Chapter 2

Electrode/electrolyte interface:

---Structure and properties

Extensive reading:
Bard, Electrochemical methods. Fundamentals and applications:
pp. 54-63

2.2 A MORE DETAILED VIEW OF INTERFACIAL POTENTIAL DIFFERENCES
2.2.1 The Physics of Phase Potentials
2.2.3 Measurement of Potential Differences
2.2.4 Electrochemical Potentials
2.2.5 Fermi Level and Absolute Potential
Introduction

Electrochemical reactions are interfacial reactions, the structure and properties of electrode / electrolytic solution interface greatly influence the reaction.

Influential factors:

(1) Chemistry factor:

Chemical composition and surface structure of the electrode: reaction mechanism – electrocatalytic effect.

(2) Electrical factor:

Potential distribution: activation energy of electrochemical reaction
2.1 Electrochemical potential

2.1.1 Electrochemical potential

For process involving useful work, \( \delta W' \) should be incorporated in the following thermodynamic expression.

\[
dG = -SdT + VdP + \delta W' + \sum \mu_i dn_i
\]

For electrochemical system, the useful work is:

\[
W' = z_i e \phi
\]

Under constant temperature and pressure, for process \( A \rightarrow B \):

\[
\Delta G_i^{A \rightarrow B} = \mu_i^B - \mu_i^A + z_i e_0 (\phi^B - \phi^A)
= (\mu_i^B + z_i e_0 \phi^B) - (\mu_i^A + z_i e_0 \phi^A)
\]
1) Definition:

\[ \Delta G_i^{A\rightarrow B} = (\mu_i^B + z_i e_0 \phi^B) - (\mu_i^A + z_i e_0 \phi^A) \]

2.1 Electrochemical potential

\[ \mu_{i}^{\alpha} + z_i e_0 \phi^\alpha = \mu_{i}^{\alpha} \]

\( z_i \) is the charge on species \( i \), \( \phi \), the inner potential, is the potential of phase \( \alpha \).

\[ \Delta G_i^{A\rightarrow B} = \mu_{i}^{B} - \mu_{i}^{A} \]

In electrochemical system, problems should be considered using electrochemical potential instead of chemical potential.
2.1 Electrochemical potential

\[ \mu_i^\alpha + z_i e_0 \phi^\alpha = \bar{\mu}_i^\alpha \]

2) Properties:

1) If \( z = 0 \) (species uncharged)

\[ \bar{\mu}_i^\alpha = \mu_i^\alpha \]

2) for a pure phase at unit activity

\[ \bar{\mu}_i^\alpha = \mu_i^{\Theta, \alpha} \]

3) for species \( i \) in equilibrium between \( \alpha \) and \( \beta \).

\[ \bar{\mu}_i^\alpha = \bar{\mu}_i^\beta \]

3) Effect on reactions

1) Reactions in a single phase: \( \phi \) is constant, no effect

2) Reactions involving two phases:
   a) without charge transfer: no effect
   b) with charge transfer: strong effect
§ 2.2 Inner, outer and surface potential

(1) Potential in vacuum:

The potential of certain point is defined as the work done by transfer unite positive charge from infinite to this point. (Only Coulombic force is concerned).

\[ \phi = \int_{\infty}^{x} F \, dx = \int_{\infty}^{x} -\varepsilon \, dx \]

\[ F = e \varepsilon \]

\( \varepsilon \) - strength of electric field
§ 2.2 Inner, outer and surface potential

(2) Potential of solid phase

Electrochemical reaction can be simplified as the transfer of electron from species in solution to inner part of an electrode.

This process can be divided into two separated steps.
The work \( W_1 \) done by moving a test charge from infinite to \( 10^{-6} \sim 10^{-7} \) m vicinity to the solid surface (only related to long-distance force) is outer potential.

Outer potential also termed as Volta Potential \( \Phi \) is the potential measured just outside a phase.

Moving unit charge from vicinity \( (10^{-6} \sim 10^{-7} \) m) into inner of the sphere overcomes surface potential \( \chi \). Short-distance force takes effect.

For hollow ball, \( \mu \) can be excluded.

