Short Course of Electrochemistry
L4: Pourbaix Diagram, EC Setup and Non-faraday Behavior

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Potential/pH Diagram of Water

Water Dissociation, E^0_{water}

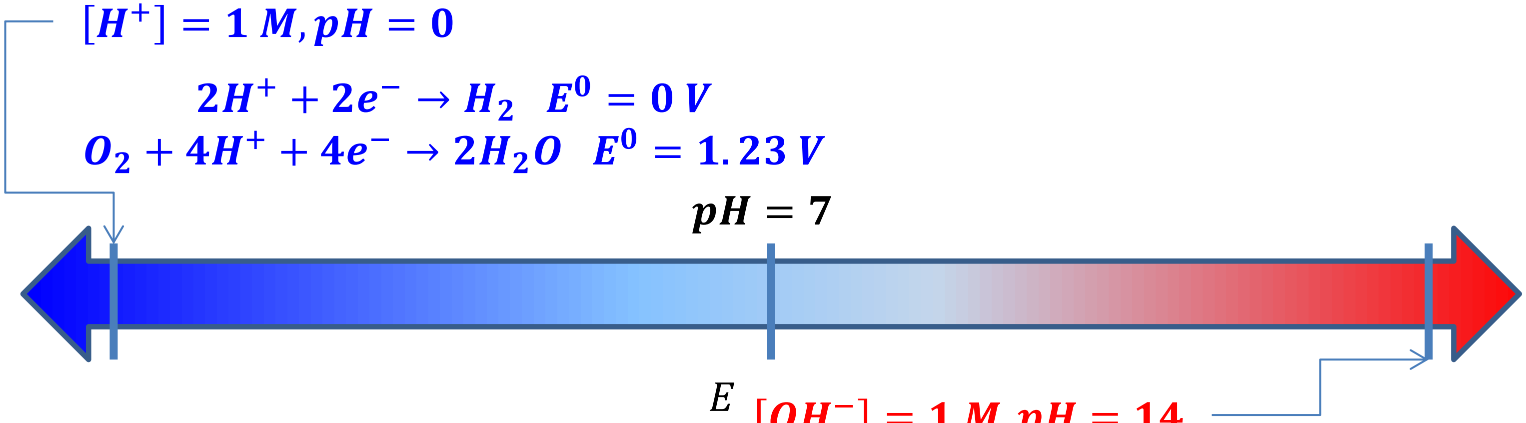
Acid solution

$2H^+ + 2e^- \rightarrow H_2$	0 (by definition)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+1.23$

Base/Neutral solution

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$+0.40$

Potential Window of Water



$[H^+] = 1\ M, pH = 0$

$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0\ V$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23\ V$

$pH = 7$

E

$[OH^-] = 1\ M, pH = 14$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^0 = -0.83\ V$

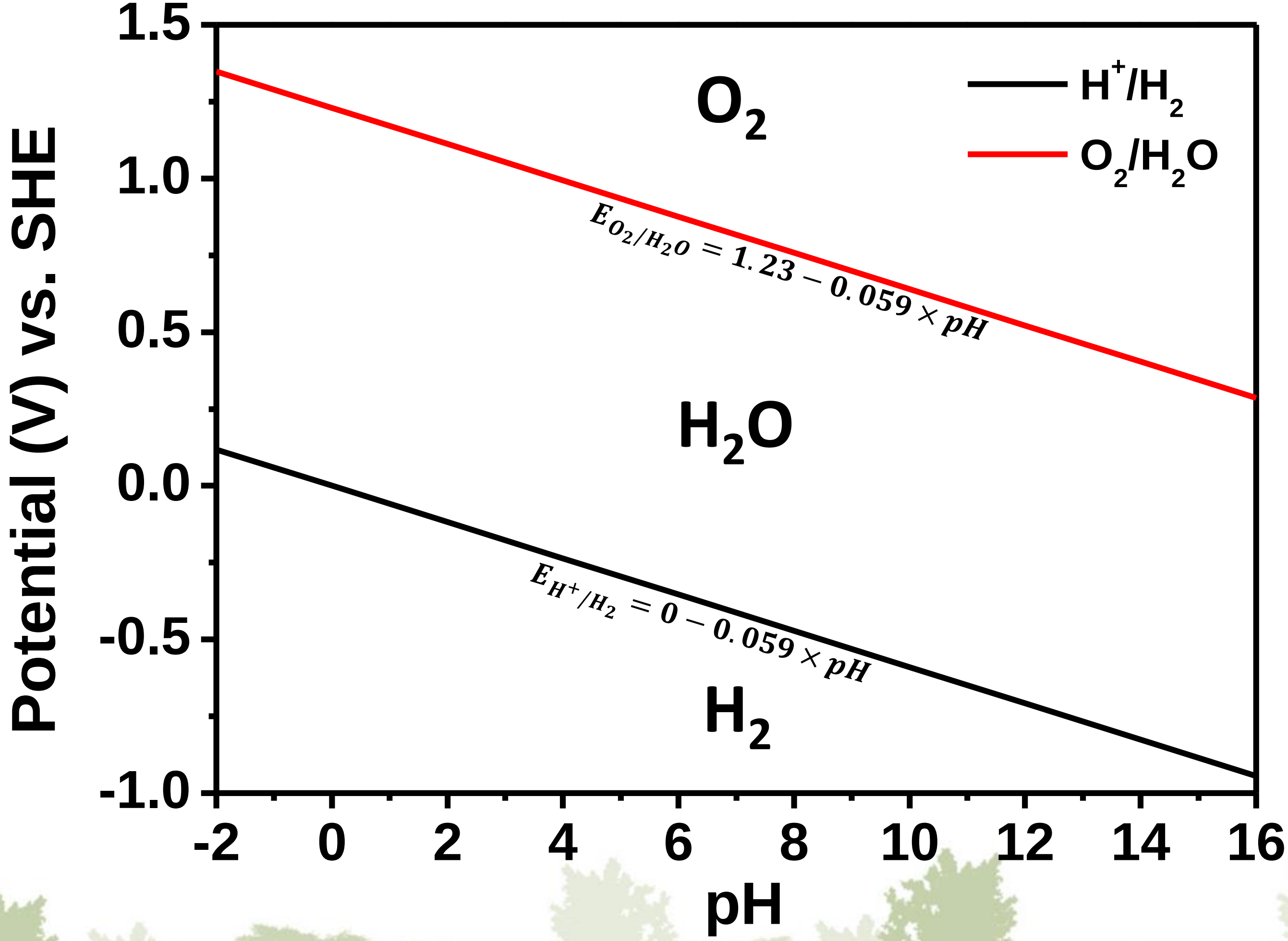
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^0 = 0.40\ V$

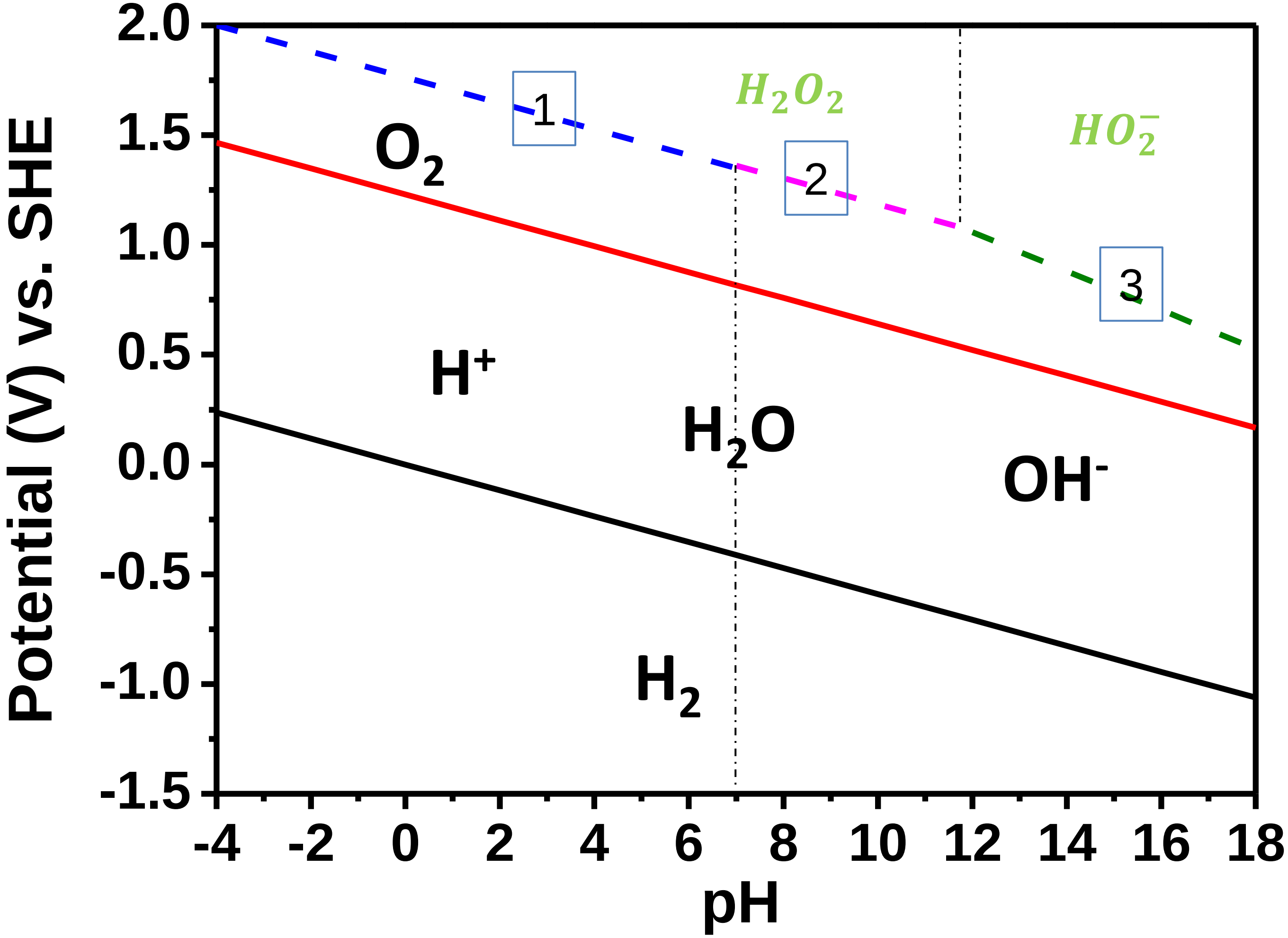
For the H^+/H_2 and O_2/H_2O at 25°C,

$$E_{H^+/H_2} = 0 + \frac{RT}{2F}\ln[H^+]^2 = 0 + 0.059\log[H^+] = 0 - 0.059 \times pH$$

$$E_{O_2/H_2O} = 1.23 + \frac{RT}{4F}\ln[H^+]^4 = 1.23 + 0.059\log[H^+] = 1.23 - 0.059 \times pH$$

