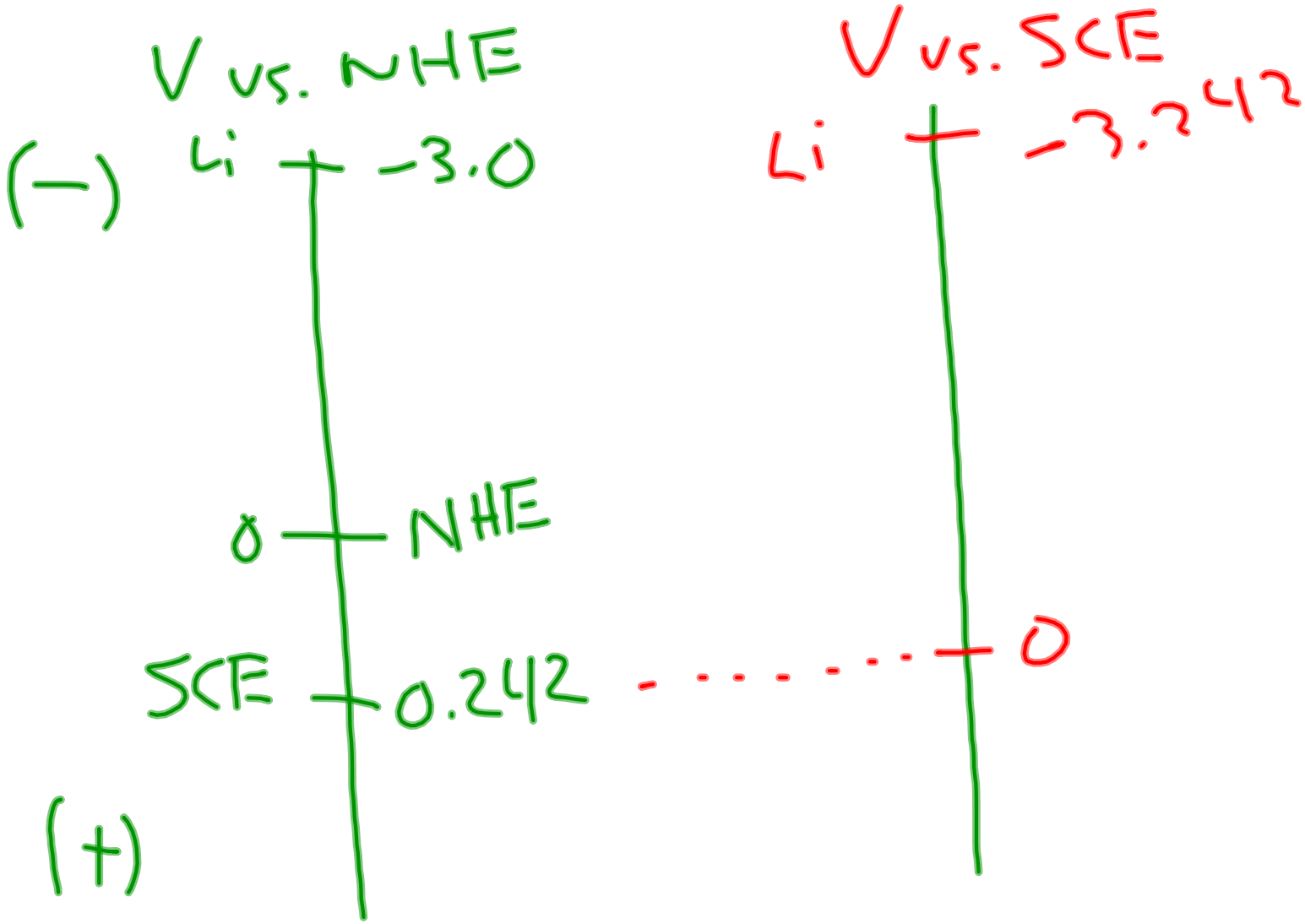
Other reference electrodes

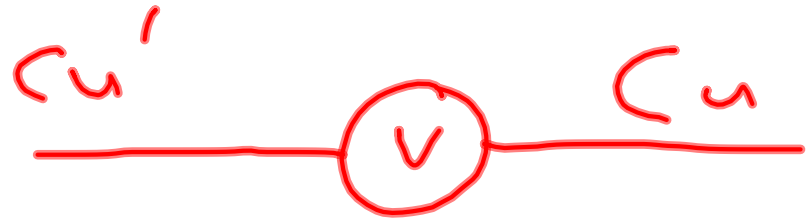
SCE = saturated calomel electrode Hg_2Cl_2

$$Hg_2Cl_2 \rightarrow Hg^0$$

$Hg/Hg_2Cl_2 / KCl$ (sat'd)