\( \chi \) arises due to the change in environment experienced by the charge (redistribution of charges and dipoles at the interface).
The total work done for moving unit charge to inner of the charged sphere is $W_1 + W_2$

$$\phi = \frac{(W_1 + W_2)}{ze_0} = \psi + \chi$$

The electrostatic potential within a phase termed the Galvani potential or inner potential ($\phi$).

If short-distance interaction, i.e., chemical interaction, is taken into consideration, the total energy change during moving unite test charge from infinite to inside the sphere:

$$W_1 + W_2 + \mu = \bar{\mu}$$

$$\bar{\mu} = \mu + ze_0\phi = \mu + ze_0(\psi + \chi)$$
§ 2.2 Inner, outer and surface potential

- **infinite**
  \( \overline{\mu_i}, \psi_i, \phi = 0 \)

- **distance**
  \( 10^{-6} \sim 10^{-7} \)
  - **hollow**
  - **inner**

- \( z_i e_0 \psi^\alpha \)
- \( z_i e_0 \phi^\alpha \)
- \( \overline{\mu_i}^\alpha \)
- \( \mu_i^\alpha \)
- \( \psi_i^\alpha \)

- **Work function**
  \( W_{e^-} \)
§ 2.2 Inner, outer and surface potential

(4) Work function and surface potential

**work function**

The minimum energy (usually measured in electron volts) needed to remove an electron from a solid to a point immediately outside the solid surface

or energy needed to move an electron from the Fermi energy level into vacuum.

\[
W_{e^-} = \mu_i + z_i e_0 \chi^\alpha
\]
For two conductors contacting with each other at equilibrium, their electrochemical potential is equal.

\[ \bar{\mu}_e^\alpha = \bar{\mu}_e^\beta \]

\[ \alpha \Delta^\beta \bar{\mu}_e^- = 0 \]

\[ \alpha \Delta^\beta \phi = \frac{\bar{\mu}_e^\alpha - \bar{\mu}_e^\beta}{e_0} \]
Chapter 2 Electrode/electrolyte interface

§ 2.3 measurability of inner potential

\[ \mu_e^- = \mu_e^- - e_0(\psi + \chi) \]

\[ \mu_e^\alpha - e_0\psi^\alpha - e_0\chi^\alpha = \mu_e^\beta - e_0\psi^\beta - e_0\chi^\beta \]

\[ e_0^{\alpha} \Delta^\beta \psi = e_0(\psi^\alpha - \psi^\beta) = (\mu_e^\alpha - e_0\chi^\alpha) - (\mu_e^\beta - e_0\chi^\beta) \]

\[ -W_e^- = \mu_e^- - e_0\chi \]

\[ \alpha \Delta^\beta \psi = -\frac{\alpha \Delta^\beta W_e^-}{e_0} \]

Different metal with different \( W_e^- \)

\[ \alpha \Delta^\beta W_e^- \neq 0 \quad \text{Therefore} \quad \alpha \Delta^\beta \psi \neq 0 \]

\[ \therefore \alpha \Delta^\beta \phi \neq 0 \]
Chapter 2 Electrode/electrolyte interface:

§ 2.3 measurability of inner potential

No potential difference between well contacting metals can be detected

\[ \alpha V^\beta = 0 \]

\[ \alpha \Delta^\beta \mu_{e^-} = 0 \]

\[ \alpha \Delta^\beta \psi \neq 0 \]

\[ \alpha \Delta^\beta \phi \neq 0 \]

Conclusion

\[ e_0 \alpha V^\beta = \mu^\beta_{e^-} - \mu^\alpha_{e^-} \]

\[ \alpha V^\beta \sim \Delta \mu_{e^-} , \text{ not } \Delta \phi \text{ nor } \Delta \Psi \]

Galvanic and voltaic potential cannot be measured using voltmeter.
If electrons can not exchange freely among the pile, i.e., poor electrical conducting between phases.

