

Electrochem

write down ΔG for $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

Reaction Quotient: $\frac{(a_c)^\gamma (a_d)^\delta}{(a_A)^\alpha (a_B)^\beta}$ equilibria only!

like $K_{sol} = [Na^+][Cl^-]$, if $> K_{eq}$, then backwards (too much of the products) etc

ΔG is for forward; $< 0 \Rightarrow$ spontaneous

$$\therefore \Delta G = \Delta G^\circ + RT \ln \frac{(a_c)^\gamma (a_d)^\delta}{(a_A)^\alpha (a_B)^\beta}$$

$$\Delta G = 0 \Rightarrow eq. \Rightarrow \Delta G^\circ = -RT \ln K_{eq}$$

$Q < K_{eq}$, 2nd term neg. so more spontaneous

for ideal gas, $a = \frac{p}{p^\circ}$ (partial pressure)

ideal sol., $a = c/c^\circ$

real sol., $a = \gamma c/c^\circ$

what's the units of a, γ ? (unitless) (γ must be unitless!)

how are values of a usually quoted?

as numerical part of γc ($c^\circ = 1M$)

what if c in M vs $mol\ kg^{-1}$??

a does not change, but γ changes!

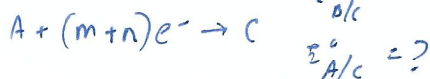
activity a

activity coefficients γ

combining two half cells: $E_{cell} = ?$



two processes in a half cell?



Use ΔG



$$\Delta G_{cell} = m \Delta G^\circ_{A/B} - n \Delta G^\circ_{C/D}$$

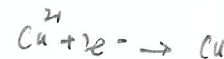
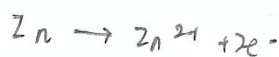
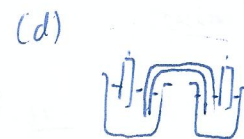
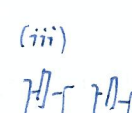
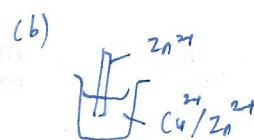
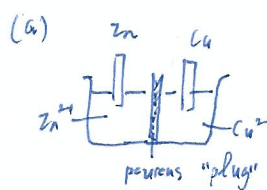
$$E^\circ_{cell} = E^\circ_{A/B} - E^\circ_{C/D}$$

$$\Delta G_{A/C} = \Delta G_{A/B} + \Delta G_{B/C}$$

$$E^\circ_{A/C} = \frac{m E^\circ_{A/B} + n E^\circ_{B/C}}{m+n}$$

no. of e^-
 $\times E^\circ \propto \text{energy}$

write down the cell eq. for:



(a) # no reaction (how would charge be transferred?)

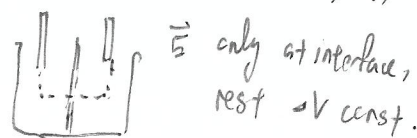
Think of it as electric field & potential gradient at each interface:

diff. no. of free electrons } diffusion of e^-
diff. conductivity

if $Cu(s)$ neutral, \leftarrow
so deposit until \rightleftharpoons
(E builds up, $\frac{+}{-}$ repel Cu^{2+})

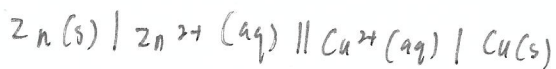
electric field $\leftrightarrow \Delta V$

to find ΔV between Zn, Cu , draw path:



e^- flow

hyp. e⁻ flow



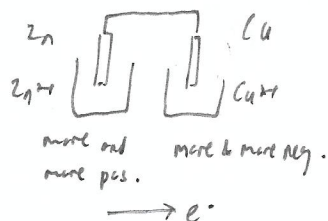
↑
phase

↑
diffusional barrier

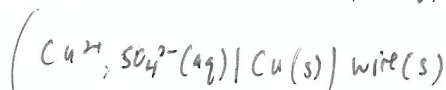
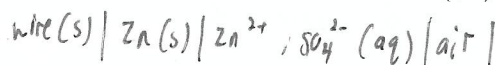
↑
interphase/
interface

(b) Cannot...

(c) (i) react, until eq. due to repulsion; then
wire same potential

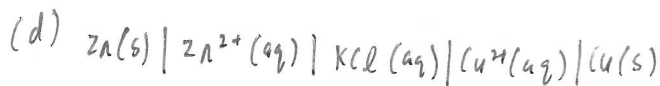


(%)

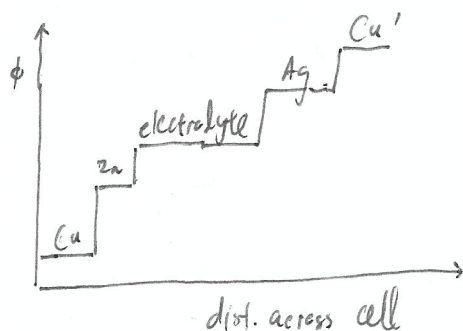


same potential! ← here counterions important?

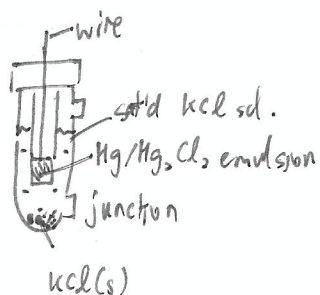
(ii) no voltmeters are ideal, so potential
measured includes the repulsion.



Vetter's representation



saturated calomel electrode



wire: half cell

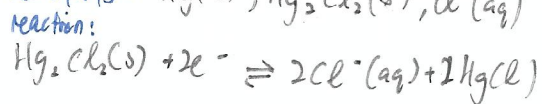
liquid junction: salt bridge etc.

saturated vs standard

ideal: $a_{\text{Cl}^-} = 1$

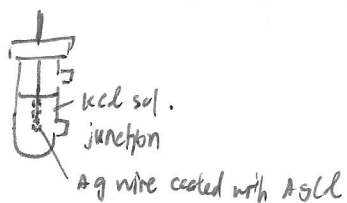
Reactants: $\text{Hg(l)}, \text{Hg}_2\text{Cl}_2(\text{s}), \text{Cl}^-(\text{aq})$

Reaction:



Notation: $\text{Cl}^-(\text{aq}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg(l)}$

silver-silver chloride electrode



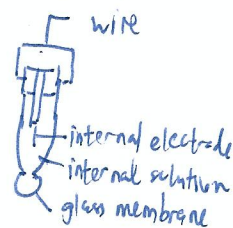
Reactants: $\text{Ag(s)}, \text{AgCl(s)}, \text{Cl}^-(\text{aq})$

Reaction: $\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-(\text{aq})$

Notation: $\text{Cl}^-(\text{aq}) | \text{AgCl(s)} | \text{Ag(s)}$

DKA-70A Corp.

About pH: glass electrode & ref. elect.



- wire to ref. elect.

- glass & ref. dipped into same electrolyte

ex:

$\text{SCE} / \text{Test sol.} / \text{Glass membrane} / \text{HCl (0.1M)} / \text{AgCl} / \text{Ag}$

glass elect.
 internal ref.