

2.1.6 Formal Potentials

γ_x : activity coefficient

- As the **ionic strength** becomes greater, the behavior of an individual ion is influenced by its nearby neighbors.
- The ionic strength depends on the concentration and charge number:
$$\mu = \frac{1}{2} \sum_1^n c_i z_i^2$$

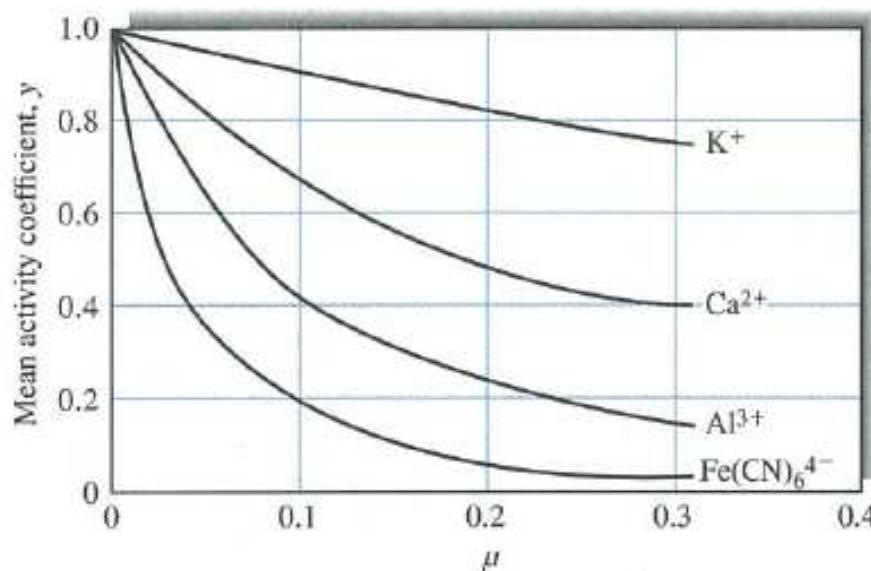
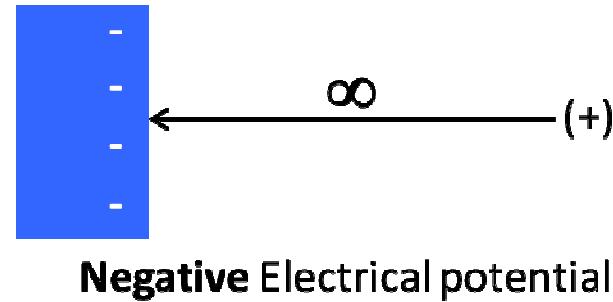
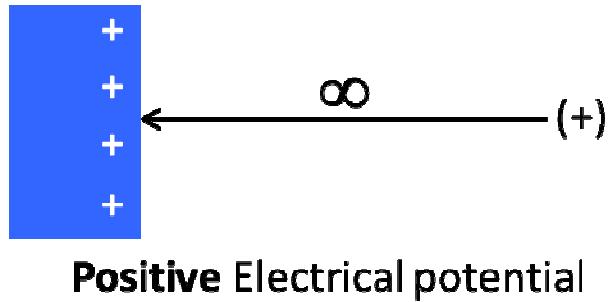


FIGURE a2-1 Effect of ionic strength on activity coefficients.

2.2.1 The Physics of Phase Potentials

- The potential at any particular point within a phase, $\phi(x, y, z)$
 - defined as the work required to bring a unit positive charge, without material interactions, from an infinite distance to point (x, y, z) .
 - independent of the path of the test charge



2.2.1 The Physics of Phase Potentials

- The work is done against a coulombic field;
→ hence we can express the potential generally as

$$\phi(x, y, z) = \int_{\infty}^{x, y, z} -\mathcal{E} \cdot d\mathbf{l}$$

where

\mathcal{E} : the electric field strength vector (i.e., the force exerted on a unit charge at any point)

$d\mathbf{l}$: an infinitesimal tangent to the path in the direction of movement.

- The difference in potential between points (x', y', z') and (x, y, z) is then

$$\phi(x', y', z') - \phi(x, y, z) = \int_{x, y, z}^{x', y', z'} -\mathcal{E} \cdot d\mathbf{l}$$

2.2.1 The Physics of Phase Potentials

- When no current passes through a conducting phase,
→ there is no net movement of charge carriers,
→ So the **electric field** at all interior points = 0.

$$\phi(x', y', z') - \phi(x, y, z) = \int_{x,y,z}^{x',y',z'} - \mathbf{E} \cdot d\mathbf{l}$$

- From the above equation,
→ the difference in potential between any two points in the interior of the phase = 0
→ Thus the entire phase is **an equipotential volume** under these conditions.
→ Its potential, ϕ , is known as the **inner potential** (or Galvani potential) of the phase.

2.2.2 Interactions Between Conducting Phases

- Consider a situation
 - where there is a **charged metal sphere** of macroscopic size, perhaps a mercury droplet 1 mm in diameter, **surrounded by a layer of uncharged electrolyte** a few millimeters in thickness.
 - This assembly is suspended in a vacuum.