\[
\Delta V = \sum_{1}^{n-1} i \Delta i+1 \psi + \left( \frac{\mu^n_{e^-} - \mu^1_{e^-}}{e_0} \right)
\]

\[
= \sum_{1}^{n-1} i \Delta i+1 \psi + n \Delta^1 \phi
\]

\[
\Delta V = \sum_{1}^{n} i \Delta i+1 \psi + \left( \frac{\mu^1_{e^-} - \mu^1_{e^-}}{e_0} \right)
\]

\[
= \sum_{1}^{n} i \Delta i+1 \psi
\]
§ 2.3 measurability of inner potential

(4) Analysis of real system

Consider the cell: \( \text{Cu|Cu}^{2+} | \text{Zn}^{2+} | \text{Zn/Cu}' \)

\[
\Delta V^{II} = \Delta V^I = \phi^I - \phi^{I'}
\]

\[
= (\phi^I - \phi^{S_1}) + (\phi^{S_1} - \phi^{S_2}) + (\phi^{S_2} - \phi^{II}) + (\phi^{II} - \phi^{I'})
\]

\[
= I \Delta S_1 \phi + S_1 \Delta S_2 \phi + S_2 \Delta II \phi + II \Delta I' \phi + II \Delta I \phi
\]

For homogeneous solution without liquid junction potential

\[
\Delta V^{II} = I \Delta S \phi + S \Delta II \phi + \text{const.}
\]

the potential between I and II depends on outer potential difference between metal and solution.
§ 2.3 measurability of inner potential

\[ I V^{II} = I \Delta^S \phi + I \Delta^{II} \phi + \text{const.} \]

Using reference with the same convention, the exact value of unknown electrode cannot be detected.

\[ I V_1^{II} = I \Delta^S \phi_1 + \text{const.} \quad I V_2^{II} = I \Delta^S \phi_2 + \text{const.} \]

\[ \Delta(I V^{II}) = \Delta(I \Delta^S \phi) \]

The value of \( I \Delta^S \phi \) is unmeasurable but the change of is \( \Delta(I \Delta^S \phi) \) can be measured.

\[ I \Delta^S \phi \]

absolute potential
§ 2.4 origination of interfacial charge

(1) Transfer of electrons

(2) Transfer of charged species
§ 2.4 origination of interfacial charge

3) Unequal dissolution / ionization

(4) specific adsorption of ions
§ 2.4 origination of interfacial charge

(5) orientation of dipole molecules

(6) Liquid-liquid interfacial charge

Different transference number
**§ 2.4 origination of interfacial charge**

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<table>
<thead>
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<tbody>
<tr>
<td>1)</td>
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<td>Liquid-liquid interfacial charge</td>
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1), 2), 3) and 6): **interphase potential**

4), 5) **surface potential**.
§ 2.4 origination of interfacial charge

Electric double layer

Electroneutrality: $q_m = -q_s$

Holmholdt double layer (1853)
§ 2.5 ideal polarizable and ideal non-polarizable electrodes

Faradaic process and non-Faradaic process
§ 2.5 ideal polarizable and ideal non-polarizable electrodes

**ideal polarizable electrode**

An electrode at which no charge transfer across the metal-solution interface occurs regardless of the potential imposed by an outside source of voltage.

No electrochemical current:

\[ i = i_{ch} \]
§ 2.5 ideal polarizable and ideal non-polarizable electrodes

Virtual ideal polarizable electrode

\[ \text{Hg electrode in KCl aqueous solution: no reaction takes place} \]

\[ \text{k}^+ + 1\text{e}^- = \text{K} \quad (-1.6 \text{ V}) \]

\[ 2\text{Hg} + 2\text{Cl}^- - 2\text{e}^- = \text{Hg}_2\text{Cl}_2 \quad (+0.1 \text{ V}) \]
§ 2.5 ideal polarizable and ideal non-polarizable electrodes

ideal non-polarizable electrode

an electrode whose potential does not change upon passage of current (electrode with fixed potential)

no charge current: \( i = i_{ec} \)

Virtual non-polarizable electrode

\[ \text{Ag(s)|AgCl(s)|Cl}^- (\text{aq.}) \]

\[ \text{Ag(s) + Cl}^- \rightarrow \text{AgCl(s) + 1e}^- \]
§ 2.5 ideal polarizable and ideal non-polarizable electrodes

For measuring the electrochemical behavior of electrode/electrolyte interface, which kind of electrode is preferred, ideal polarizable electrode or ideal non-polarizable electrode?
§ 2.5 Interfacial structure

**Experimental methods:**

1) Electro-capillary curve measurement
2) Differential capacitance measurement

Surface charge-dependence of surface tension:

1) Why does *surface tension* change with increasing of surface charge density?