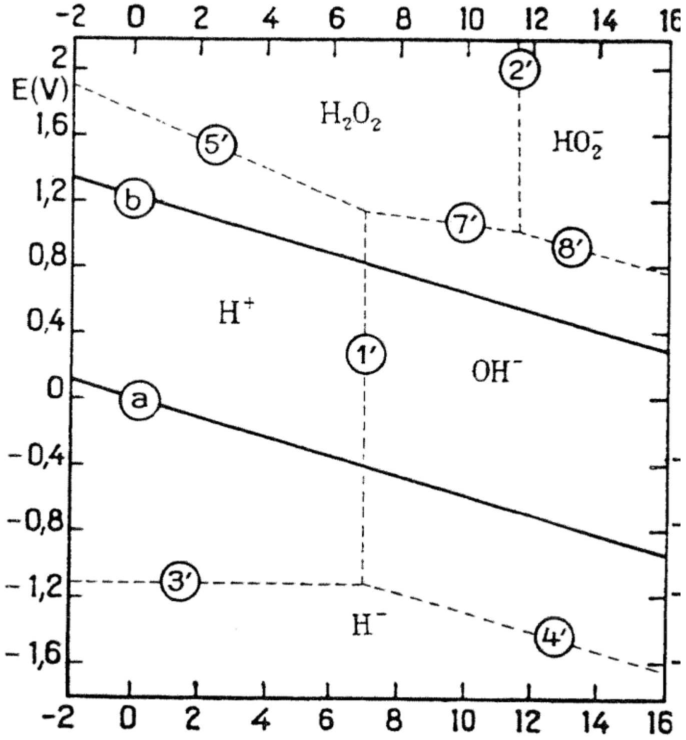
Potential/pH Diagram of Water (Pourbaix Diagram)





1. $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.763\,V \Rightarrow E = 1.763 - 0.059pH + 0.0295\log[H_2O_2]$
2. $H_2O_2 + H^+ + 2e^- \rightarrow OH^- + H_2O \quad E^0 = 1.362\,V \Rightarrow E = 1.362 - 0.0295pH + 0.0295\log\frac{[H_2O_2]}{[OH^-]}$
3. $HO_2^- + 2H^+ + 2e^- \rightarrow OH^- + H_2O = \quad E^0 = 1.706 \Rightarrow E = 1.706 - 0.059pH + 0.0295\log\frac{[HO_2^-]}{[OH^-]}$

*Assume that $[H_2O_2]$ and $[HO_2^-]$ are equal to 1 M.



1. $\mathbf{H_2O} = OH^- + H^+$ $\log(OH^-) = -14.00 + pH$

2. $H_2O_2 = HO_2^- + H^+$ $\log\frac{(HO_2^-)}{(H_2O_2)} = -11.63 + pH$

3. $H^- = H^+ + 2e^-$ $E_0 = -1.125 + 0.0295 \log\frac{(H^+)}{(H^-)}$

4. $H^- + \mathbf{H_2O} = OH^- + 2H^+ + 2e^-$ $E_0 = -0.711 - 0.0591\,pH + 0.0295 \log\frac{(OH^-)}{(H^-)}$

5. $2\mathbf{H_2O} = H_2O_2 + 2H^+ + 2e^-$ $E_0 = 1.776 - 0.0591\,pH + 0.0295 \log(H_2O_2)$

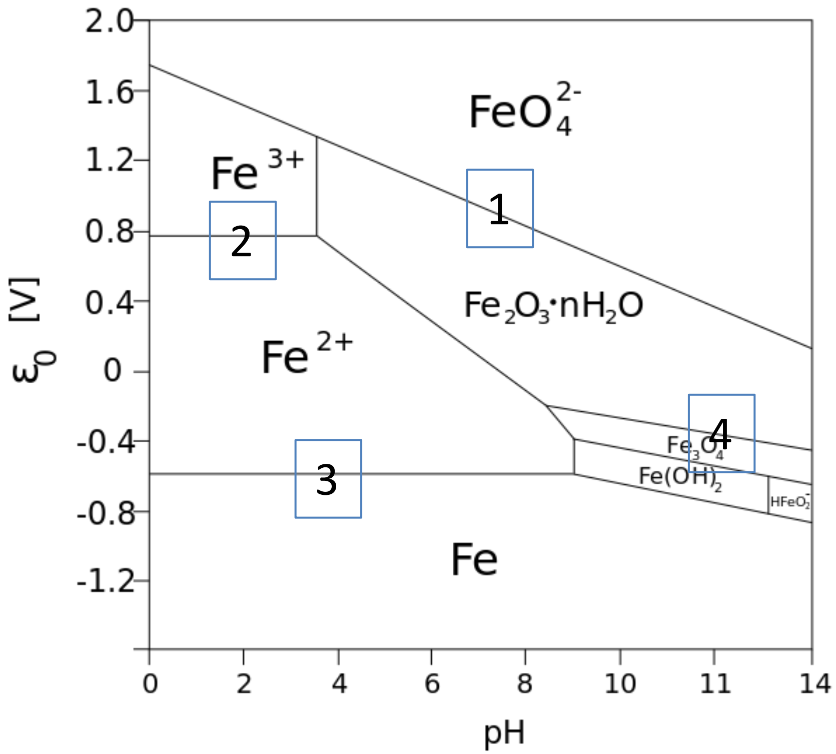
6. $2\mathbf{H_2O} = HO_2^- + 3H^+ + 2e^-$ $E_0 = 2.119 - 0.0886\,pH + 0.0295 \log(HO_2^-)$

7. $OH^- + \mathbf{H_2O} = H_2O_2 + H^+ + 2e^-$ $E_0 = 1.362 - 0.0295\,pH + 0.0295 \log\frac{(H_2O_2)}{(OH^-)}$

8. $OH^- + \mathbf{H_2O} = HO_2^- + 2H^+ + 2e^-$ $E_0 = 1.706 - 0.0591\,pH + 0.0295 \log\frac{(HO_2^-)}{(OH^-)}$

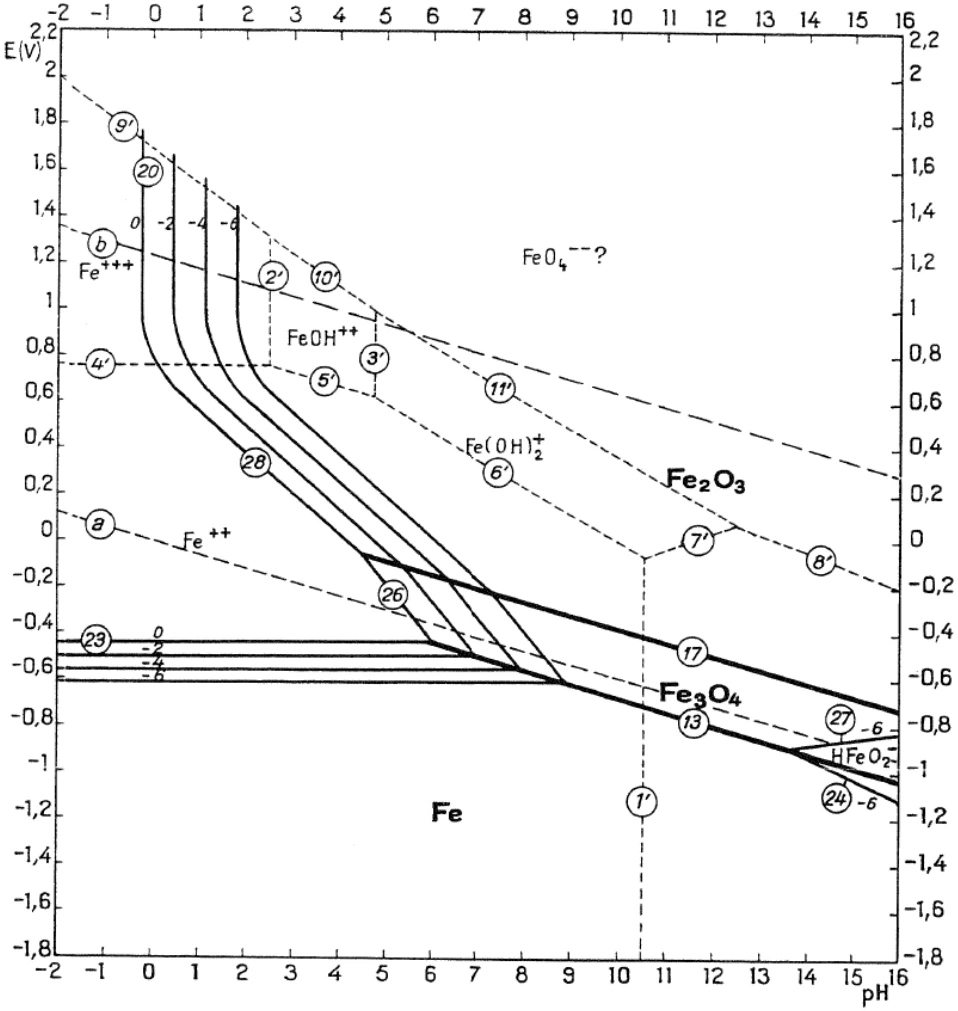
Atlas of Electrochemical Equilibria in Aqueous Solutions, Marcel Pourbaix, 1974

Potential/pH Diagram of Iron



1. $FeO_4^{2-} + 5H^+ + 4e^- \rightarrow Fe^{3+} + 4H_2O \quad E^0 = 1.700\ V$
2. $Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^0 = 0.771\ V$
3. $Fe^{2+} + 2e^- \quad E^0 = -0.447\ V$
4. $3Fe_2O_3 + 2H^+ + 2e^- \rightarrow 2Fe_3O_4 \quad E^0 = 0.221\ V$*

Potential/pH Diagram of Iron



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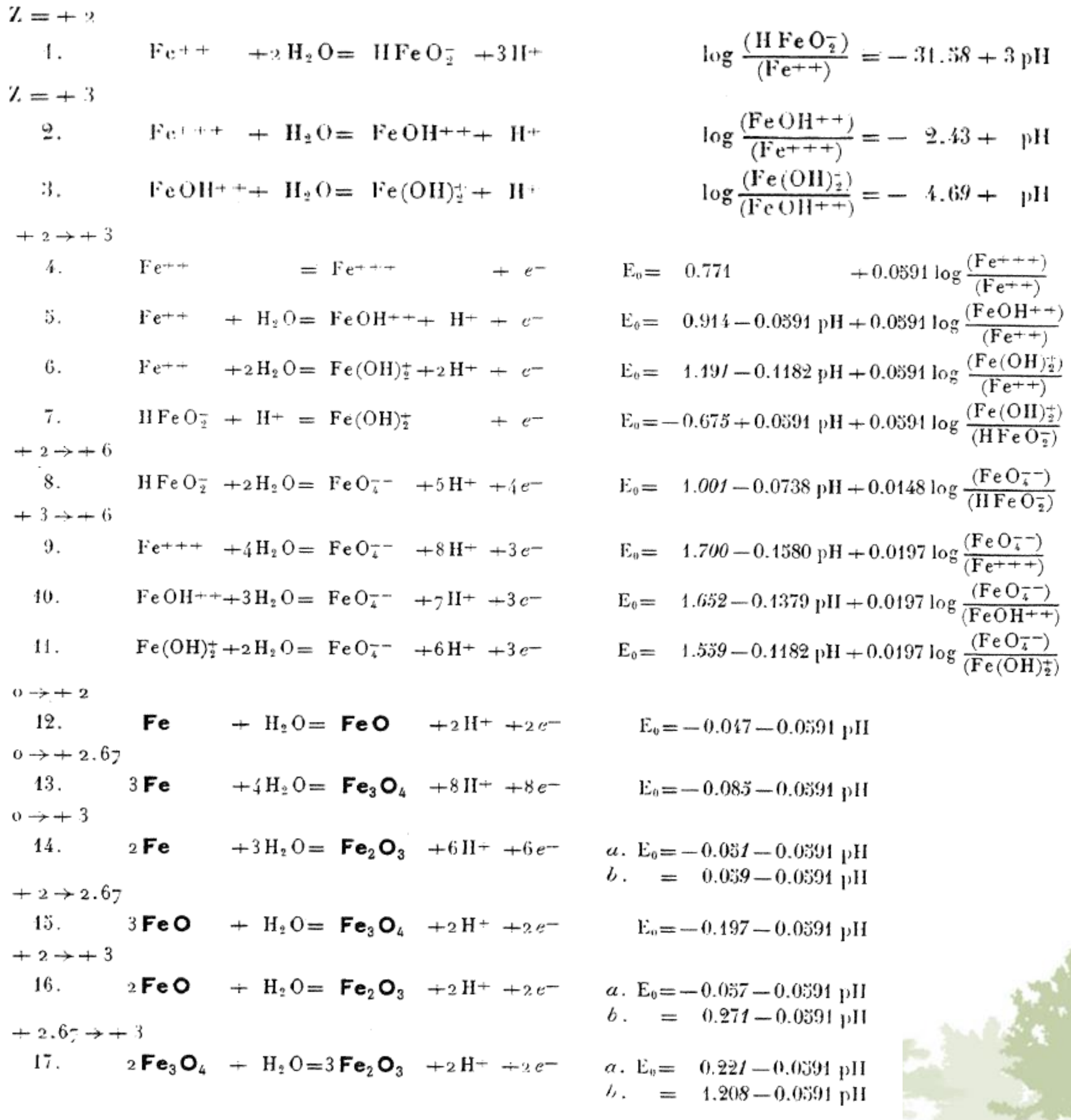