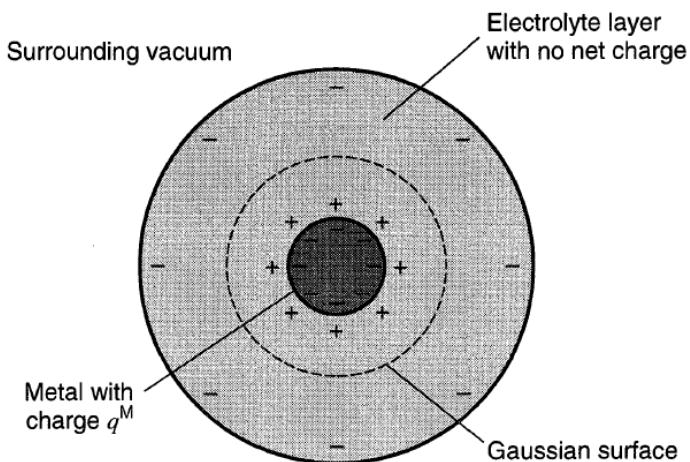
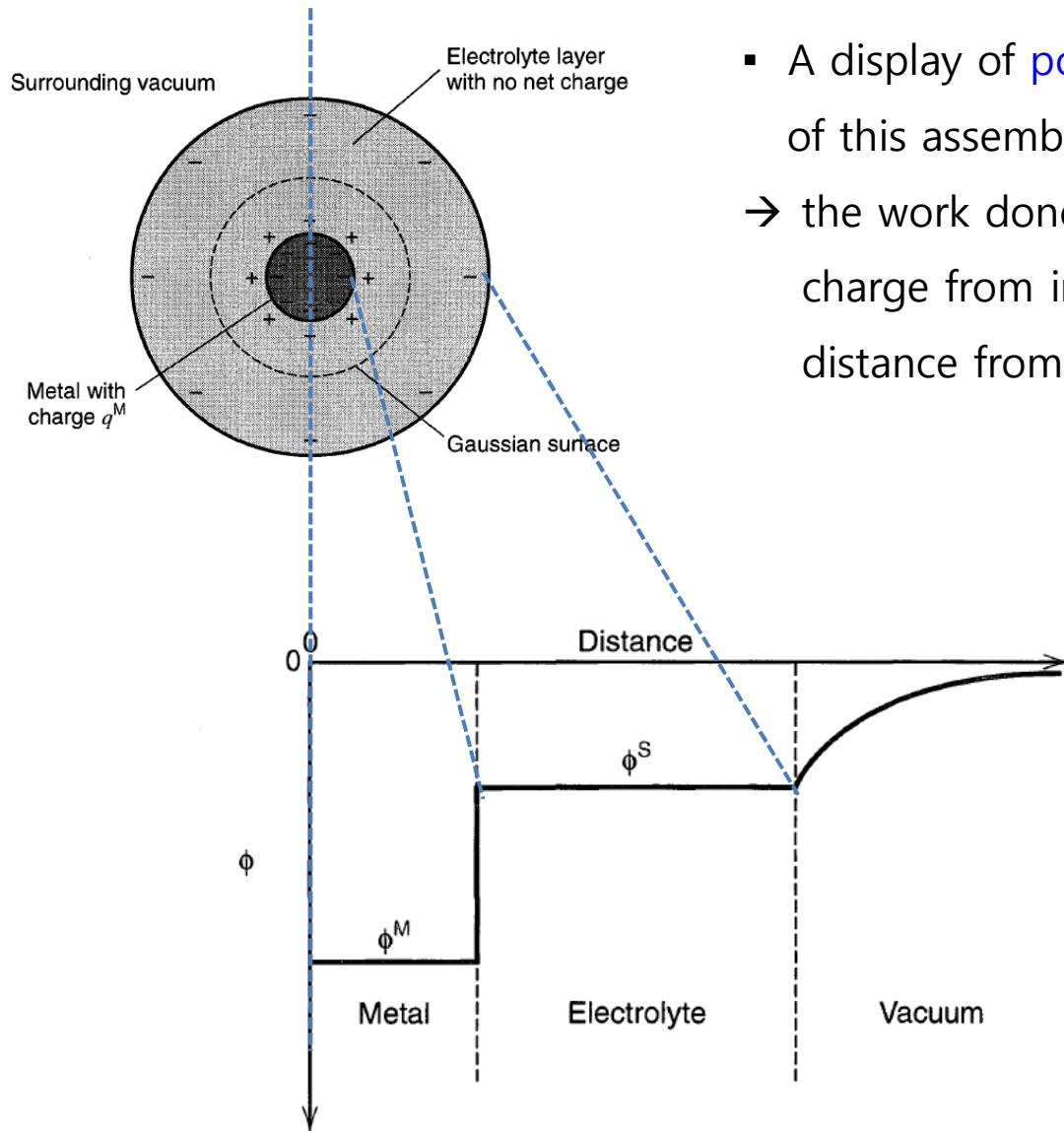


Figure 2.2.2 Cross-sectional view of the interaction between a metal sphere and a surrounding electrolyte layer. The Gaussian enclosure is a sphere containing the metal phase and part of the electrolyte.

2.2.2 Interactions Between Conducting Phases



- A display of potential vs. distance from the center of this assembly
→ the work done to bring a unit positive test charge from infinitely far away to a given distance from the center.
- Within the electrolyte, ϵ is zero everywhere,
→ so there is no work in moving the test charge, and the potential is constant at ϕ^S .
- At the metal-solution interface, there is a strong field because of the double layer

2.2.2 Interactions Between Conducting Phases

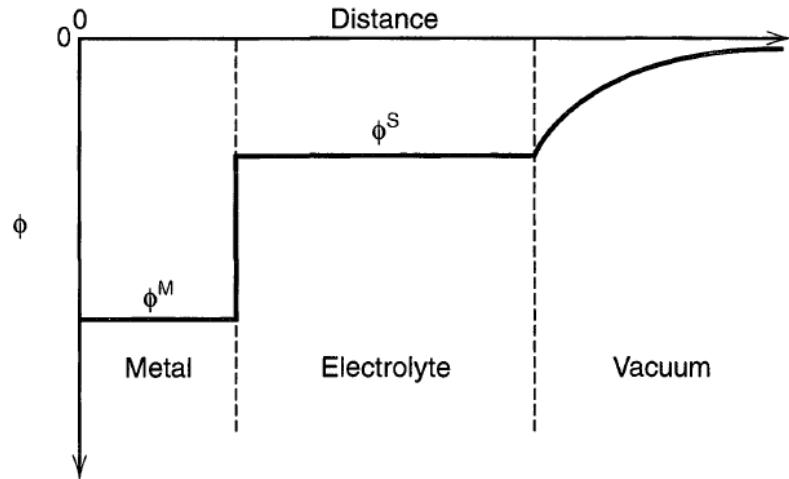


Figure 2.2.3 Potential profile through the system shown in Figure 2.2.2. Distance is measured radially from the center of the metallic sphere.

- The difference $\Delta\phi (\phi^M - \phi^S)$, called the [interfacial potential difference](#),
→ depends on the [charge imbalance](#) at the interface and the [physical size](#) of the interface.