2) Through which way can we notice the change of surface tension?
§ 2.5 Interfacial structure

(1) Electro-capillary curve measurement

Experimental setup for Electrocapillary curve measurement

Electrocapillary curves for mercury and different electrolytes at 18 °C.
§ 2.5 Interfacial structure

(1) Electro-capillary curve measurement

The Gibbs adsorption isotherm

\[ n_i = n_i^\alpha + n_i^\beta + n_i^\sigma \]

\[ n_i^\sigma = n_i - n_i^\alpha - n_i^\beta \]

\[ \Gamma = \frac{n_i^\sigma}{A} \]

\[ dG^\sigma = -SdT + \sigma dA + \sum_i \mu_i dn_i^\sigma \]

When \( T \) is fixed

\[ dG^\sigma = \sigma dA + \sum_i \mu_i dn_i^\sigma \]
§ 2.5 Interfacial structure

(1) Electro-capillary curve measurement

$$dG^\sigma = \sigma dA + \sum_i \mu_i dn_i^\sigma$$

Integration gives

$$G^\sigma = \sigma A + \sum \mu_i n_i^\sigma$$

$$dG^\sigma = \sigma dA + Ad\sigma + \sum \mu_i dn_i^\sigma + \sum n_i^\sigma d\mu$$

$$Ad\sigma + \sum_i n_i^\sigma d\mu = 0$$

$$d\sigma = -\Sigma \Gamma_i d\mu_i$$

Gibbs adsorption isotherm

$$d\sigma = -\Sigma \Gamma_i d\mu_i - q d\varphi$$

$$\Gamma_{e^-} = \frac{-q}{F}$$

$$d\mu_{e^-} = -Fd\varphi$$
§ 2.5 Interfacial structure

(1) Electro-capillary curve measurement

Lippman equation

\[ d\sigma = -\Sigma \Gamma_i d\mu_i - q d\varphi \]

When the composition of solution keeps constant

\[ d\sigma = -q d\phi \]

\[ q = -\left( \frac{\partial \sigma}{\partial \phi} \right)_{\mu_1, \mu_2, \cdots \mu_1} \]

Zero charge potential: \( \varphi_0 \) (\( \varphi_{pzc} \): potential at which the electrode bears zero charge)

\[ \sigma = \sigma_m - \frac{C}{2} \varphi^2 \]
\section*{\textsection 2.5 Interfacial structure}

(1) Electro-capillary curve measurement

Theoretical deduction of 
\[ \sigma = \sigma_m - \frac{C}{2} \phi^2 \]

\[ -d\sigma = q d\phi; \quad q = C\phi; \]

\[ -d\sigma = C\phi d\phi \]

\[ -\int_{\sigma}^{\sigma_m} d\sigma = C \int_{\phi}^{\phi_0} \phi d\phi \]

\[ - (\sigma_m - \sigma) = \frac{C}{2} (\phi_0^2 - \phi^2) \]
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

\[ q = \int_{\varphi_1}^{\varphi_2} c(\varphi) \cdot d\varphi \]

Differential capacitance
The double layer capacitance can be measured with ease using electrochemical impedance spectroscopy (EIS) through data fitting process.
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

\[ C_d = C(\varphi) \]

Differential capacitance curves

Integration of capacitance for charge density
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

Dependence of differential capacitance on potential of different electrolytes.

Charge density on potential
Figure 13.2.3  Charge density on the electrode vs. potential for mercury immersed in 1 M solutions of the indicated electrolytes at 25°C. The potentials are plotted with respect to the PZC for each electrolyte. [Reprinted with permission from D. C. Grahame, Chem. Rev., 41, 441 (1947). Copyright 1947, American Chemical Society.]
Figure 13.2.5  Surface excesses vs. potential for mercury in 0.1 \textit{M} KF. Potentials are referenced both to a NCE and the potential of zero charge, \( E_z \). [From data in D. C. Grahame and B. A. Soderberg, \textit{J. Chem. Phys.}, 22, 449 (1954).]
Figure 13.2.6 Surface excesses vs. charge density on the electrode for mercury in 0.1 M KBr. [Reprinted with permission from M. A. V. Devanathan and S. G. Canagaratna, *Electrochim. Acta*, 8, 77 (1963). Copyright 1963, Pergamon Press PLC.]
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