$Z = +2$

1. $Fe^{++} + 2H_2O = HFeO_2^- + 3H^+ \qquad \log \frac{(HFeO_2^-)}{(Fe^{++})} = -31.58 + 3\,pH$

$Z = +3$

2. $Fe^{+++} + H_2O = FeOH^{++} + H^+ \qquad \log \frac{(FeOH^{++})}{(Fe^{+++})} = -2.43 + pH$

3. $FeOH^{++} + H_2O = Fe(OH)_2^+ + H^+ \qquad \log \frac{(Fe(OH)_2^+)}{(FeOH^{++})} = -4.69 + pH$

$+2 \rightarrow +3$

4. $Fe^{++} = Fe^{+++} + e^- \qquad E_0 = 0.771 + 0.0591 \log \frac{(Fe^{+++})}{(Fe^{++})}$

5. $Fe^{++} + H_2O = FeOH^{++} + H^+ + e^- \qquad E_0 = 0.914 - 0.0591\,pH + 0.0591 \log \frac{(FeOH^{++})}{(Fe^{++})}$

6. $Fe^{++} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^- \qquad E_0 = 1.197 - 0.1182\,pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(Fe^{++})}$

7. $HFeO_2^- + H^+ = Fe(OH)_2^+ + e^- \qquad E_0 = -0.675 + 0.0591\,pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(HFeO_2^-)}$

$+2 \rightarrow +6$

8. $HFeO_2^- + 2H_2O = FeO_4^{--} + 5H^+ + 4e^- \qquad E_0 = 1.001 - 0.0738\,pH + 0.0148 \log \frac{(FeO_4^{--})}{(HFeO_2^-)}$

$+3 \rightarrow +6$

9. $Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3e^- \qquad E_0 = 1.700 - 0.1580\,pH + 0.0197 \log \frac{(FeO_4^{--})}{(Fe^{+++})}$

10. $FeOH^{++} + 3H_2O = FeO_4^{--} + 7H^+ + 3e^- \qquad E_0 = 1.652 - 0.1379\,pH + 0.0197 \log \frac{(FeO_4^{--})}{(FeOH^{++})}$

11. $Fe(OH)_2^+ + 2H_2O = FeO_4^{--} + 6H^+ + 3e^- \qquad E_0 = 1.559 - 0.1182\,pH + 0.0197 \log \frac{(FeO_4^{--})}{(Fe(OH)_2^+)}$

$0 \rightarrow +2$

12. $\mathbf{Fe} + H_2O = \mathbf{FeO} + 2H^+ + 2e^- \qquad E_0 = -0.047 - 0.0591\,pH$

$0 \rightarrow +2.67$

13. $3\mathbf{Fe} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 8e^- \qquad E_0 = -0.085 - 0.0591\,pH$

$0 \rightarrow +3$

14. $2\mathbf{Fe} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 6e^- \qquad$ a. $E_0 = -0.051 - 0.0591\,pH$
b. $= 0.059 - 0.0591\,pH$

$+2 \rightarrow 2.67$

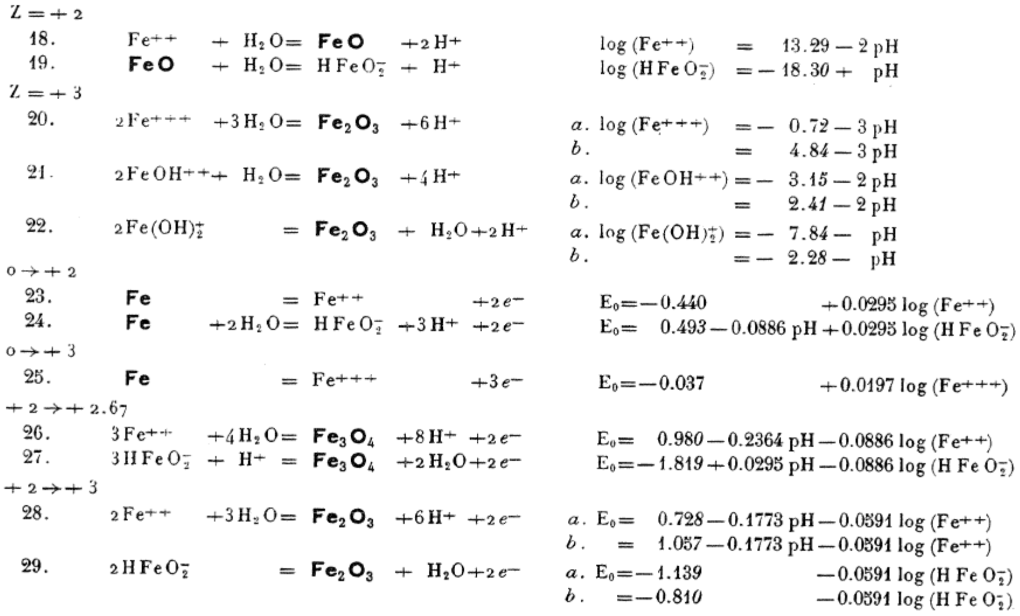
15. $3\mathbf{FeO} + H_2O = \mathbf{Fe_3O_4} + 2H^+ + 2e^- \qquad E_0 = -0.197 - 0.0591\,pH$

$+2 \rightarrow +3$

16. $2\mathbf{FeO} + H_2O = \mathbf{Fe_2O_3} + 2H^+ + 2e^- \qquad$ a. $E_0 = -0.057 - 0.0591\,pH$
b. $= 0.271 - 0.0591\,pH$

$+2.67 \rightarrow +3$

17. $2\mathbf{Fe_3O_4} + H_2O = 3\mathbf{Fe_2O_3} + 2H^+ + 2e^- \qquad$ a. $E_0 = 0.221 - 0.0591\,pH$
b. $= 1.208 - 0.0591\,pH$



$Z = +2$

18. $Fe^{++} + H_2O = \mathbf{FeO} + 2H^+$ $\qquad \log(Fe^{++}) = 13.29 - 2\,pH$

19. $\mathbf{FeO} + H_2O = HFeO_2^- + H^+$ $\qquad \log(HFeO_2^-) = -18.30 + pH$

$Z = +3$

20. $2Fe^{+++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+$ $\qquad a.\ \log(Fe^{+++}) = -0.72 - 3\,pH$
$\qquad b.\ = 4.84 - 3\,pH$

21. $2FeOH^{++} + H_2O = \mathbf{Fe_2O_3} + 4H^+$ $\qquad a.\ \log(FeOH^{++}) = -3.15 - 2\,pH$
$\qquad b.\ = 2.41 - 2\,pH$

22. $2Fe(OH)_2^+ = \mathbf{Fe_2O_3} + H_2O + 2H^+$ $\qquad a.\ \log(Fe(OH)_2^+) = -7.84 - pH$
$\qquad b.\ = -2.28 - pH$

$0 \rightarrow +2$

23. $\mathbf{Fe} = Fe^{++} + 2e^-$ $\qquad E_0 = -0.440 + 0.0295 \log(Fe^{++})$

24. $\mathbf{Fe} + 2H_2O = HFeO_2^- + 3H^+ + 2e^-$ $\qquad E_0 = 0.493 - 0.0886\,pH + 0.0295 \log(HFeO_2^-)$

$0 \rightarrow +3$

25. $\mathbf{Fe} = Fe^{+++} + 3e^-$ $\qquad E_0 = -0.037 + 0.0197 \log(Fe^{+++})$

$+2 \rightarrow +2.67$

26. $3Fe^{++} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 2e^-$ $\qquad E_0 = 0.980 - 0.2364\,pH - 0.0886 \log(Fe^{++})$

27. $3HFeO_2^- + H^+ = \mathbf{Fe_3O_4} + 2H_2O + 2e^-$ $\qquad E_0 = -1.819 + 0.0295\,pH - 0.0886 \log(HFeO_2^-)$

$+2 \rightarrow +3$

28. $2Fe^{++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 2e^-$ $\qquad a.\ E_0 = 0.728 - 0.1773\,pH - 0.0591 \log(Fe^{++})$
$\qquad b.\ = 1.057 - 0.1773\,pH - 0.0591 \log(Fe^{++})$