0.242 V vs. NHE


V vs. NHE
(−)
Li
−3.0
0
NHE
SCE
0.242
(+)
V vs. SCE
Li
−3.242
0

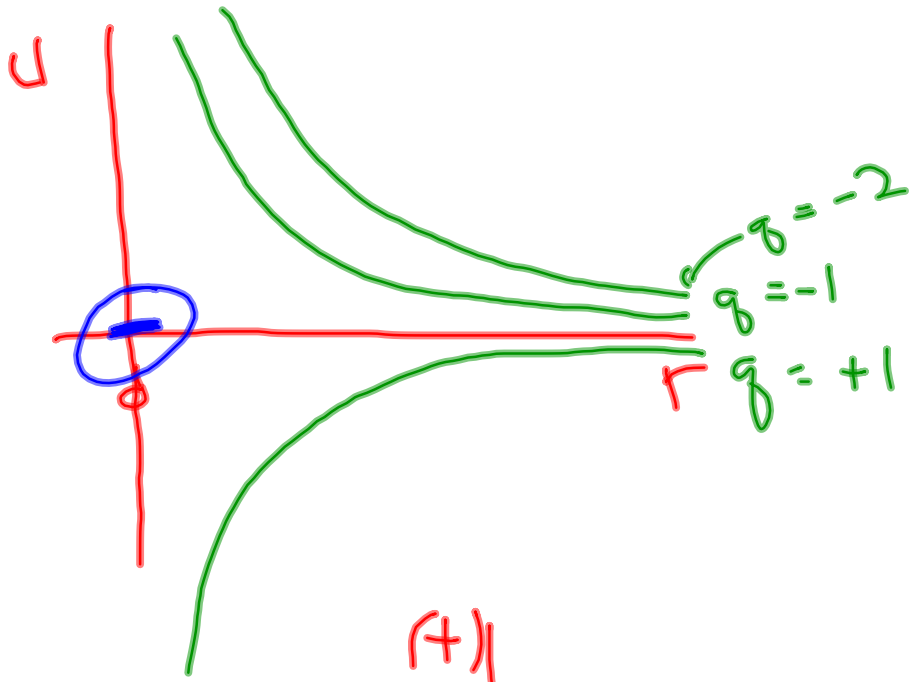


$$V = \phi^{Cu'} - \phi^{Cu}$$