Dependence of differential capacitance on concentration

Potential-dependent

Concentration-dependent

Minimum capacitance at potential of zero charge ($E_{\text{pzc}}$)

36 μF cm$^{-2}$;

18 μF cm$^{-2}$;

differential capacitance curves for an Hg electrode in NaF aqueous solution
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

Surface excess charge

\[ q = \Gamma_+ + \Gamma_- \]

\[ z_+ F \Gamma_+ + z_- F \Gamma_- = q_s = -q \]

\[ M_{v^+} A_{v^-} \rightleftharpoons v_+ M^{z+} + v_- A^{z-} \]

\[ v_+ z_+ = v_- z_- \]

\[ d \mu_{MA} = v_+ d \mu_+ + v_- d \mu_- \]
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

\[ d\sigma + \sum \Gamma_i d\mu_i = 0 \]
\[ d\sigma = -qd\varphi - \sum \Gamma_i d\mu_i \]
\[ = -qd\varphi - \Gamma_+ d\mu_+ - \Gamma_- d\mu_- \]

\[ d\varphi = d\varphi_{W.E.} + d\varphi_{R.E.} \]

For R.E. in equilibrium with cation

\[ d\mu_+ = z_+ F d\varphi_{R.E.} \]
\[ d\mu_{MA} = v_+ d\mu_+ + v_- d\mu_- \]

For any electrolyte

\[ \Gamma_+ = -v_+ \left( \frac{\partial\sigma}{\partial\mu_{MA}} \right)_{\varphi_{R.E.}} \]
\[ \Gamma_- = -v_- \left( \frac{\partial\sigma}{\partial\mu_{MA}} \right)_{\varphi_{R.E.}} \]
§ 2.5 Interfacial structure

(2) Differential capacitance measurement

Surface excess curves
§ 2.6 Models for electric double layer

1) Helmholtz model (1853)

Electrode possesses a charge density resulted from excess charge at the electrode surface ($q_m$), this must be balanced by an excess charge in the electrolyte ($-q_s$)
§ 2.6 Models for electric double layer

1) Helmholtz model (1853)

\[ C = \frac{\varepsilon_0 \varepsilon_r}{A d} \]

\[ q = \frac{\varepsilon_0 \varepsilon_r V}{A d} \]

\( q \) charge on electrode (in Coulomb)

Equivalent to a capacitor:

“dielectric” medium

Charge on electrode (in Coulomb)
Charge on the electrode is confined to surface but same is not true for the solution. Due to interplay between electrostatic forces and thermal randomizing force particularly at low concentrations, it may take a finite thickness to accumulate necessary counter charge in solution.
§ 2.6 Models for electric double layer

(2) Gouy-Chappman layer (1910, 1913)

Gouy and Chapman quantitatively described the charge stored in the diffuse layer, \( q_d \) (per unit area of electrode):

**Boltzmann distribution**

\[
C_+(x) = C^0 \exp\left(-\frac{\phi_x F}{RT}\right)
\]

\[
C_-(x) = C^0 \exp\left(\frac{\phi_x F}{RT}\right)
\]

**Poisson equation**

\[
\frac{\partial^2 \phi}{\partial x^2} = -\frac{\partial E}{\partial x} = -\frac{4\pi \rho_x}{\varepsilon}
\]

\[
\rho_x = F[C_+(x) - C_-(x)]
\]
§ 2.6 Models for electric double layer

(2) Gouy-Chappman layer (1910, 1913)

\[
\rho_x = C^0 F \left[ \exp \left( - \frac{\varphi_x F}{RT} \right) - \exp \left( \frac{\varphi_x F}{RT} \right) \right]
\]

\[
\frac{\partial^2 \varphi_x}{\partial x^2} = - \frac{4\pi C^0 F}{\varepsilon} \left[ \exp \left( - \frac{\varphi_x F}{RT} \right) - \exp \left( \frac{\varphi_x F}{RT} \right) \right]
\]

\[
\frac{\partial^2 \varphi_x}{\partial x^2} = \frac{1}{2} \cdot \frac{\partial}{\partial \varphi_x} \left( \frac{\partial \varphi_x}{\partial x} \right)^2
\]

\[
\frac{\partial}{\partial \varphi_x} \left( \frac{\partial \varphi_x}{\partial x} \right)^2 = - \frac{8\pi C^0 F}{\varepsilon} \left[ \exp \left( - \frac{\varphi_x F}{RT} \right) - \exp \left( \frac{\varphi_x F}{RT} \right) \right]
\]