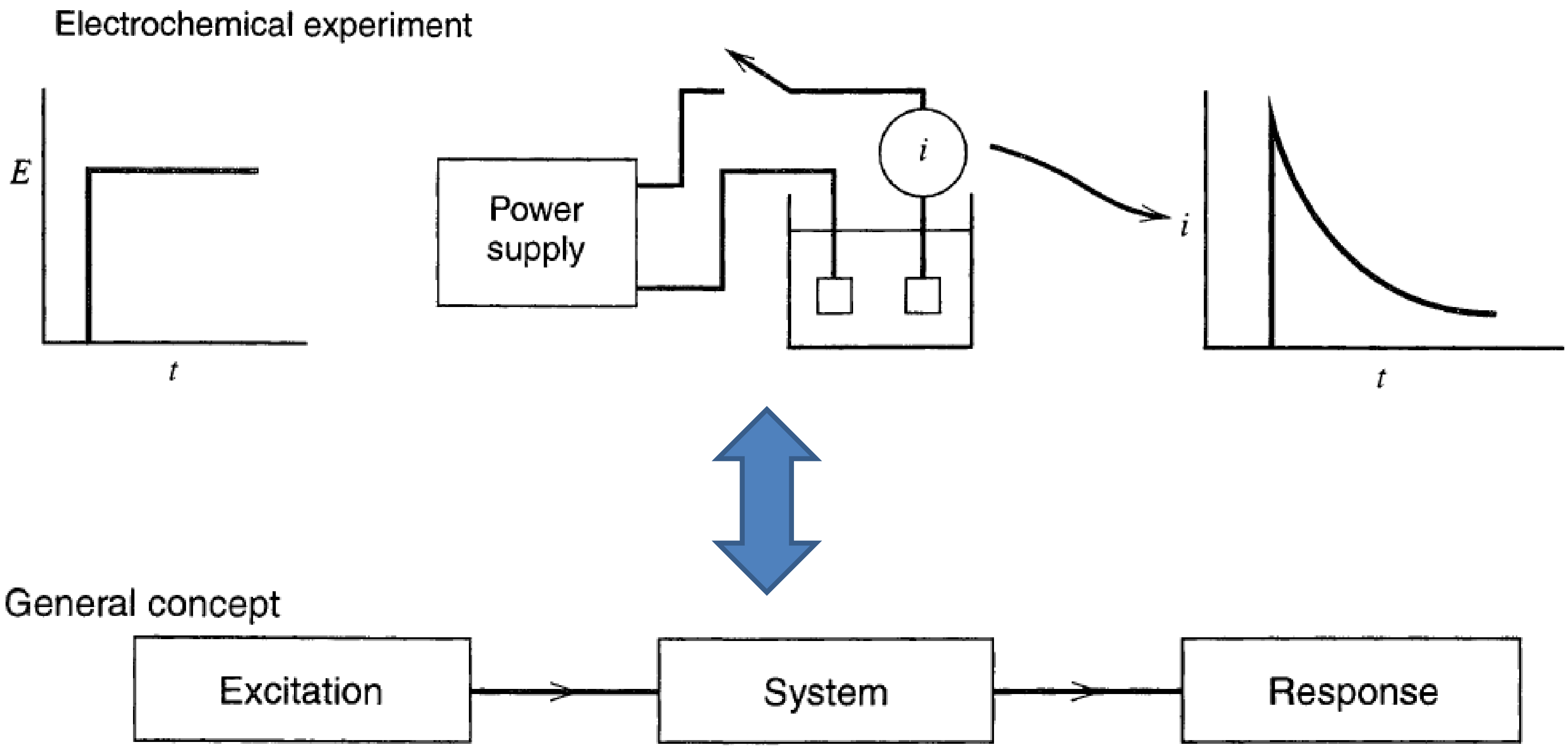
29. $2HFeO_2^- = \mathbf{Fe_2O_3} + H_2O + 2e^-$ $\qquad a.\ E_0 = -1.139 - 0.0591 \log(HFeO_2^-)$
$\qquad b.\ = -0.810 - 0.0591 \log(HFeO_2^-)$

Setup of Measuring Electrochemistry

Electrochemical Measurement

- **Generally, we want the following data,**
    - Potential, E
    - Current, i
    - Time, t
    - The relations between E vs. i vs. t

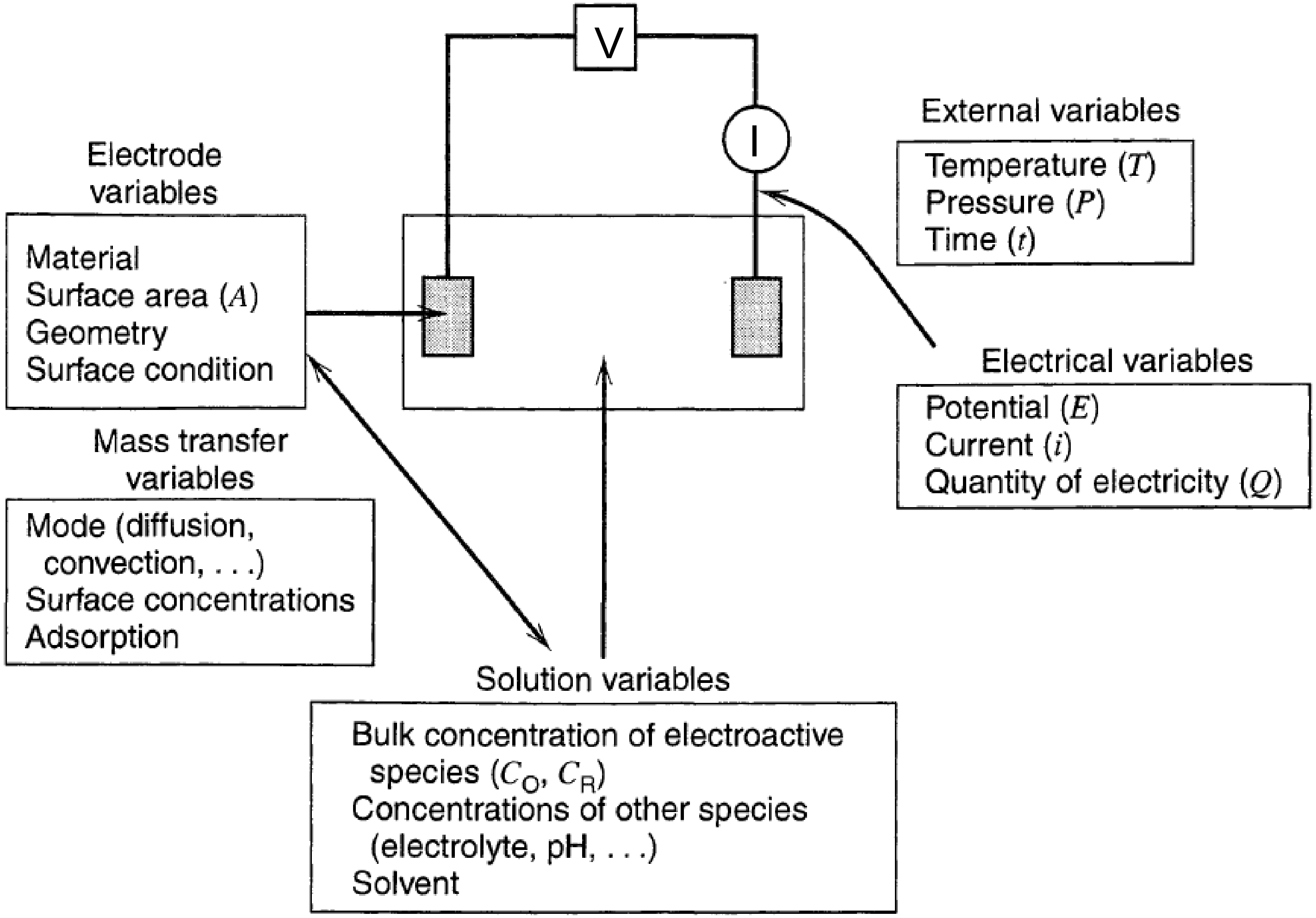
General Concepts of EC Measurement



Electrochemical experiment

General concept

Factors of EC Measurement



Electrode variables

- Material
- Surface area (*A*)
- Geometry
- Surface condition

Mass transfer variables

- Mode (diffusion, convection, . . .)
- Surface concentrations
- Adsorption

External variables

- Temperature (*T*)
- Pressure (*P*)
- Time (*t*)

Electrical variables

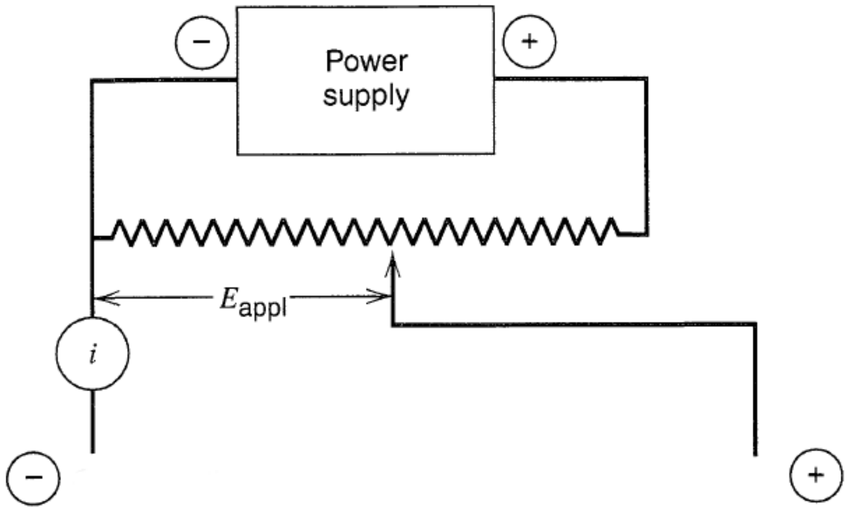
- Potential (*E*)
- Current (*i*)
- Quantity of electricity (*Q*)

Solution variables

- Bulk concentration of electroactive species (C_O, C_R)
- Concentrations of other species (electrolyte, pH, . . .)
- Solvent

Potential? Current?

Example: 0.1 M HCl electrolysis



$$2H^+ + 2e^- \rightarrow H_2 \qquad 2Cl^- \rightarrow Cl_2 + 2e^-$$

$$E = -0.059\ \text{V} \qquad E = -1.419\ \text{V}$$

$$2H^+ + 2Cl^- \rightarrow H_2 + Cl_2$$

$$E_{cell} = -1.478\ \text{V}$$

- **If you are doing the HCl electrolysis, then:**
  - Can you know the current (*i*)?
    - Yes.
  - If E_{appl} is varied by time (*t*), can you know the curve of E_{appl} vs. *i*?
    - Yes.
  - If E_{appl} = 1.5 V, can you know the curve *of i vs. t*?
    - Yes.
  - Can you know the individual potentials of the anode and cathode?
    - ?
  - Can you know the individual "ionic flows" of the anode and cathode?
    - ?

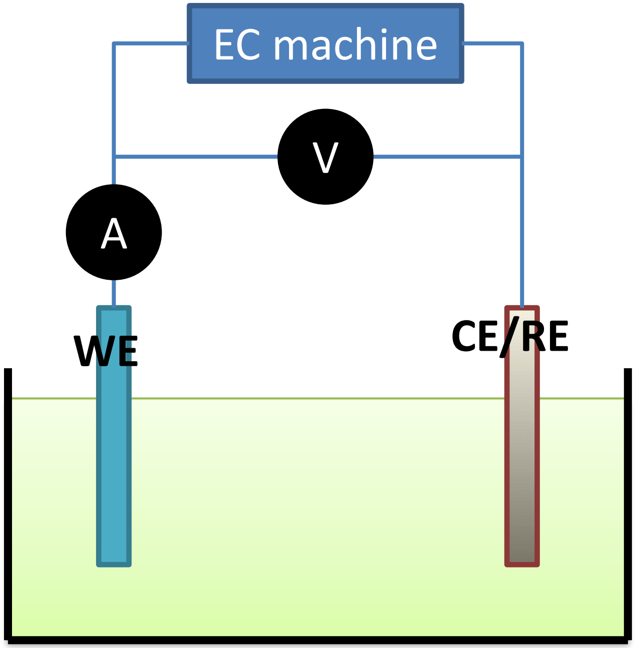
How to know …

- **Generally, we only concern about the "electrochemical reactions" of the "individual electrode".**
  - Potential
  - Current
  - Time
- **Therefore, we need the "known reference point"!**