2.2.3 Measurement of Potential Differences

- Unfortunately, $\Delta\phi$ cannot be measured for a single interface by voltmeters
→ voltmeters require two electrodes
- Consider $\Delta\phi$ at the interface Zn/Zn²⁺, Cl⁻.
→ We want to measure the $\Delta\phi$
→ Need to construct the electrochemical cell including several interfaces



2.2.3 Measurement of Potential Differences

- The potential profile through the cell is expected as shown in the figure of:

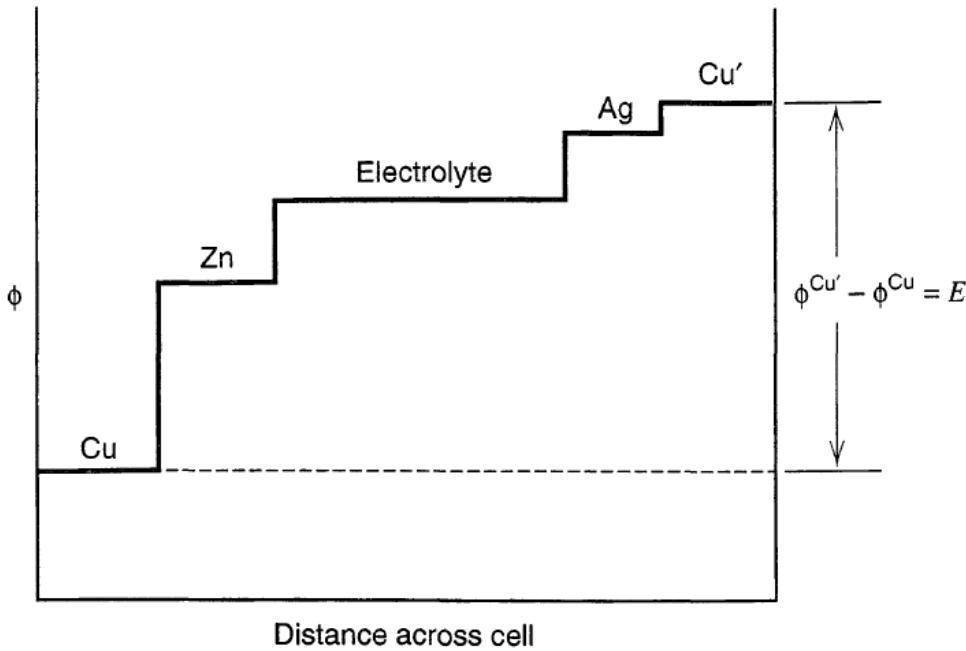


Figure 2.2.5 Potential profile across a whole cell at equilibrium.

- A measured cell potential (E)
 - a sum of several interfacial differences, none of which we can evaluate independently

2.2.3 Measurement of Potential Differences

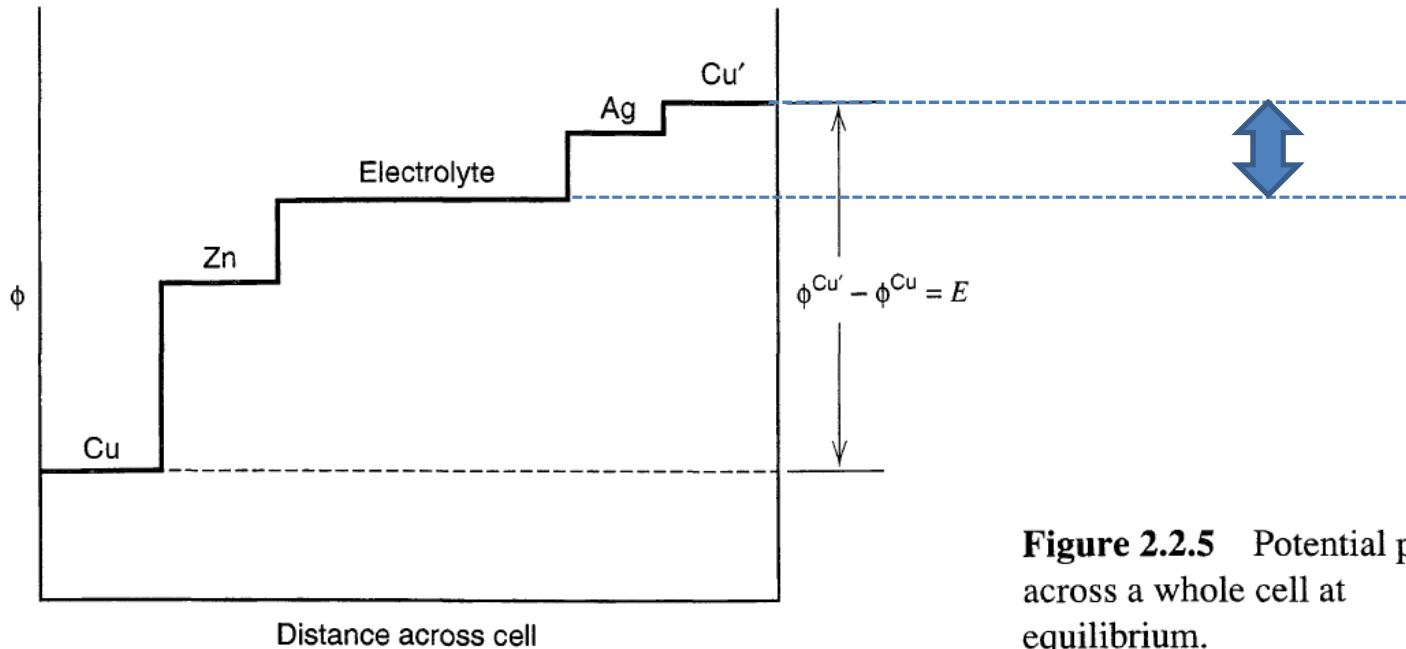


Figure 2.2.5 Potential profile across a whole cell at equilibrium.

- The silver/electrolyte junction can be fixed if the activities of the participants in its half-reaction remain fixed (Reference electrode).
→ it is possible to focus on a single interfacial potential difference between zinc and the electrolyte

2.2.4 Electrochemical Potentials

- Let us consider the interface Zn/Zn²⁺, Cl⁻ (aqueous) and focus on zinc ions in metallic zinc and in solution.
 - In the metal - Zn²⁺: fixed in a lattice of positive zinc ions, with free electrons permeating the structure
 - In solution - Zn²⁺: hydrated and interacted with Cl⁻
- The energy state of Zn²⁺ depends on
 - i) the chemical environment by short-range forces
 - chemical potential: μ_i^α for species i in phase α
 - ii) the energy required to bring the +2 charge to the location in question, disregarding the chemical effects
 - proportional to the potential ϕ at the location
 - $z_i F \phi^\alpha$ for species i with charge z_i in phase α

2.2.4 Electrochemical Potentials

- Introduce the electrochemical potential $\bar{\mu}_i^\alpha$ for species i with charge z_i in phase α

$$\boxed{\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha}$$

- The **chemical potential** μ_i^α is defined as

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

→ where n_i is the number of moles of i in phase α .