Integrate from \( x = d \) to \( x = \infty \)
§ 2.6 Models for electric double layer

(2) Gouy-Chappman layer (1910, 1913)

For 1:1 electrolyte

\[
q = \sqrt{\frac{\varepsilon RT c^0}{2\pi}} \left[ \exp\left( \frac{\phi_1 F}{2RT} \right) - \exp\left( - \frac{\phi_1 F}{2RT} \right) \right]
\]

For Z:Z electrolyte

\[
q = \sqrt{\frac{\varepsilon RT c^0}{2\pi}} \left[ \exp\left( \frac{|z|\phi_1 F}{2RT} \right) - \exp\left( - \frac{|z|\phi_1 F}{2RT} \right) \right]
\]
§ 2.6 Models for electric double layer

(2) Gouy-Chappman layer (1910, 1913)

\[ q_d = -\left(8RT \varepsilon C^* \right)^{1/2} \sinh \frac{zF \phi_0}{2RT} \]

Experimentally, it is easier to measure the differential capacitance:

\[ C_d = \frac{zF(2\varepsilon C^*)^{1/2}}{RT} \cosh \frac{zF \phi_0}{2RT} \]

\[ \sinh x = \frac{e^x - e^{-x}}{2} \quad \text{Hyperbolic functions} \]
Figure 13.3.3  Potential profiles through the diffuse layer in the Gouy–Chapman model. Calculated for a $10^{-2}$ $M$ aqueous solution of a 1:1 electrolyte at 25°C. $1/\kappa = 30.4$ Å.

**TABLE 13.3.1 Characteristic Thickness of the Diffuse Layer$^a$**

<table>
<thead>
<tr>
<th>$C^*(M)^b$</th>
<th>$1/\kappa$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>9.6</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>30.4</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>96.2</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>304</td>
</tr>
</tbody>
</table>

$^a$For a 1:1 electrolyte at 25°C in water.

$^b$C* = $n^0/N_A$ where $N_A$ is Avogadro’s number.
§ 2.6 Models for electric double layer

(2) Gouy-Chapman layer (1910, 1913)

For a 1:1 electrolyte at 25 °C in water, the predicted capacitance from Gouy-Chapman Theory.

1) Minimum in capacitance at the potential of zero charge

2) dependence of $C_d$ on concentration
§ 2.6 Models for electric double layer

(3) Stern double layer (1924)

Combination of Helmholtz and Guoy-Chapman Models

The potential drop may be broken into 2:

\[ \varphi_m - \varphi_s = (\varphi_m - \varphi_2) + (\varphi_2 - \varphi_s) \]
§ 2.6 Models for electric double layer

(3) Stern double layer (1924)

\[ \varphi_m - \varphi_s = (\varphi_m - \varphi_2) + (\varphi_2 - \varphi_s) \]

Inner layer + diffuse layer

This may be seen as 2 capacitors in series:

\[ \frac{1}{C_t} = \frac{1}{C_i} + \frac{1}{C_d} \]

\( C_i \): inner layer capacitance

\( C_d \): diffuse layer capacitance - given by Gouy-Chapman
Total capacitance ($C_t$) dominated by the smaller of the two.