Electrochemical Cell

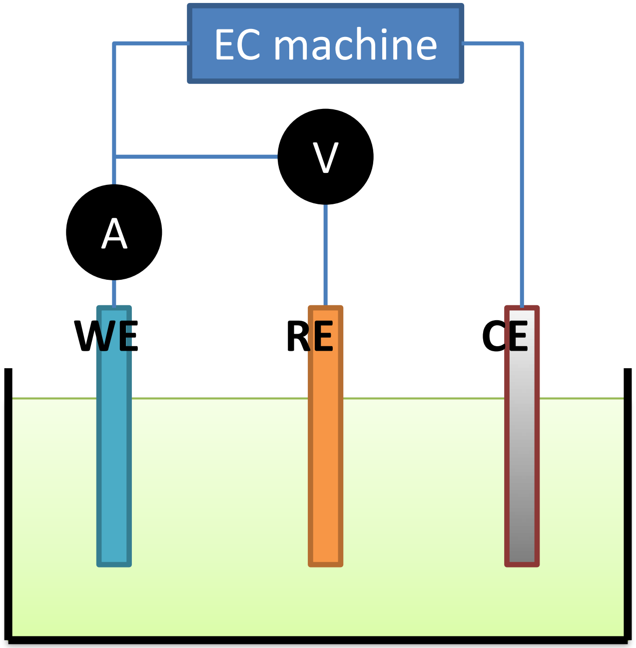
Working electrode (WE): An electrode of interest
Counter electrode (CE): Any convenient electrode (e.g. Pt)
Reference electrode (RE): A reference point

Two-electrode cell



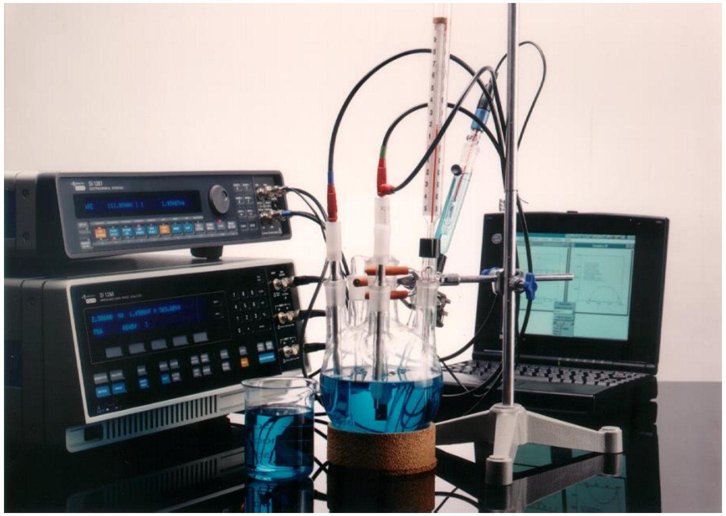
Potential: $E_{WE} - E_{CE/RE}$
Current: WE ↔ CE

Three-electrode cell



Potential: $E_{WE} - E_{RE}$
Current: WE ↔ CE

Modern Electrochemical Machine

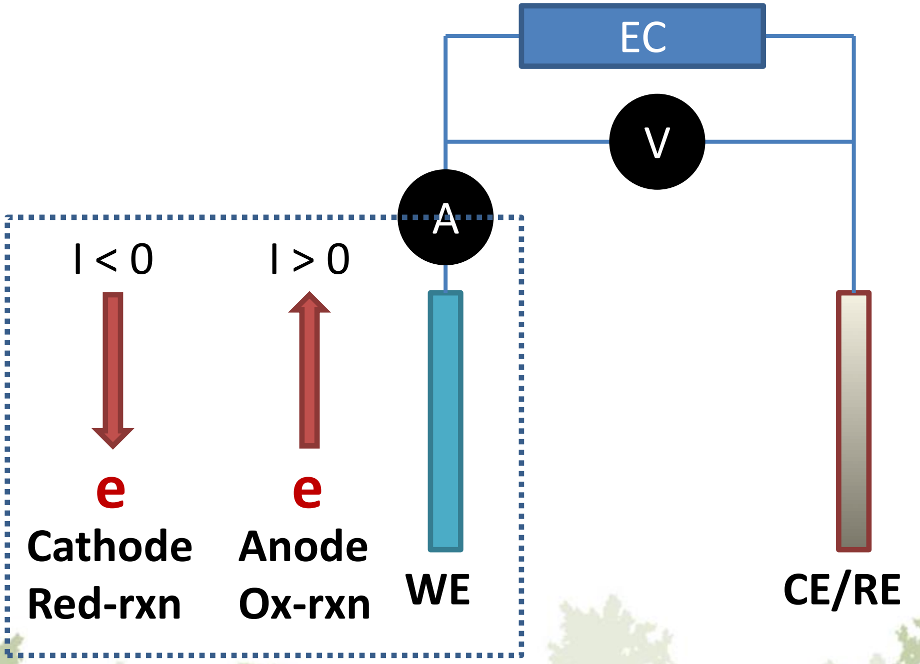


Solartron

- **For modern EC machines,**
  - You always read the potential and current of WE from the machine.
  - You cannot read the potential and current of CE or RE from the machine, for most cases.

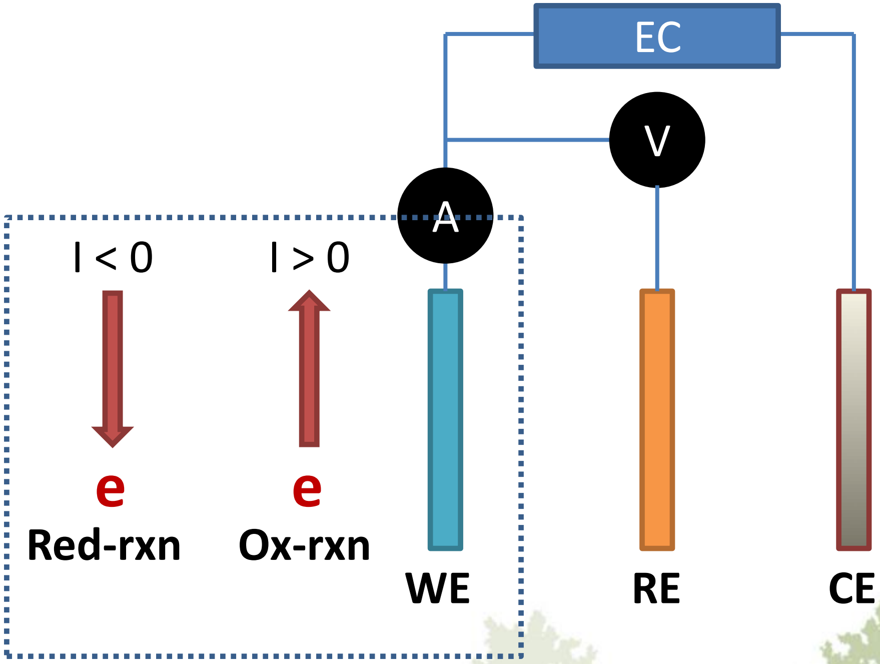
Definitions of Current and Potential, Two-electrode cell

- **Potential, $E_{WE} – E_{RE/CE}$**
- **Current, WE ↔ CE/RE**
  - Current > 0, WE: anode, oxidation; CE/RE: cathode, reduction.
  - Current < 0, WE: cathode, reduction; CE/RE: anode, oxidation.



Definitions of Current and Potential, Three-electrode cell

- **Potential, $E_{WE} - E_{RE}$**
- **Current, WE ↔ CE**
    - Current > 0, WE: anode, oxidation
    - Current < 0, WE: cathode, reduction

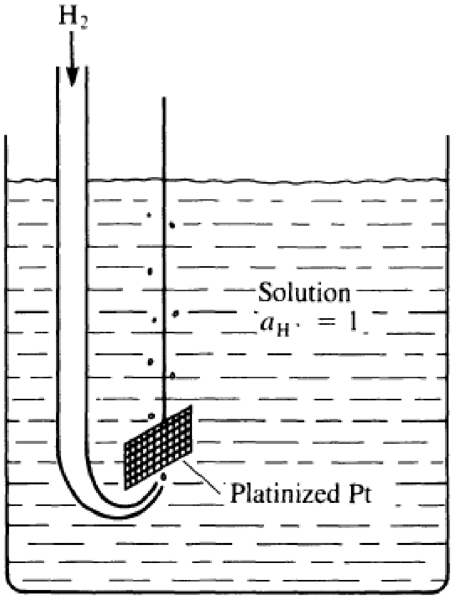


Reference Electrode

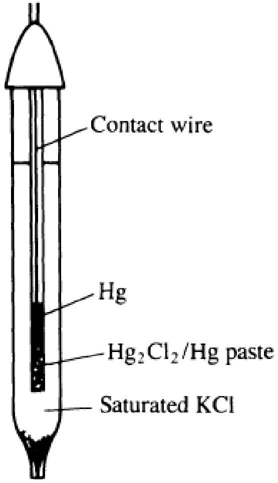
- A reference electrode is an electrode of a well-known electrode potential.
- A good reference electrode needs to have a potential that is stable with time and with temperature and which is not altered by small perturbations to the system—that is, by the passage of a small current.

Types of Reference Electrodes

Reversible hydrogen electrode (RHE)



Saturated calomel electrode (SCE)



$$Hg_{(l)} + Cl^- \Leftrightarrow Hg_2Cl_{2(S)}$$

$$E(25^O C, Sat.\,KCl) = 0.244\text{ V}$$

Ag/AgCl electrode

$$Ag_{(s)} + Cl^- \Leftrightarrow AgCl_{(S)}$$

$$E(25^O C, Sat.\,KCl) = 0.197\text{ V}$$

Hg/HgO Electrode (for alkaline solution)

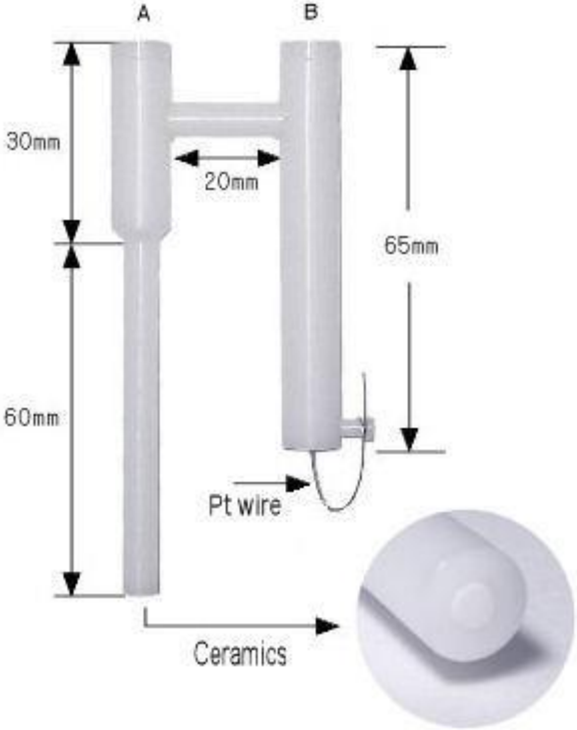


Fig. 1

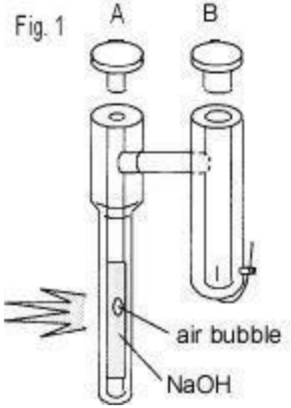
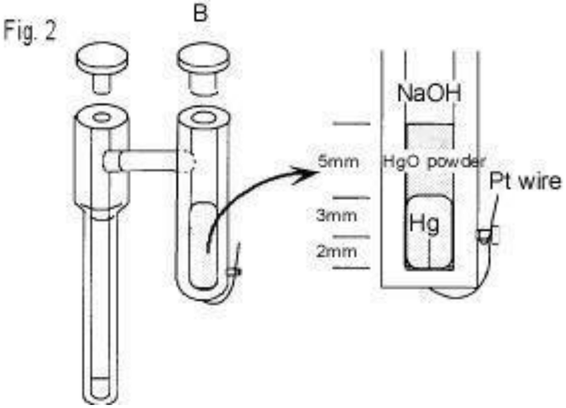


