

Liquid Junction Potentials---occur at the boundary between two solutions that have different ionic compositions---

-Exist for all reference electrodes that are separated from sample solution by frit, or some other type of electrolytic contact interface---to prevent bulk mixing of the reference electrode electrolyte with the sample solution

-Occur at all liquid-liquid junctions--but magnitude of E_j value is dependent on the exact method of forming junction----

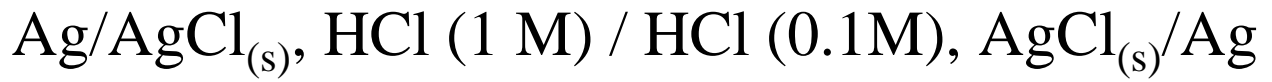
-restrained junction----e.g., microporous frit

-free flowing junction----simply bringing two solutions in contact---but no mixing!

theory for junction potential calculations is always based on “free flowing” type junction;

In cases of constrained junction---adsorption of sample species onto the solid support can greatly alter the E_j value by changing the mobilities of the ions across the junction due to electrostatic effects

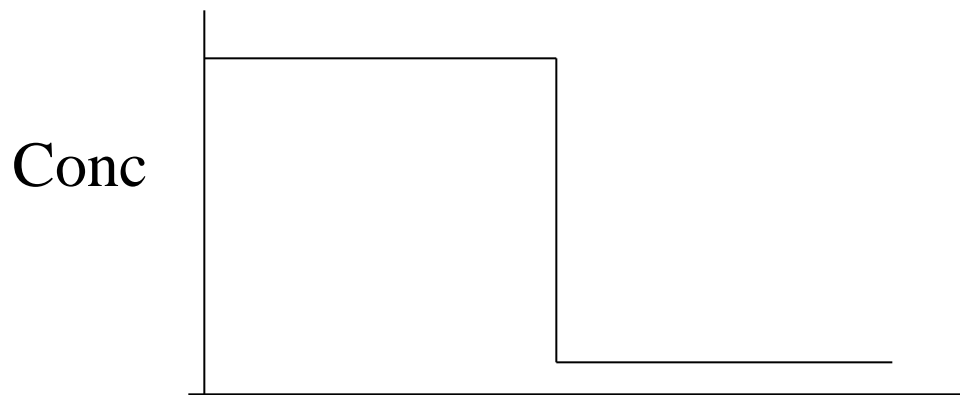
Origin of liquid junction potentials:



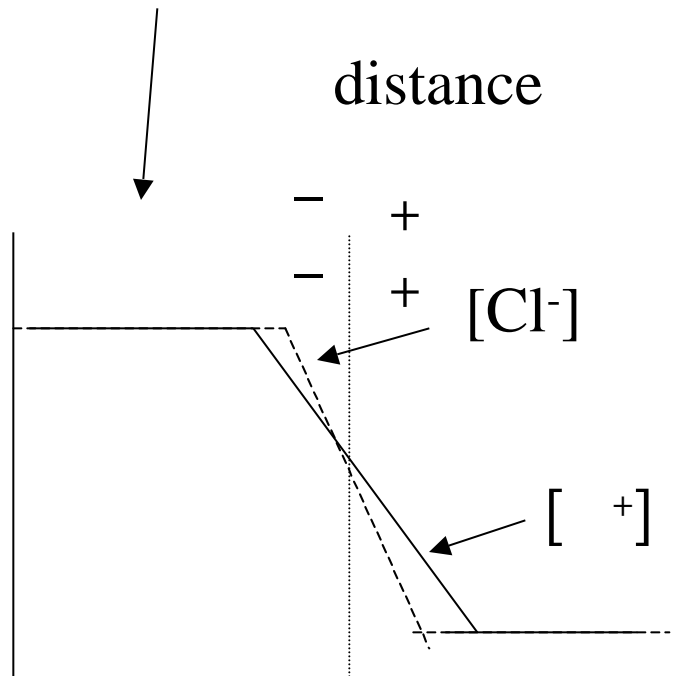
- = E_j E_j

↑

at t=0;



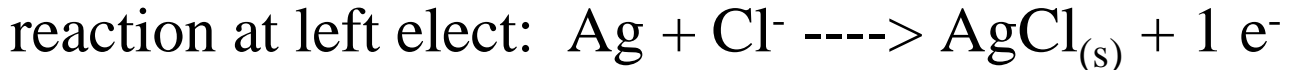
at steady-state--
time--t:



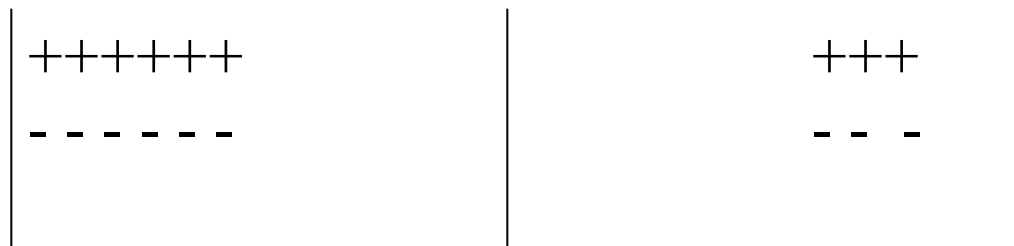
get breakdown of electroneutrality at the interface--
 flux of H^+ and Cl^- at interface depend on two forms
 of ionic movement-----diffusion: dC/dx and mobility
 and migration: movement of ions in electric field

as move from to phases---each element (plane)
 of solution has more + than previous segment--

If cell were allowed to discharge spontaneously--
 (short the two electrodes)



initial:

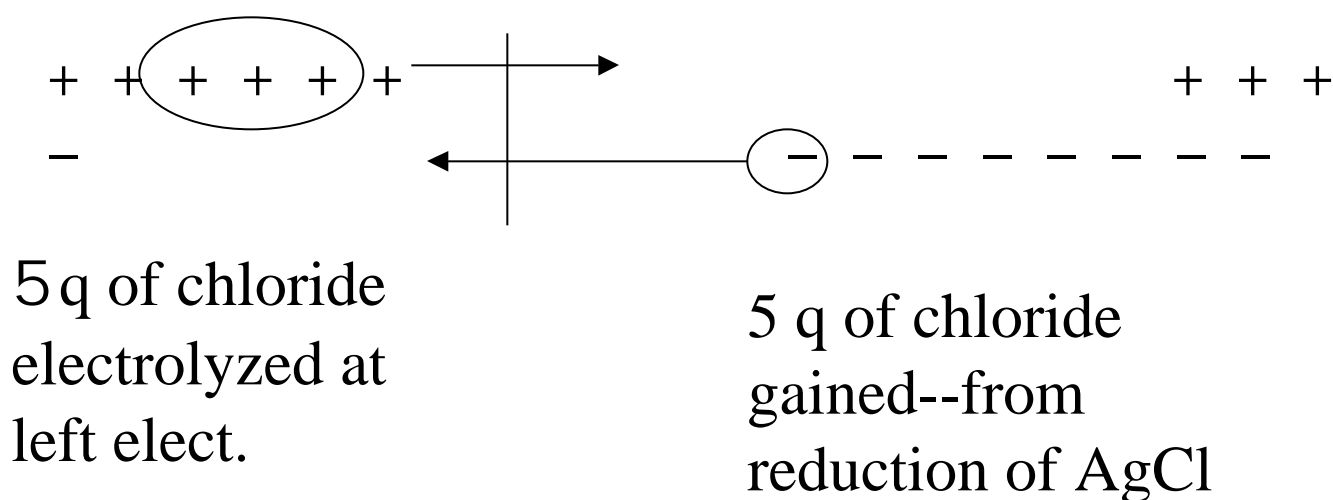


as cell discharges---chloride ion builds up in phase-
 and H^+ build up in phase-----but this can't happen-
 bulk of phases must be electroneutral----

Therefore---ions move between phases to compensate
 build-up of excess charge!

for every 5 q (coulombs) of charge that passes in external circuit---then 5 q of charge must transfer in electrolyte soln to maintain electroneutrality---

H⁺ moves from to phase---and Cl⁻ moves from to .



after time t---you pass q total charge---

$f(q)/F =$ moles of HCl added to side---due to generation of Cl⁻ and movement of H⁺

f= fraction of current carried by movement of H⁺ ions

1-f=fraction of current carried by Cl⁻ ions

$f = t_+$; $1-f = t_-$ ----cation and anion transference numbers, respectively

for simple electrolyte---same electrolyte on each side of junction---- $t_+ + t_- = 1$

Different methods to measure transference # of electrolyte solutions-----

---Hittorf method---use electrolytic cell--starting with same concentration of electrolyte in all parts of a long tube---then pass current for given time---and measure concentration of electrolyte at different portions of tube!