- The **electrochemical potential** $\bar{\mu}_i^\alpha$ is defined as

$$\bar{\mu}_i^\alpha = \left(\frac{\partial \bar{G}}{\partial n_i} \right)_{T,P,n_j \neq i}$$

→ where the electrochemical free energy differs from the chemical free energy, G , by the inclusion of effects from the large-scale electrical environment

2.2.4 Electrochemical Potentials

(a) Properties of the Electrochemical Potential

1. For an uncharged species: $\bar{\mu}_i^\alpha = \mu_i^\alpha$ $\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha$
2. For any substance: $\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln a_i^\alpha$
→ where $\mu_i^{0\alpha}$ is the standard chemical potential, and a_i^α is the activity of species i in phase α.
3. For a pure phase at unit activity (e.g., solid Zn, AgCl, Ag, or H₂ at unit fugacity):
 $\bar{\mu}_i^\alpha = \mu_i^{0\alpha}$ $\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln a_i^\alpha$
4. For electrons in a metal ($z = -1$): $\bar{\mu}_e^\alpha = \mu_e^{0\alpha} - F \phi^\alpha$ $\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln a_i^\alpha$
→ activity effects can be disregarded
5. For equilibrium of species i between phases α and β: $\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta$

2.2.4 Electrochemical Potentials

(b) Reactions in a Single Phase

- Consider the acid-base equilibrium within a single conducting phase:
(ϕ is constant everywhere)



- At the equilibrium

$$\bar{\mu}_{\text{HOAc}} = \bar{\mu}_{\text{H}^+} + \bar{\mu}_{\text{OAc}^-}$$

$$\mu_{\text{HOAc}} = \mu_{\text{H}^+} + F\phi + \mu_{\text{OAc}^-} - F\phi$$

$$\mu_{\text{HOAc}} = \mu_{\text{H}^+} + \mu_{\text{OAc}^-}$$

- The ϕ terms drop out of relations involving electrochemical potentials, and only chemical potentials remain.
→ ϕ exerts no effect on a chemical equilibrium.

2.2.4 Electrochemical Potentials

(c) Reactions Involving Two Phases Without Charge Transfer

- Let us now examine the **solvability equilibrium**



- One can consider separate equilibria involving Ag^+ and Cl^- in solution and in the solid.

$$\begin{aligned}\bar{\mu}_{\text{Ag}}^{\text{AgCl}} &= \bar{\mu}_{\text{Ag}}^s \\ \bar{\mu}_{\text{Cl}}^{\text{AgCl}} &= \bar{\mu}_{\text{Cl}}^s \\ \bar{\mu}_{\text{AgCl}}^{\text{AgCl}} &= \bar{\mu}_{\text{Ag}}^{\text{AgCl}} + \bar{\mu}_{\text{Cl}}^{\text{AgCl}}\end{aligned}\quad \left. \vphantom{\bar{\mu}_{\text{Ag}}^{\text{AgCl}} = \bar{\mu}_{\text{Ag}}^s}\right\} \quad \mu_{\text{AgCl}}^{0\text{AgCl}} = \bar{\mu}_{\text{Ag}}^s + \bar{\mu}_{\text{Cl}}^s$$

$$\mu_{\text{AgCl}}^{0\text{AgCl}} = \mu_{\text{Ag}}^{0s} + RT \ln a_{\text{Ag}}^s + F\phi^s + \mu_{\text{Cl}}^{0s} + RT \ln a_{\text{Cl}}^s - F\phi^s$$

$$\rightarrow \mu_{\text{AgCl}}^{0\text{AgCl}} - \mu_{\text{Ag}}^{0s} - \mu_{\text{Cl}}^{0s} = RT \ln (a_{\text{Ag}}^s a_{\text{Cl}}^s) = RT \ln K_{\text{sp}}$$

2.2.4 Electrochemical Potentials

$$\mu_{\text{AgCl}}^{0\text{AgCl}} - \mu_{\text{Ag}^+}^{0\text{s}} - \mu_{\text{Cl}^-}^{0\text{s}} = RT \ln (a_{\text{Ag}^+}^{\text{s}} a_{\text{Cl}^-}^{\text{s}}) = RT \ln K_{\text{sp}}$$

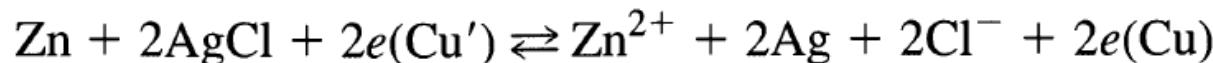
: where K_{sp} is the solubility product

- Note that the ϕ^{s} and ϕ^{AgCl} terms canceled
- Since the final result depends only on chemical potentials
 - ➔ The equilibrium is unaffected by the potential difference across the interface.
 - ➔ This is a general feature of interphase reactions without transfer of charge
- However, when charge transfer does occur,
 - ➔ the ϕ terms will not cancel and the interfacial potential difference strongly affects the chemical process.

2.2.4 Electrochemical Potentials

(d) Formulation of a Cell Potential

- Consider the cell written in the form of: $\text{Cu}/\text{Zn}/\text{Zn}^{2+},\text{Cl}^-/\text{AgCl}/\text{Ag}/\text{Cu}'$