Fig. 2



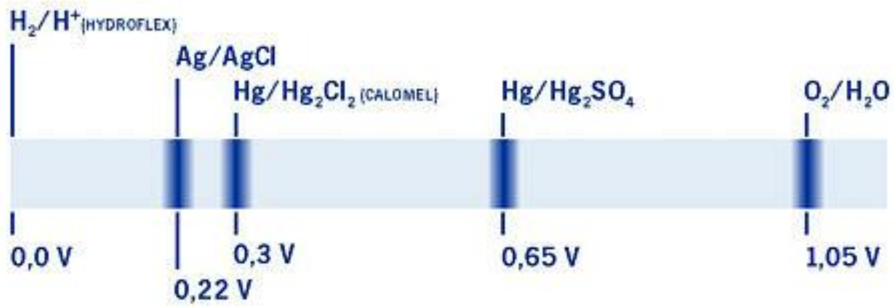
$$HgO_{(s)} + H_2O + 2e^- \Leftrightarrow Hg_{(l)} + 2OH^-$$

$$E(25^O C, 0.1\,\mathrm{M}\ NaOH) = 0.165\,\mathrm{V}$$

Ref.: http://www.als-japan.com/RE-6H_Reference_electrode.html

Potentials of Reference Electrodes

Acid solution



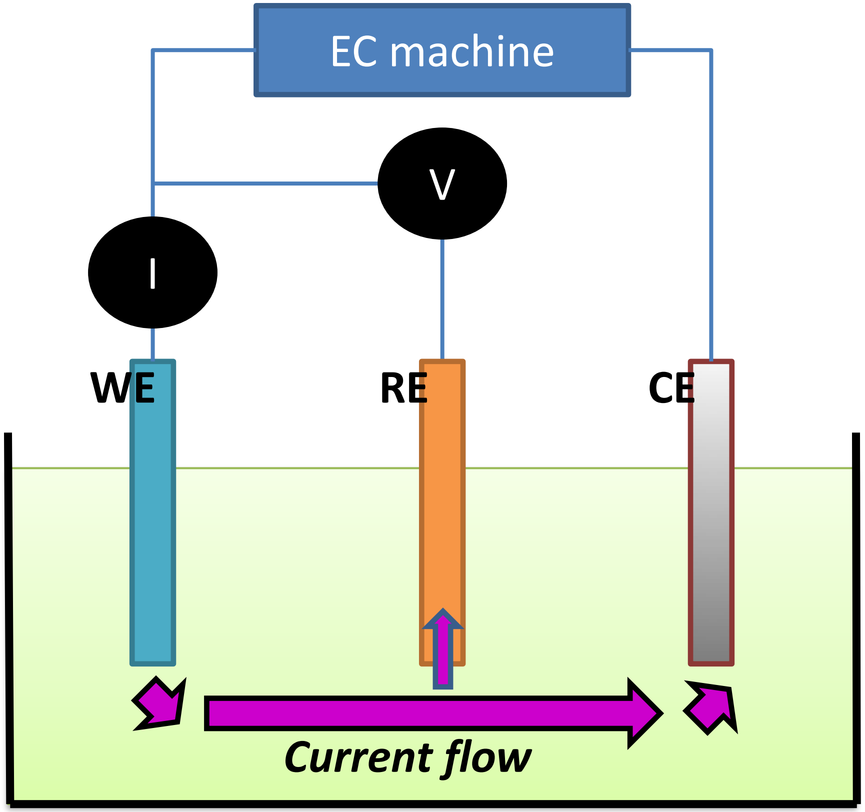
Alkaline solution

Ref.: http://www.gaskatel.de/english/hydroflex/potential.html

Counter Electrode

- **Counter electrode can be any convenient one, because its electrochemical properties do not affect the working electrode.**
- **It is usually chosen to be an electrode that does not produce substances by electrolysis that will reach the working electrode surface and cause interfering reactions there.**
- **Because the current flows trough the counter electrode, the optional material is highly conductive and very stable.**
- **General counter electrode:**
    - Platinum
    - Graphite
    - Other stable materials in a wide range of potential
- **The area of counter electrode is as large as possible. (Two-fold area of the working electrode)**

Current Flow and Potential-Loss

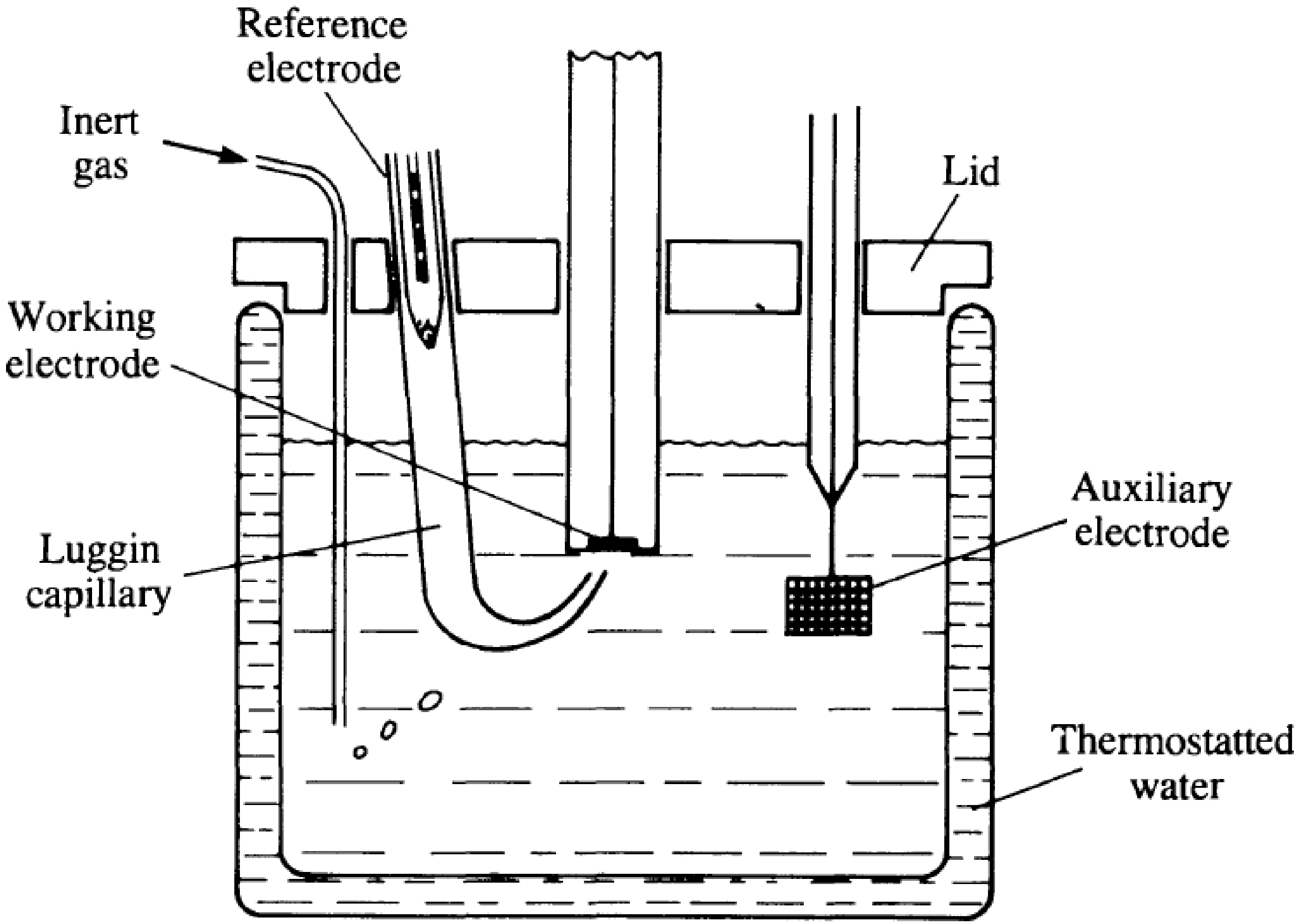


Potential: E_{WE} — E_{RE}

Current: WE ↔ CE

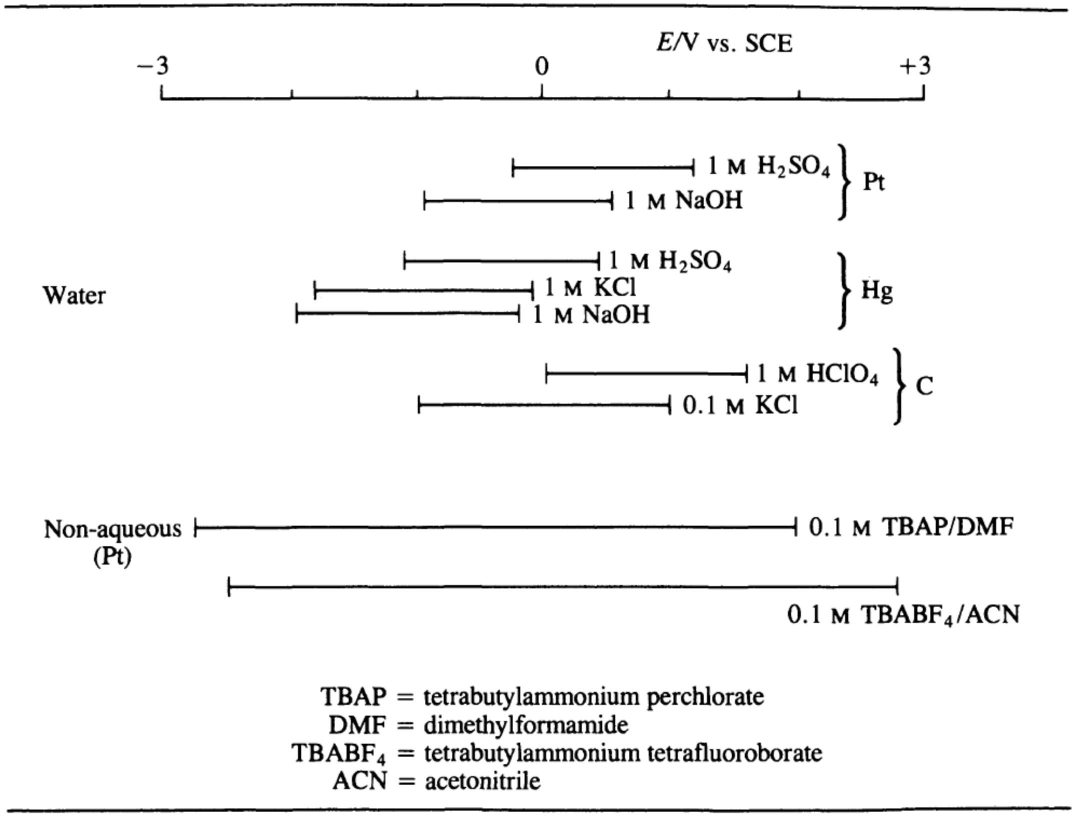
- **The potential-loss is caused by the solution resistance (R_s).**
  - $E_{iR\text{-free}} = E_{measured} + iR_s$
- **Small current flows into the reference electrode, resulting in the current-loss and potential-loss.**
  - To solve this problem, the resistance (R_u) between the RE and WE should as larger as possible.
  - $R_u = x/\kappa A$
    - x: Distance between WE and RE
    - A: Tip area of RE
    - κ: Solution conductivity