### Table

<table>
<thead>
<tr>
<th>At low $c^0$</th>
<th>At high $c^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_d$ dominant</td>
<td>$C_i$ dominant</td>
</tr>
<tr>
<td>$C_d \approx C_t$</td>
<td>$C_i \approx C_t$</td>
</tr>
</tbody>
</table>
§ 2.6 Models for electric double layer

(3) Stern double layer (1924)

Stern equation for double layer

\[ C_i = \frac{q}{\varphi - \varphi_1} \]

\[ \varphi = \varphi_1 + \frac{1}{C_i} \sqrt{\frac{\varepsilon RT c^0}{2\pi}} \left[ \exp\left( \frac{\varphi_1 F}{2RT} \right) - \exp\left( -\frac{\varphi_1 F}{2RT} \right) \right] \]

Discussion:

When \( c^0 \) and \( |\varphi| \) are very small

\[ \varphi = \varphi_1 + \frac{1}{C_i} \sqrt{\frac{\varepsilon RT}{2\pi}} \left( \frac{\varphi_1 F}{2RT} \right) \sqrt{c^0} \]
§ 2.6 Models for electric double layer

(3) Stern double layer (1924)

Discussion:

When $c^0$ and $|\varphi|$ are very large

\[
\varphi \approx \varphi_1 + \frac{1}{C_i} \sqrt{\frac{\varepsilon RT}{2\pi}} \exp \left( \frac{\varphi_1 F}{2RT} \right) \sqrt{c^0}
\]

\[
\approx \frac{1}{C_i} \sqrt{\frac{\varepsilon RT}{2\pi}} \exp \left( \frac{\varphi_1 F}{2RT} \right) \sqrt{c^0}
\]

\[
C_d = \frac{dq}{d\varphi_1} = \frac{F}{2RT} \sqrt{\frac{\varepsilon RTc^0}{2\pi}} \left[ \exp \left( \frac{\varphi_1 F}{2RT} \right) + \exp \left( -\frac{\varphi_1 F}{2RT} \right) \right]
\]

$C_d$ plays a role at low potential near to the p. z. c.
\[
\frac{1}{C_d} = \frac{x_2}{\varepsilon \varepsilon_0} + \frac{1}{(2\varepsilon \varepsilon_0 z^2 e^2 n^0 / kT)^{1/2} \cosh(z_e \phi_2 / 2kT)}
\]

\[
\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}
\]

Figure 13.3.6  (a) A view of the differential capacitance in the Gouy–Chapman–Stern (GCS) model as a series network of Helmholtz-layer and diffuse-layer capacitances. (b) Potential profile through the solution side of the double layer, according to GCS theory. Calculated from (13.3.23) for 10^{-2} M 1:1 electrolyte in water at 25°C.
Fitting result of Stern Model.

Fitting of Gouy-Chapman model to the experimental results

§ 2.6 Models for electric double layer
(3) Stern double layer (1924)
§ 2.6 Models for electric double layer

(4) BDM model

Bockris-Devanathan-Muller, 1963

Only electrostatic adsorption

Not only electrostatic adsorption
§ 2.6 Models for electric double layer

(4) BDM model

- **Inner Helmholtz plane (IHP)** \( \phi_1 \)
- **Outer Helmholtz plane (OHP)** \( \phi_2 \)

- Specially adsorbed anion
- Solvated cation

Weak Solvation and strong interaction let anions approach electrode and become specifically adsorbed.
§ 2.6 Models for electric double layer

(4) BDM model

Dielectric saturation

\[ d_i \varepsilon_i = 5-6 \quad d_o \varepsilon_i = 40 \]

\[ C_d = C^i = \frac{\varepsilon_i}{4\pi d_i} \]

If the diameter of adsorbed water molecules was assumed as \(2.7 \times 10^{-10} \text{ m}, \varepsilon_i = 6\), then

\[ C_c \approx \frac{\varepsilon_i}{4\pi d_i} = \frac{1}{9 \times 10^{11}} \times \frac{6}{4 \times 3.1416 \times 2.7 \times 10^{-8}} = 20 \mu\text{F} \cdot \text{cm}^{-2} \]

The theoretical estimation is close to the experimental results, 18-20 \( \mu\text{F} \cdot \text{cm}^{-2} \), which suggests the reasonability of the BDM model.
Summary: What have been solved, what have not?
§ 2.6 Models for electric double layer

(5) Gramham Model-specific adsorption

Triple layer
Specifically adsorbed anions
Helmholtz (inner / outer) plane
Figure 13.3.8 Calculated potential profiles in the double layer for mercury in contact with aqueous 0.3 M NaCl at 25°C. Potentials given with respect to the PZC in NaF. At positive electrode potentials the profile has a sharp minimum because chloride is specifically adsorbed.