- At the equilibrium

$$\begin{aligned}\bar{\mu}_{\text{Zn}}^{\text{Zn}} + 2\bar{\mu}_{\text{AgCl}}^{\text{AgCl}} + 2\bar{\mu}_{\text{e}}^{\text{Cu}'} &= \bar{\mu}_{\text{Zn}^{2+}}^{\text{s}} + 2\bar{\mu}_{\text{Ag}}^{\text{Ag}} + 2\bar{\mu}_{\text{Cl}^-}^{\text{s}} + 2\bar{\mu}_{\text{e}}^{\text{Cu}} \\ 2(\bar{\mu}_{\text{e}}^{\text{Cu}'} - \bar{\mu}_{\text{e}}^{\text{Cu}}) &= \bar{\mu}_{\text{Zn}^{2+}}^{\text{s}} + 2\bar{\mu}_{\text{Ag}}^{\text{Ag}} + 2\bar{\mu}_{\text{Cl}^-}^{\text{s}} - \bar{\mu}_{\text{Zn}}^{\text{Zn}} - 2\bar{\mu}_{\text{AgCl}}^{\text{AgCl}}\end{aligned}$$

$$2(\bar{\mu}_{\text{e}}^{\text{Cu}'} - \bar{\mu}_{\text{e}}^{\text{Cu}}) = -2F(\phi^{\text{Cu}'} - \phi^{\text{Cu}}) = -2FE$$

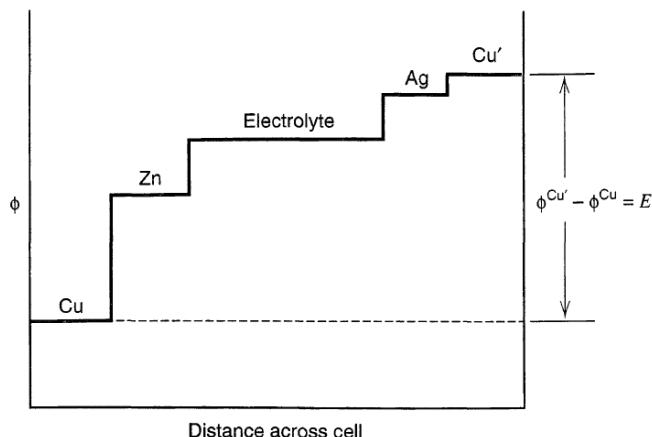


Figure 2.2.5 Potential profile across a whole cell at equilibrium.

2.2.4 Electrochemical Potentials

$$\bar{\mu}_{\text{Zn}}^{\text{Zn}} + 2\bar{\mu}_{\text{AgCl}}^{\text{AgCl}} + 2\bar{\mu}_{\text{e}}^{\text{Cu}'} = \bar{\mu}_{\text{Zn}^{2+}}^{\text{s}} + 2\bar{\mu}_{\text{Ag}}^{\text{Ag}} + 2\bar{\mu}_{\text{Cl}^-}^{\text{s}} + 2\bar{\mu}_{\text{e}}^{\text{Cu}}$$

$$2(\bar{\mu}_{\text{e}}^{\text{Cu}'} - \bar{\mu}_{\text{e}}^{\text{Cu}}) = \bar{\mu}_{\text{Zn}^{2+}}^{\text{s}} + 2\bar{\mu}_{\text{Ag}}^{\text{Ag}} + 2\bar{\mu}_{\text{Cl}^-}^{\text{s}} - \bar{\mu}_{\text{Zn}}^{\text{Zn}} - 2\bar{\mu}_{\text{AgCl}}^{\text{AgCl}}$$

$$2(\bar{\mu}_{\text{e}}^{\text{Cu}'} - \bar{\mu}_{\text{e}}^{\text{Cu}}) = -2F(\phi^{\text{Cu}'} - \phi^{\text{Cu}}) = -2FE$$

→ $-2FE = \mu_{\text{Zn}^{2+}}^{0\text{s}} + RT \ln a_{\text{Zn}^{2+}}^{\text{s}} + 2F\phi^{\text{s}} + 2\mu_{\text{Ag}}^{0\text{Ag}} + 2\mu_{\text{Cl}^-}^{0\text{s}}$
 $+ 2RT \ln a_{\text{Cl}^-}^{\text{s}} - 2F\phi^{\text{s}} - \mu_{\text{Zn}}^{0\text{Zn}} - 2\mu_{\text{AgCl}}^{0\text{AgCl}}$

$$\Delta G^0 = \mu_{\text{Zn}^{2+}}^{0\text{s}} + 2\mu_{\text{Cl}^-}^{0\text{s}} + 2\mu_{\text{Ag}}^{0\text{Ag}} - \mu_{\text{Zn}}^{0\text{Zn}} - 2\mu_{\text{AgCl}}^{0\text{AgCl}}$$

→ $-2FE = \Delta G^0 + RT \ln a_{\text{Zn}^{2+}}^{\text{s}} (a_{\text{Cl}^-}^{\text{s}})^2$
 $\Delta G^0 = -2FE^0$

→ $E = E^0 - \frac{RT}{2F} \ln(a_{\text{Zn}^{2+}}^{\text{s}})(a_{\text{Cl}^-}^{\text{s}})^2$

: which is the **Nernst equation** for the cell.

2.2.4 Electrochemical Potentials

Determine. Cell rxn? Its emf? Spontaneous?



$$E = E^0 + \frac{0.0257}{n} \ln \frac{a_{\text{O}}^{\nu_{\text{o}}}}{a_{\text{R}}^{\nu_{\text{R}}}} = E^0 + \frac{0.0591}{n} \log \frac{a_{\text{O}}^{\nu_{\text{o}}}}{a_{\text{R}}^{\nu_{\text{R}}}}$$