Three-electrode Cell Setup



Supporting electrolytes

- **In order to minimize the phenomenon of migration of the electroactive ions caused by the electric field and to confine the interfacial potential difference to the distance of closest approach of solvated ions to the electrode, the addition of a solution containing a high concentration of inert electrolyte, called supporting electrolyte, is necessary.**



TBAP = tetrabutylammonium perchlorate
DMF = dimethylformamide
$TBABF_4$ = tetrabutylammonium tetrafluoroborate
ACN = acetonitrile

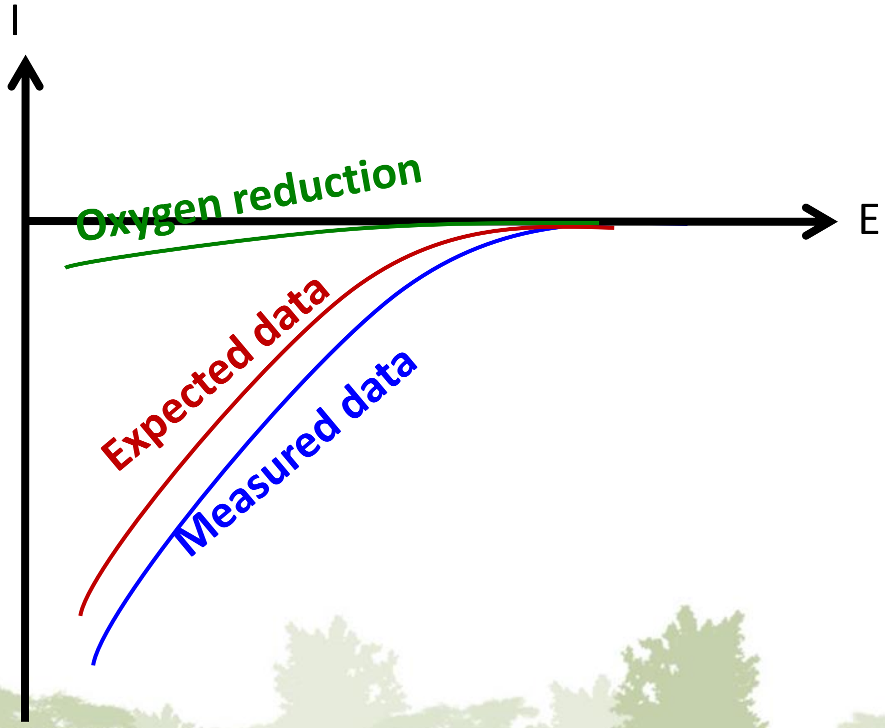
All care must be taken to ensure that the supporting electrolyte is truly inert in the potential range of the experiment, not reacting with the electrode or with the products of the electrode reaction (except when desired).

Oxygen Involved in EC

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23\,\mathrm{V}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^0 = 0.401\,\mathrm{V}$$

- **Oxygen (0.2 atm) is slightly heavier than air, and is dissolved appreciably (~10^{-4} M) in solutions open to the atmosphere, which results in the by-reaction, the oxygen reduction reaction, especially doing the experiments for the reduction reaction.**



How to Remove Oxygen

- **The solution is purged by inert gases, N_2 and Ar.**
  - Ar has the advantage of being heavier than air and not escaping easily from the cell, whereas N_2 is lighter than air.
  - However, N_2 is much less expensive than Ar.
- **Gas purity is very important, and ultra-pure gases should always be preferred.**
- **If necessary the gas can be further purified to remove any remaining traces of oxygen.**

Some Tips for EC Measurement

- **Clean, clean and clean!**
  - Clean everything before starting experiments!
  - For most of EC measurements, the current is at mA-level or even at μA-level. In other words, any impurity can strongly affect the result.
- **Take good care of the reference electrode just like to cherish your …**
  - Change the solution in the regular period (1 month); make the calibration in the regular period (2 month).
  - The tip of reference electrode is made by ceramic membrane or polymer membrane. Don’t tough or even strike it!
  - Based on previous experiences, bad data comes from bad maintenance of reference electrode, for most cases.

Some Tips for EC Measurement

- **Design EC measurement carefully!**
  - Check the papers before starting measurements.
  - What potential range should you set?
  - What current range should you set?
  - Which scan rate should you set?
  - Which solutions or supporting electrolytes should you use?
  - Are you sure that every setup is correct and reasonable?
- **Look before you leap! (三思而後行) – Think before you press “RUN” button!**
  - Confirm, check and think again!
  - Do the data meet to your expectation?
  - Are there some unexpected signals in the data?
- **Store the data to other place immediately.**
  - You must know, “Accidents will Happen later”!

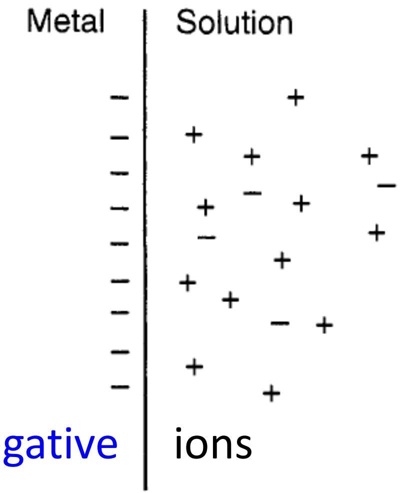
Non-faraday’s Behavior of Electrochemistry

Non-Faradaic Process

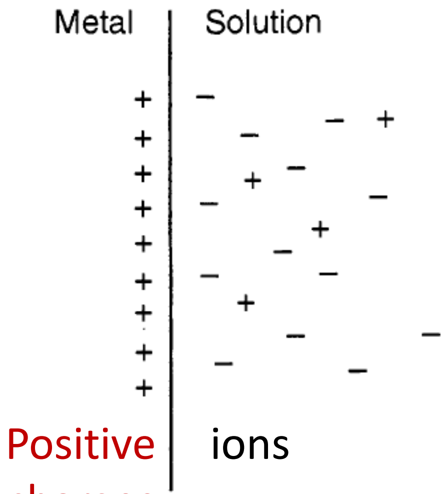
- A given electrode-solution interface will show a range of potentials where no charge-transfer reactions occur because such reactions are thermodynamically or kinetically unfavorable.
- However, processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface can change with changing potential or solution composition. These processes are called non-faradaic processes.
- Although charge does not cross the interface external currents can flow (at least transiently) when the potential, electrode area, or solution composition changes.
- Non-Faradaic process comes from Interfacial region of electrolyte double-layer region (major) and space charge region (minor).
- In most cases, Fraradaic current >> non-Faradaic current.

Double Layer (DL) vs. Capacitor

Metal-solution interface

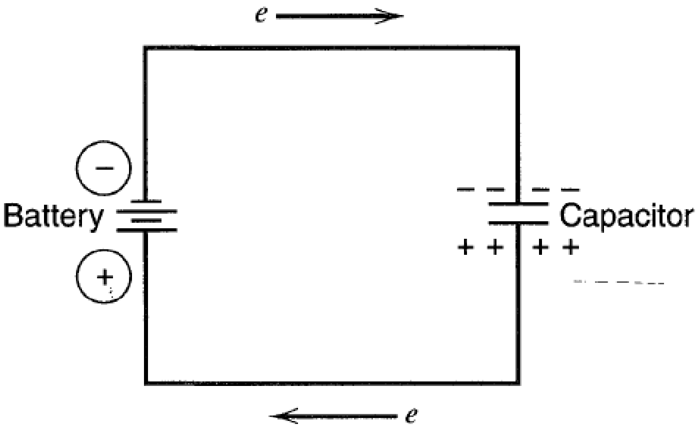


Negative charges ions



Positive charges ions

Capacitor



Equations in Capacitor

Capacitance is also a measure of the amount of electrical energy stored (or separated) for a given electric potential

Don't be confused Faraday constant (coulomb/mol) with farad (F, coulomb/V)!

$$C\ (\text{capacitance}) = \frac{q\ (\text{coulomb})}{E\ (\text{potential})}$$

$$\text{Unit}: 1\text{F} = 1\frac{\text{C}}{\text{V}},$$

$$\text{F}: \text{farad},\ \text{C}: \text{coulomb},\ \text{V}: \text{potential}$$

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

$$\varepsilon_r: \text{dielectric constant}, \varepsilon_0: 8.854\times10^{-12}\ \text{F/m},$$

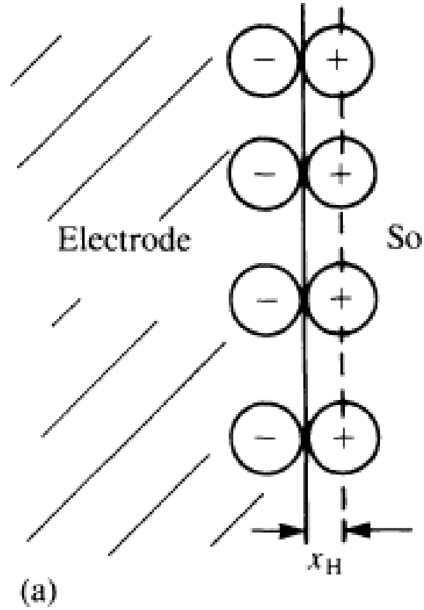
$$\text{d}: \text{distance between two plates}, \text{A}: \text{Area}$$

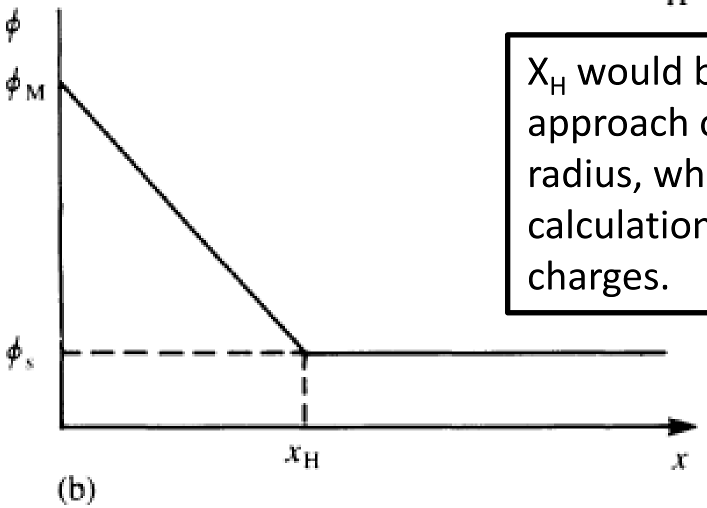
Energy stored in a capacitance is found by integrating this equation. Starting with an uncharged capacitance (q = 0) and moving charge from one plate to the other until the plates have charge +Q and −Q requires the work W

$$dW = \frac{q}{C}dq$$

$$W_{\text{charge}} = \int_0^Q \frac{q}{C}dq = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2$$

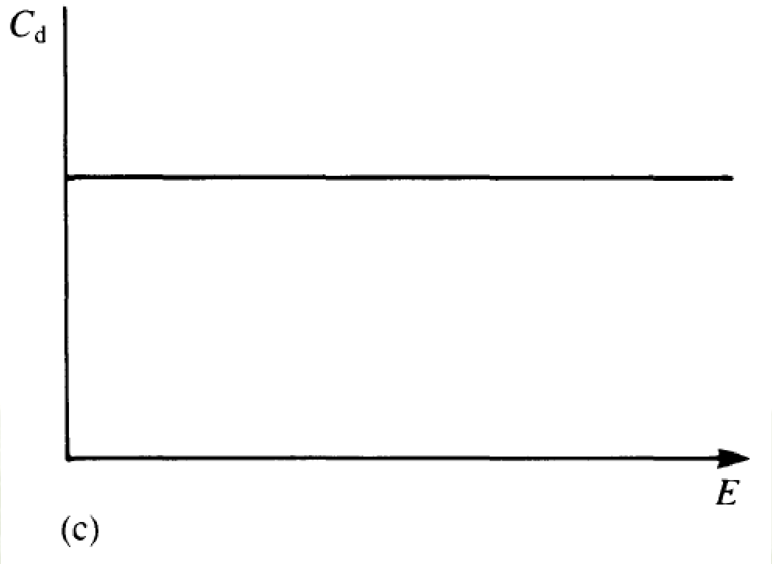
DL Model I: Helmholtz





$$C_{d,H} = \frac{\epsilon_r \epsilon_0}{x_H}$$

X_H would be the distance of closest approach of the charges, i.e. ionic radius, which, for the purpose of calculation, were treated as point charges.