Potential energy

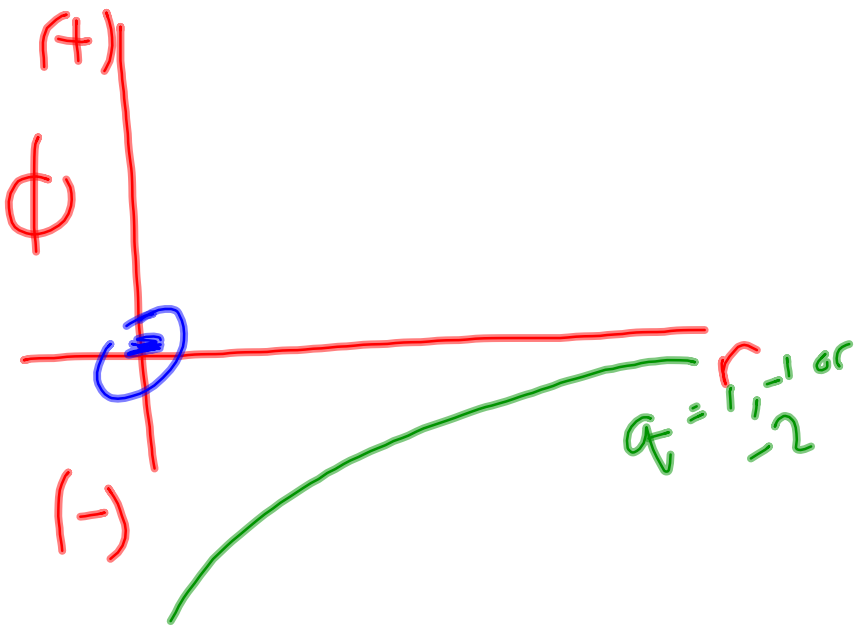
$$U = \frac{q_1 q_2}{4\pi\epsilon r}$$

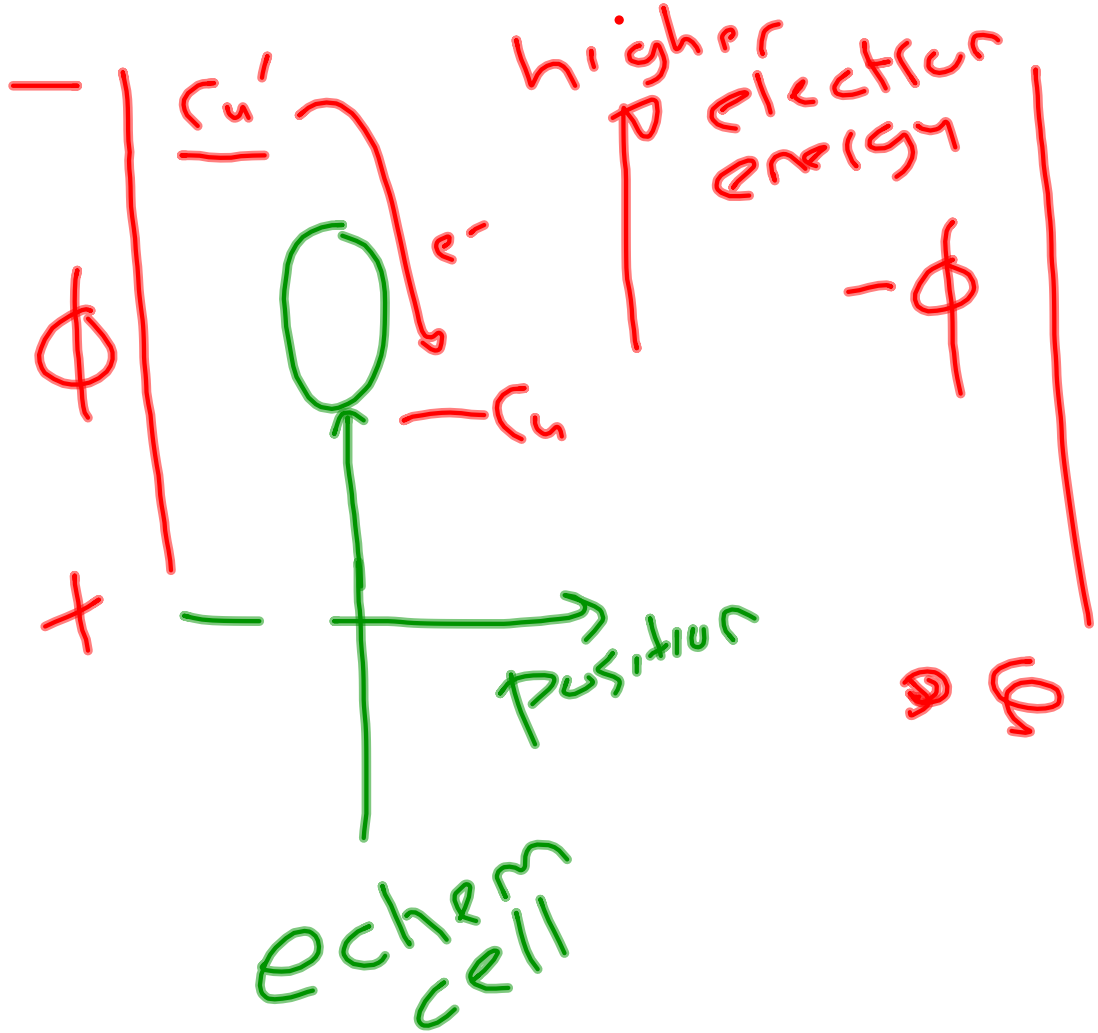
Coulomb's Law.