2.3.1 Potential Differences at an Electrolyte-Electrolyte Boundary

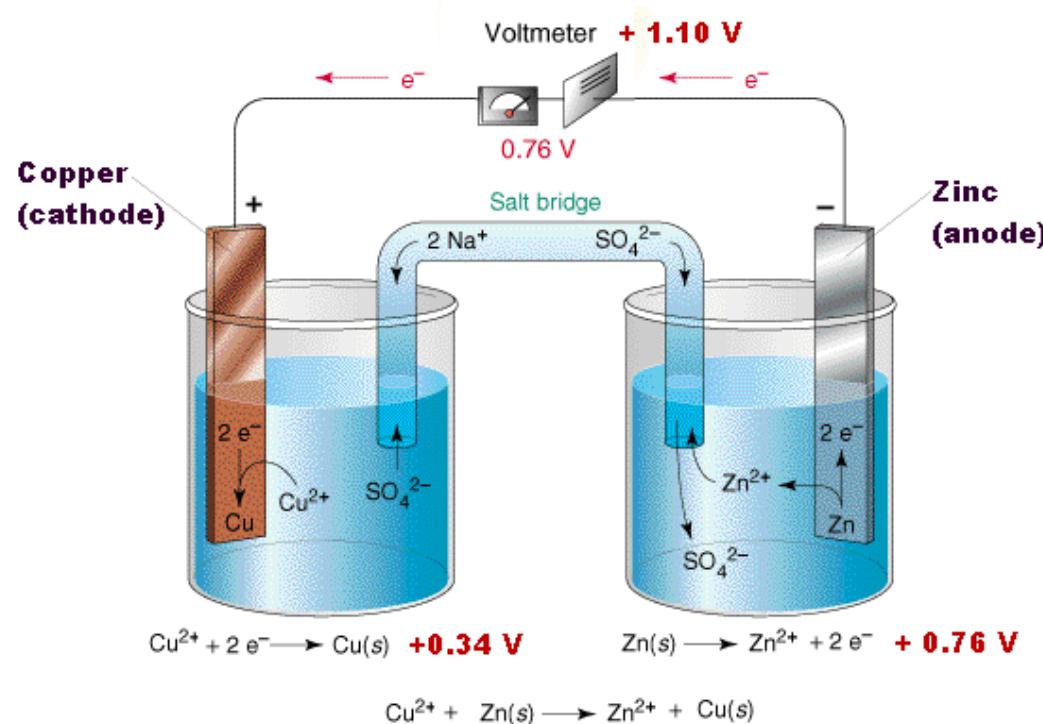
2.3 LIQUID JUNCTION POTENTIALS

2.3.1 Potential Differences at an Electrolyte-Electrolyte Boundary

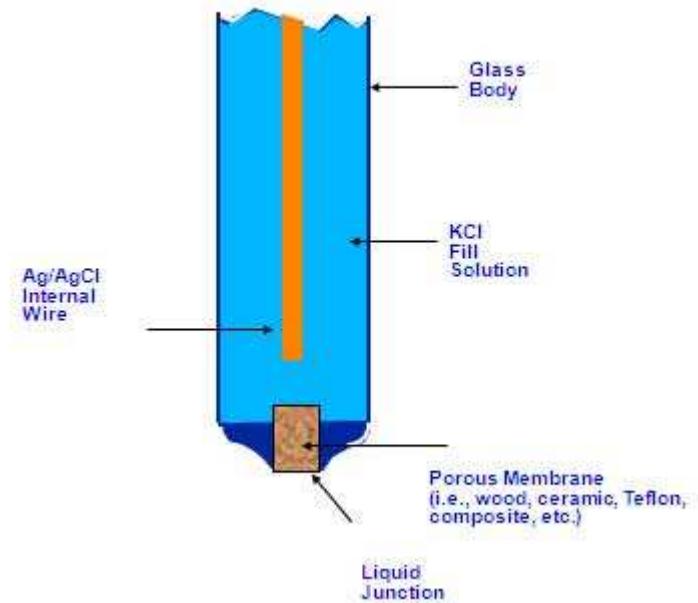
- To this point, the potential differences in equilibrium electrochemical systems are considered by thermodynamics.
- However, many **real cells** are **not** at equilibrium,
 - The electrochemical cells **include** different electrolytes around the two electrodes.
 - **An interface between the two solutions** where mass transport processes work to **mix the solutes**.
 - Examples: salt bridge, reference electrode
- Unless the solutions are the **same initially**,
 - the **liquid junction** will **not** be at equilibrium, because **net flows of mass** occur continuously across it.

2.3.1 Potential Differences at an Electrolyte-Electrolyte Boundary

- Examples for liquid junction: salt bridge, reference electrode

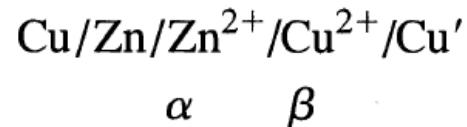


The Basic Reference Electrode



2.3.1 Potential Differences at an Electrolyte-Electrolyte Boundary

- For example,



- The corresponding equilibrium processes can be described as:

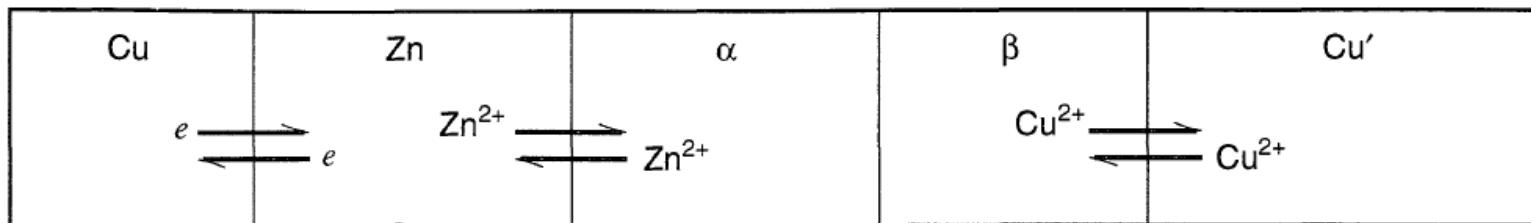


Figure 2.3.1 Schematic view of the phases in cell (2.3.1). Equilibrium is established for certain charge carriers as shown, but at the liquid junction between the two electrolyte phases α and β , equilibrium is not reached.

- The overall cell potential (sum of several interfacial differences) at null current is then

$$E = (\phi^{\text{Cu}'} - \phi^\beta) - (\phi^{\text{Cu}} - \phi^\alpha) + (\phi^\beta - \phi^\alpha) \quad \rightarrow \quad \phi^{\text{Cu}'} - \phi^{\text{Cu}} = E$$

2.3.1 Potential Differences at an Electrolyte-Electrolyte Boundary

$$E = (\phi^{\text{Cu}'} - \phi^\beta) - (\phi^{\text{Cu}} - \phi^\alpha) + (\phi^\beta - \phi^\alpha)$$

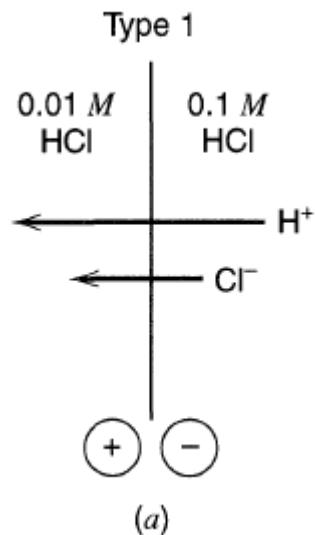


the interfacial potential
differences
at the copper and zinc
electrodes

the potential difference
between the electrolytes,
→ Liquid junction potential.