---Moving boundary method---

current in cell is obviously dependent on movement of ions---and migration of ions depends on conductance of solution---

therefore--by measuring conductivity of electrolyte you should be able to relate transference # with conductivity of given electrolyte

$$\text{Conductance} = L = 1/R_{\text{soln}} = K (A/l)$$

$L = \text{conductance} \text{ --- Siemens, }^{-1}$
 $= \text{specific conductivity --- siemens/cm}$

$A = \text{area of electrodes used for conductance measurement --- or cross-sectional area of solution between the two electrodes}$

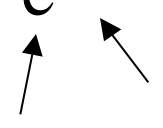
$l = \text{distance between electrodes}$

recall --- $R_u = x/KA$ same eqn as above -- except reciprocal -- and $x =$

$$K = F \sum_i |z_i| \mu_i C_i$$

$\mu_i = \text{mobility of ion in electric field --- } \text{cm}^2 \text{sec}^{-1} \text{V}^{-1}$

ions in solution will have continuous velocity v only when electric force strength = frictional drag

electric force = $z_i e$

 $\text{charge on electron}$
 $\text{V/cm} = \text{field strength}$

frictional drag ---can estimate with Stokes eqn:

$$F = 6\pi\eta r v$$

η : viscosity (poise)
 r : hydrated radius of ion
 v : velocity of ion

set frictional drag = electric force, and solve for

$$v / F = \mu_i = \frac{|z_i|e}{6\pi\eta r}$$

*movement of ions by migration usually much faster than by diffusion!

Therefore---transference # is contribution by given ion to total conductivity

$$t_i = \frac{|z_i|\mu_i C_i}{\sum_j |z_j|\mu_j C_j}$$

for 1:1 electrolytes (e.g., HCl, NaCl, KCl, etc.)--
for HCl:

$$t_{H^+} = \frac{|z_{H^+}| \mu_{H^+} C_{H^+}}{|z_{Cl^-}| \mu_{Cl^-} C_{Cl^-} + |z_{H^+}| \mu_{H^+} C_{H^+}}$$

but since absolute value of charges is equal---and
 $C_{H^+} = C_{Cl^-}$; then:

$$t_{H^+} = \frac{\mu_{H^+}}{\mu_{Cl^-} + \mu_{H^+}} \quad \text{or} \quad t_+ = \frac{\mu_+}{\mu_- + \mu_+}$$


thus for Type 1 junctions:

intuitively---if $t_+ = t_-$ then $\mu_+ = \mu_-$ ---and $E_j = 0$ --
call equitransferent electrolyte---neither ion outraces
other across junction due to concentration gradient--

If $t_+ = 1$ and $t_- = 0$ ---then this would mean that
interface between two solutions was only permeable
to t_+ ions in electrolyte-----

Then we can treat potential difference in accordance
with phase boundary potential:

$$\phi_{\beta} - \phi_{\alpha} = \frac{\mu_{H^+}^{o(\alpha)} - \mu_{H^+}^{o(\beta)}}{zF} + \frac{RT}{zF} \ln \frac{a_{H^+}^{\alpha}}{a_{H^+}^{\beta}}$$



 this term is zero---since standard free energy of ion in each of the two aqueous solutions should be the same!

Then for containing 0.1 M HCl, and containing 1 M HCl, $E_j = + 59 \text{ mV}$ or 0.059 V (at 25° C)

Actual E_j must be between these two extreme values since Cl^- does have mobility across interface (unless interface region had high concentration of negatively charged sites---e.g. thin membrane---)

some fraction of E_j is due to gradient of H^+
 some fraction of E_j is due to gradient of Cl^-

$$\phi_{\beta} - \phi_{\alpha} = (t_+) \frac{RT}{z_{H^+} F} \ln \frac{a_{H^+}^{\alpha}}{a_{H^+}^{\beta}} + (t_-) \frac{RT}{z_{\text{Cl}^-} F} \ln \frac{a_{\text{Cl}^-}^{\alpha}}{a_{\text{Cl}^-}^{\beta}}$$

$$\phi_{\beta} - \phi_{\alpha} = (t_{+} - t_{-}) \frac{RT}{F} \ln \frac{a_1^{\alpha}}{a_2^{\beta}}$$

where $a_1 = a_{M^{+}} = a_{A^{-}} = a_{MA}$

$a_2 = a_{M^{+}} = a_{A^{-}} = a_{MA}$

since single ion activities cannot be measured---we can only measure mean activities---and hence we can make above assumptions to simplify previous equation!