$$\phi = \frac{U}{q}$$

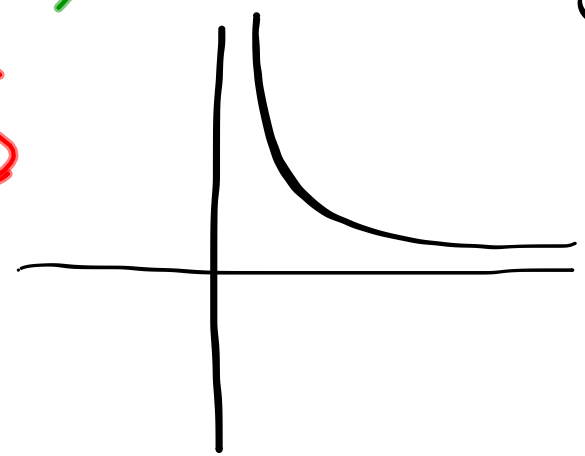
$$= \frac{I}{C} = V$$




Cu'
e-
Cu
higher electron energy
$-\phi$
ϕ
+
position
echem cell

the th

the



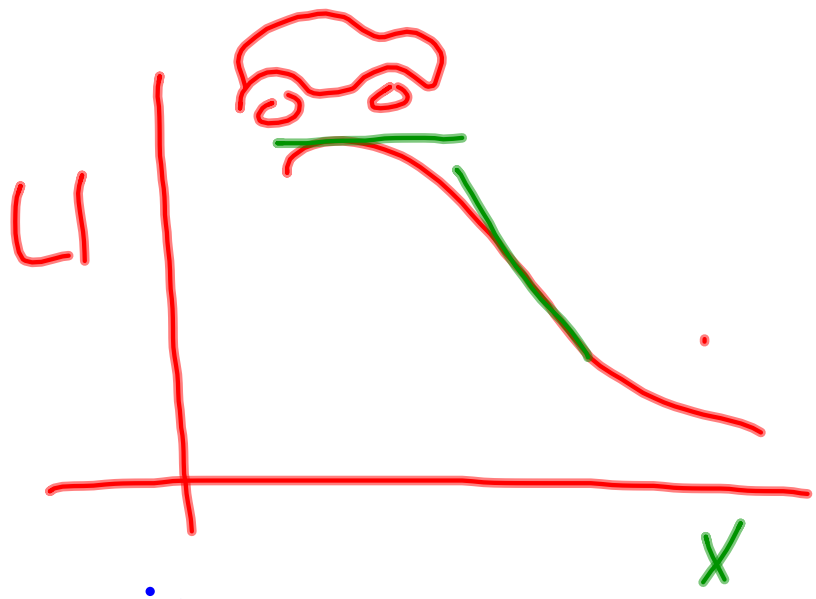
No current, uniform good conductor

metal, electrolyte, semiconductor

- no excess charges in the bulk body of the conductor

- ϕ is a constant in the bulk

$\Rightarrow \mathcal{E}$ = electric field is zero in bulk

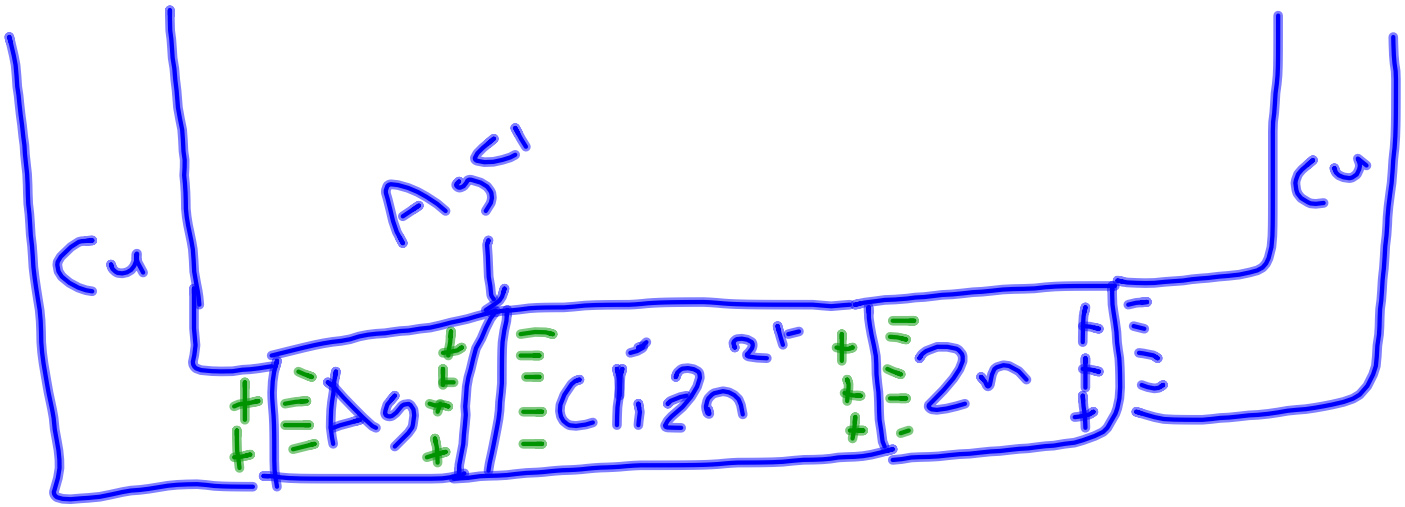


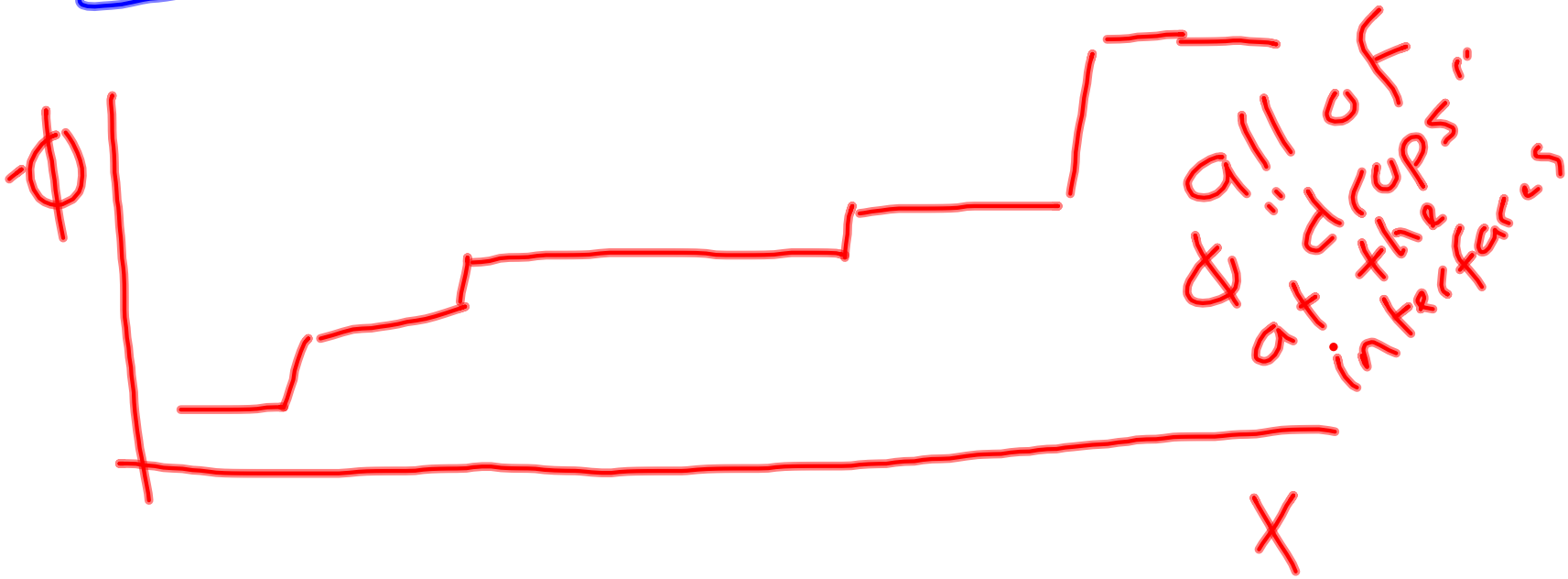
$$F = -\frac{dU}{dx}$$

electric field

$$F = -\frac{dU}{dx} = -\frac{d(q\phi)}{dx} = -q\frac{d\phi}{dx}$$

$$\mathcal{E} = \frac{F}{q} = -\frac{d\phi}{dx}$$


Cu
Ag
Ag+
Cl, Zn2+
Zn
Cu


φ
x
all of "drops" at the interfaces

$$\bar{\mu} = \mu + zF\phi$$

μ = chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_j, T, P, j \neq i}$$

When no ϕ,

μ or G is the criterion for equilibrium

For a pure substance

$$G = G_m n$$

G_m = molar free energy

When ϕ is present

then $\bar{\mu}$ is the criterion for eq.

At. eq $\quad \bar{\mu}_e^{Au} = \bar{\mu}_e^{Na}$

$$\mu_e^{Au} - F\phi^{Au} = \mu_e^{Na} - F\phi^{Na}$$

$$-F(\phi^{Au} - \phi^{Na}) = \mu_e^{Na} - \mu_e^{Au}$$