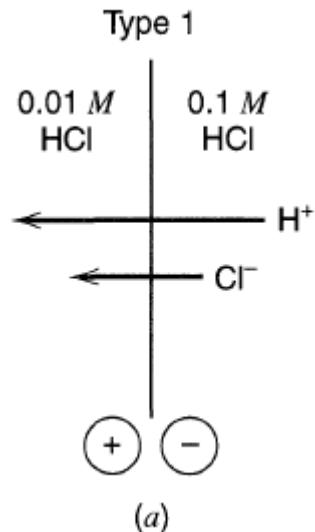
2.3.2 Types of Liquid Junctions

- Consider the boundary shown in the figure



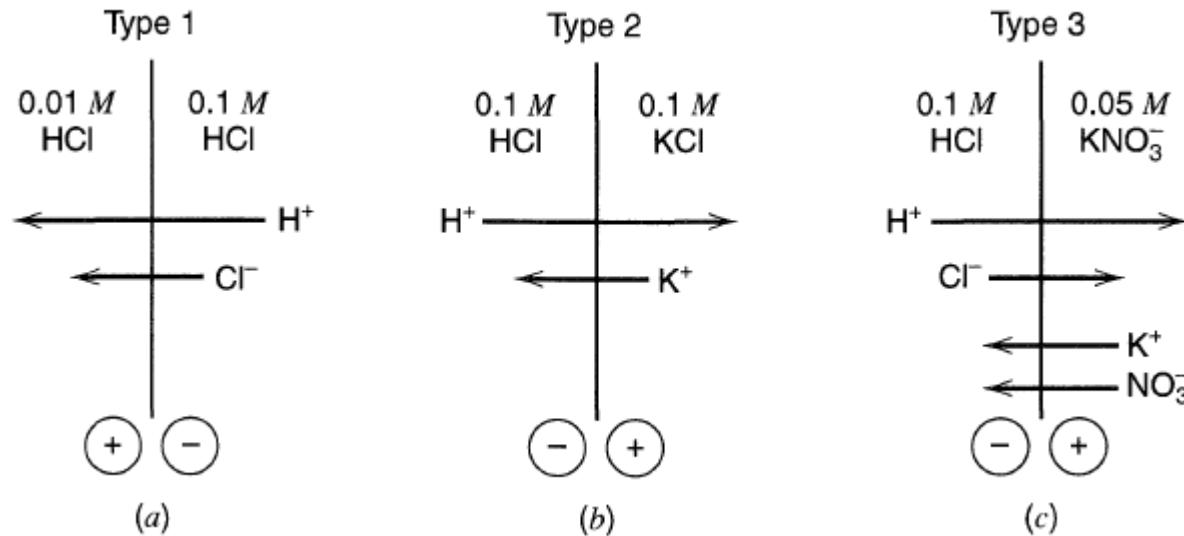
- At the junction, there is a steep concentration gradient in H^+ and Cl^-
 - Hence both ions tend to diffuse from right to left.
- Since the H^+ has a much larger mobility than Cl^- ,
 - H^+ initially penetrates the dilute phase at a higher rate.
- This process gives
 - a positive charge to the dilute phase and a negative charge to the concentrated one,
 - Results in that a boundary potential difference develops.
- However, the corresponding electric field then retards the movement of H^+ and speeds up the passage of Cl^-
 - until the two cross the boundary at equal rates (migration vs diffusion).

2.3.2 Types of Liquid Junctions



- Thus, there is a **detectable steady-state potential**,
 - which is **not due to an equilibrium** process
 - From its origin, this interfacial potential is sometimes called a **diffusion potential**.
- Even though the boundary region **cannot be at equilibrium**,
 - it has a composition that is **effectively constant** over long time period

2.3.2 Types of Liquid Junctions

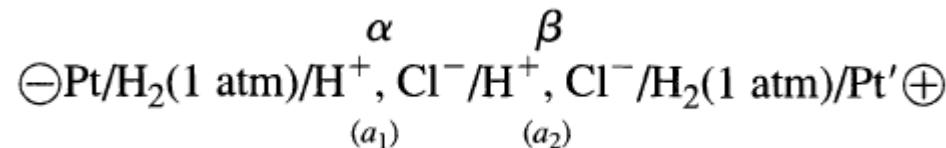


- Classify liquid junctions into three types:
 1. Figure (a): Two solutions of the same electrolyte at different concentrations
 2. Figure (b): Two solutions at the same concentration with different electrolytes having an ion in common
 3. Figure (c): Two solutions not satisfying conditions 1 or 2

2.3.2 Types of Liquid Junctions

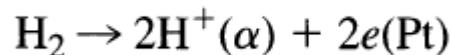
Conductance, Transference Numbers, and Mobility

- Consider the cell:

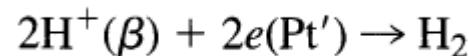


: where $a_2 > a_1$

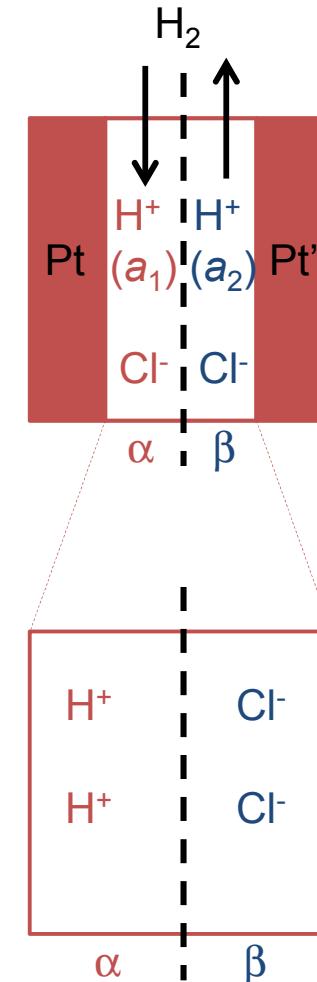
- When the cell operates **galvanically**,
→ an **oxidation** occurs at the left electrode,



- And a **reduction** happens on the right,

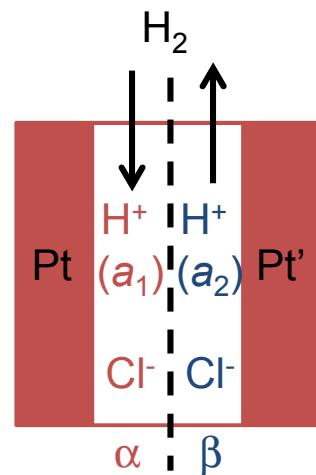


- Therefore, there is a tendency to build up
→ a **positive charge** in the α phase and a **negative charge** in β .