for HCl junction---if $t_{H^{+}} = 0.82$, and $t_{Cl^{-}} = 0.18$
then $E_j = + 37.7 \text{ mV}$ or 0.0377 V .

for Type II and Type III junctions---we cannot make these simplistic assumptions----

t_i values are changing considerably as you go across junctions, since concentrations of the ions are different---and the gradients for all the different ions present on each side are different!-

See next handwritten pages for derivation of equation based on first two terms of Nernst-Planck equation!

①

Derivation of Henderson Eqn

- Driving force for ions to cross interface is gradient of electrochemical potential (\bar{u}_i)

$$\bar{u}_i = \mu_i^\circ + RT \ln C_i + z_i F \phi \quad (1)$$

- Flux of given ion = $J_i = -u_i^{(M)} C_i \frac{d\bar{u}_i}{dx}$ (2)

$$u_i^{(M)} = \text{mobility of ion} = \frac{D_i}{RT} \quad (D_i = \text{diffusion coeff.})$$

- at steady-state - diffusion layer thickness not changing; i.e. $dx = \text{constant}$

and $\frac{d\bar{u}_i}{dx} = 0$ since standard free energy for each ion in the two aqueous solutions is the same

$$\therefore J_i = -u_i^{(M)} C_i RT \frac{d \ln C_i}{dx} - z_i F u_i^{(M)} C_i \frac{d\phi}{dx} \quad (3)$$

For potentiometry - zero net current

$$\therefore \sum J_i = 0$$

Solve above for $\frac{d\phi}{dx} = E_j$

$$\frac{d\phi}{dx} = - \frac{RT}{F} \frac{\sum z_i u_i^{(M)} C_i \frac{d \ln C_i}{dx}}{\sum z_i^2 u_i^{(M)} C_i} \quad (4)$$

(A)

but $L_i = \frac{E_i}{RT}$

$$\therefore \frac{dV}{V} = - \frac{RT}{E_i} \ln C_i$$

$$\frac{E_i}{RT}$$

what t_i is at eq^{nt} must know how

Integrate (6) from $x=0$ to $x=L$

$x = d$ also

$$E_i = \frac{RT}{L} = - \frac{RT}{L}$$

to solve assume ΔG

True but here

$$\frac{E_i}{RT} = \frac{1}{L} \ln \frac{C_i}{C_i^0}$$

HENDONOV EQU

$$E_i = \frac{RT}{L} \ln \frac{C_i}{C_i^0}$$

$$E_j = (t_+ - t_-) \frac{RT}{L} \ln \frac{C_j}{C_j^0}$$

(7)

For type I Junctions - 1:1 electrolyte on both sides
e.g. HCl/HCl

$$E_j = \frac{\mu_{+}^{\ominus} - \mu_{-}^{\ominus}}{\mu_{+}^{\ominus} + \mu_{-}^{\ominus}} \quad (1) \quad \frac{RT}{F} \ln \frac{\cancel{E_j} [z_i] \mu_{i(\alpha)}^m C_{i(\alpha)}}{\cancel{E_j} [z_i] \mu_{i(\beta)}^m C_{i(\beta)}}$$

$$\text{but } t_+ = \frac{\mu_{+}^m}{\mu_{+}^m + \mu_{-}^m}$$

$$\text{and } t_- = \frac{\mu_{-}^m}{\mu_{+}^m + \mu_{-}^m}$$

$$\therefore t_+ - t_- = \frac{\mu_{+}^{\ominus} - \mu_{-}^{\ominus}}{\mu_{+}^{\ominus} + \mu_{-}^{\ominus}} =$$

$$\therefore E_j = (t_+ - t_-) \frac{RT}{F} \ln \frac{C_{i(\alpha)}}{C_{i(\beta)}}$$

For HCl Junction -

$$t_+ = 0.82$$

$$t_- = 0.18$$

$$E_j = 37.2 \text{ mV}$$