2.3.2 Types of Liquid Junctions

Given that $a_1 = 0.01 \text{ M}$, $a_2 = 0.1 \text{ M}$, emf ?

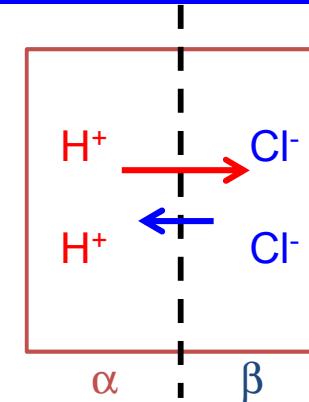


2.3.2 Types of Liquid Junctions

- This tendency is overcome by the movement of ions (electroneutrality):
→ H^+ to the right and Cl^- to the left.
- For each mole of electrons passed,
→ 1 mole of H^+ is produced in α , and 1 mole of H^+ is consumed in β .
→ The total amount of H^+ and Cl^- migrating across the boundary between α and β must equal 1 mole.
- The fractions of the current carried by H^+ and Cl^-
→ are called their transference numbers (or transport numbers).
- If we let t_+ be the transference number for H^+ and t_- be that for Cl^- , then clearly,

$$t_+ + t_- = 1$$

→ In general, for an electrolyte containing many ions, i,



$$\sum_i t_i = 1$$

2.3.2 Types of Liquid Junctions

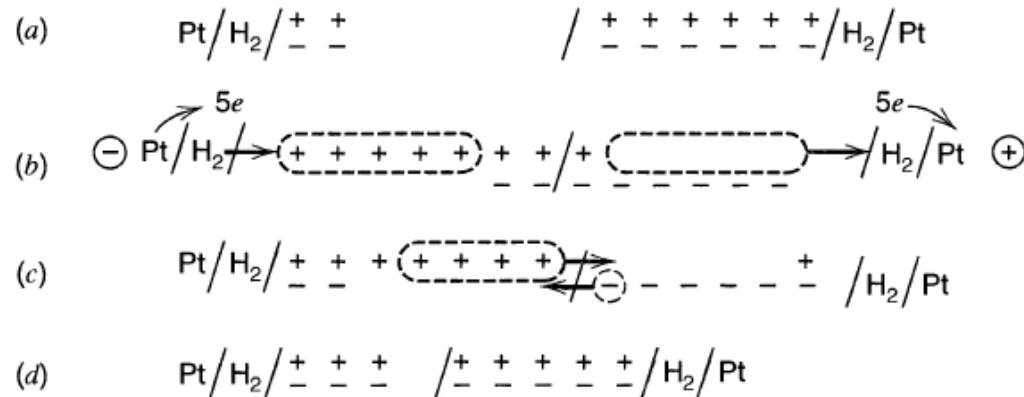


Figure 2.3.3 Schematic diagram showing the redistribution of charge during electrolysis of a system featuring a high concentration of HCl on the right and a low concentration on the left.

- (a) The cell initially features a higher activity of hydrochloric acid (+ as H^+ , - as Cl^-) on the right
- (b) hence discharging it spontaneously produces H^+ on the left and consumes it on the right. → Assume that five units of H^+ are reacted.
- (c) For hydrochloric acid, $t_+ \sim 0.8$ and $t_- \sim 0.2$
→ Therefore, four units of H^+ must migrate to the right and one unit of Cl^- to the left to maintain electroneutrality.
- (d) The final state of the solution

2.3.2 Types of Liquid Junctions

- Transference numbers are determined by the kinetics of ionic conduction (resistance or conductance)
- The value of conductance L for a segment of solution immersed in an electric field is defined as

$$L = \kappa A/l$$

- directly proportional to the cross-sectional area (A) perpendicular to the field vector
- inversely proportional to the length (l) of the segment along the field.
- The proportionality constant is the conductivity, κ ,
: which is an intrinsic property of the solution

- Conductance, L ,
- is given in units of siemens ($S = \Omega^{-1}$),
- Conductivity, κ
- is expressed in $S \text{ cm}^{-1}$ or $\Omega^{-1} \text{ cm}^{-1}$

2.3.2 Types of Liquid Junctions

- Since the **passage of current** through the solution is accomplished by **the independent movement of different species**
→ κ : the sum of contributions from all ionic species, i.
- Each component of κ
→ is **proportional** to the **concentration** of the ion, the magnitude of its **charge** $|z_i|$, and some index of its **migration velocity**.

$$\kappa = F \sum_i |z_i| u_i C_i$$

- That index is the **mobility**, u_i
→ The **limiting velocity** of the ion in an **electric field of unit strength**.
→ Mobility usually carries dimensions of $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (i.e., cm/s per V/cm).

2.3.2 Types of Liquid Junctions

- When a field of strength \mathcal{E} is applied to an ion,
 - It will accelerate under the force imposed by the field until the frictional drag exactly counterbalances the electric force.
 - Then, the ion continues its motion at that terminal velocity.

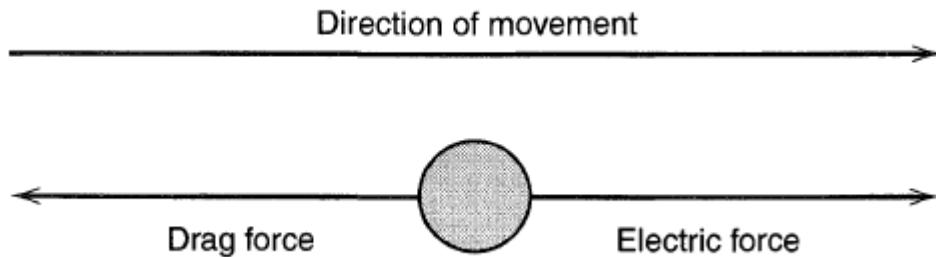


Figure 2.3.4 Forces on a charged particle moving in solution under the influence of an electric field. The forces balance at the terminal velocity.