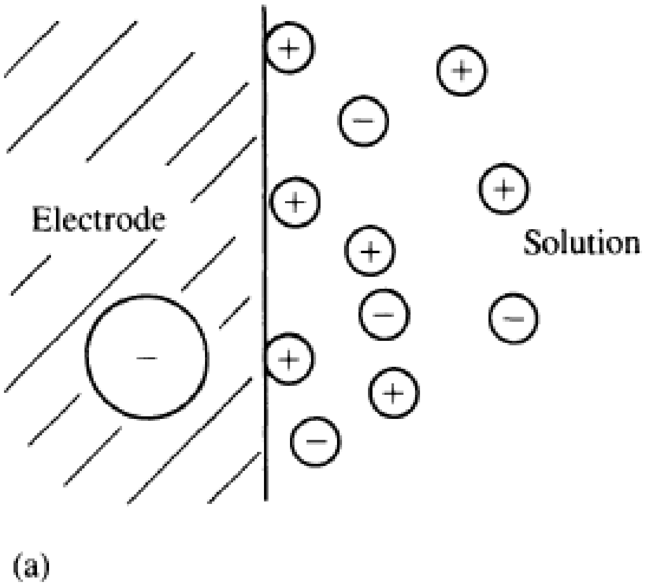


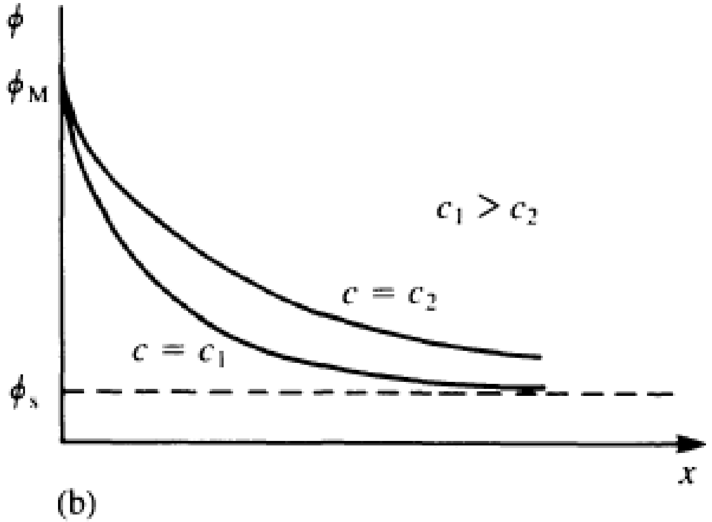
a) **Rigid arrangement of ions.**
b) **Variation of the electrostatic potential, Φ, with distance x, from the electrode.**
c) **Variation of C_d with applied potential.**

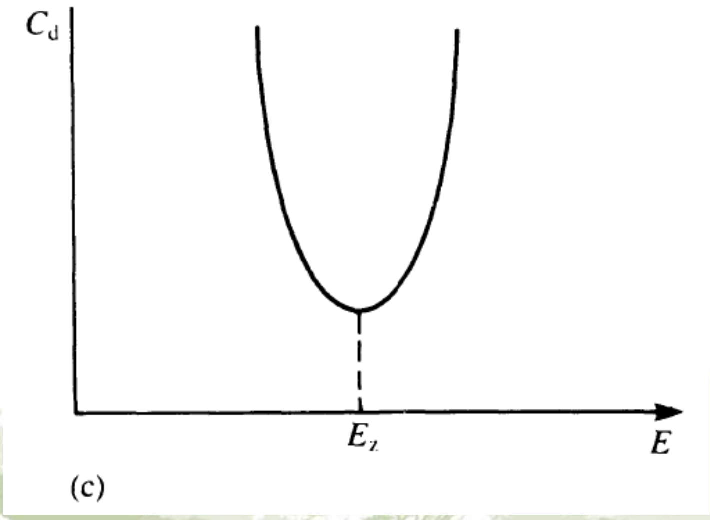
See “chapter 13.3” for more information (Bard).

DL Model II: Gouy-Chapman

As called: Diffuse double layer







a) **Arrangement of the ions in a diffuse way.**
b) **Variation of the electrostatic potential, Φ, with distance, x, from the electrode, showing effect of ion concentration.**
c) **Variation of C_d with potential, showing the minimum at the point of zero charge E_z.**

See “chapter 13.3” for more information (Bard).

DL Model II: Gouy-Chapman, Equation

Boltzmann's law

$$n_i = n_i^0 \exp\left[\frac{-z_i e \phi_\Delta}{k_B T}\right]$$

where $\phi_\Delta = \phi - \phi_S$ and n_i^0 is the numerical concentration of ions i in bulk solution.

$$x = 0 \qquad \phi_\Delta = \phi_{\Delta,0}$$

$$x \rightarrow \infty \qquad \phi_\Delta \rightarrow 0 \quad (\partial \phi_\Delta / \partial x) = 0$$

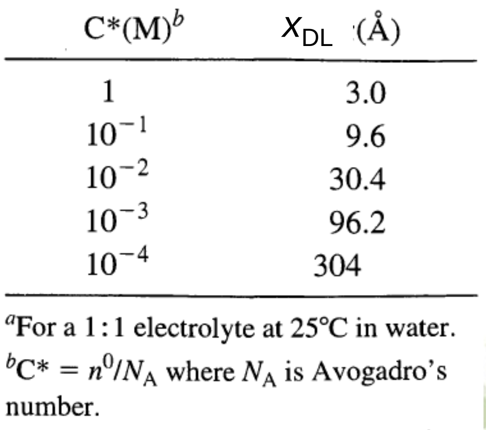
$$\boxed{x_{DL} = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{2 n_i^0 z^2 e^2}\right)^{1/2}}$$

The **diffuse layer is clearly quite thin** by comparison to the distance scale encountered **in typical diffusion layers for faradaic experiments**. It becomes thicker as the concentration of electrolyte falls.

$$\boxed{C_{d,GC} = \frac{\partial \sigma_M}{\partial \phi_{\Delta,0}} = \left(\frac{2 z^2 e^2 \epsilon_r \epsilon_0 n_i^0}{k_B T}\right)^{1/2} \cosh\left(\frac{z e \phi_{\Delta,0}}{2 k_B T}\right)}$$

For dilute aqueous solutions at 298 K,

$$\boxed{C_{d,GC} = 228 z c_\infty^{1/2} \cosh(19.5 z \phi_{\Delta,0})\ \mu\text{F cm}^{-2}}$$



$C^*(M)^b$	x_{DL} (Å)
1	3.0
10^{-1}	9.6
10^{-2}	30.4
10^{-3}	96.2
10^{-4}	304

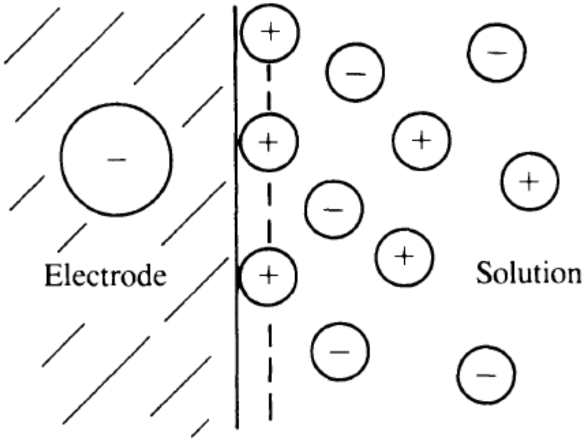
[a] For a 1:1 electrolyte at 25°C in water.

[b] $C^* = n^0/N_A$ where N_A is Avogadro's number.

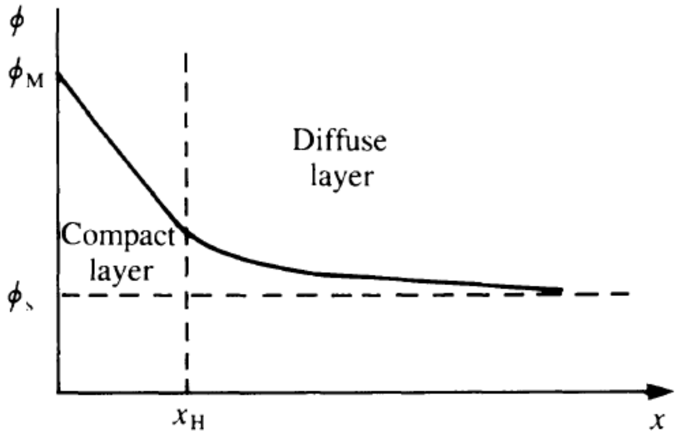
See "chapter 13.3" for more information (Bard).

DL Model III: Stern

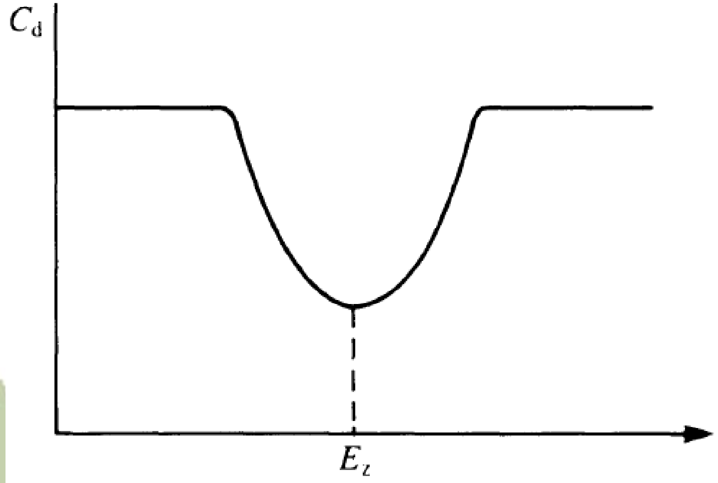
Stern combined the Helmholtz model for values of potential far from E_z with the Gouy-Chapman model for values close to E_z.



(a)



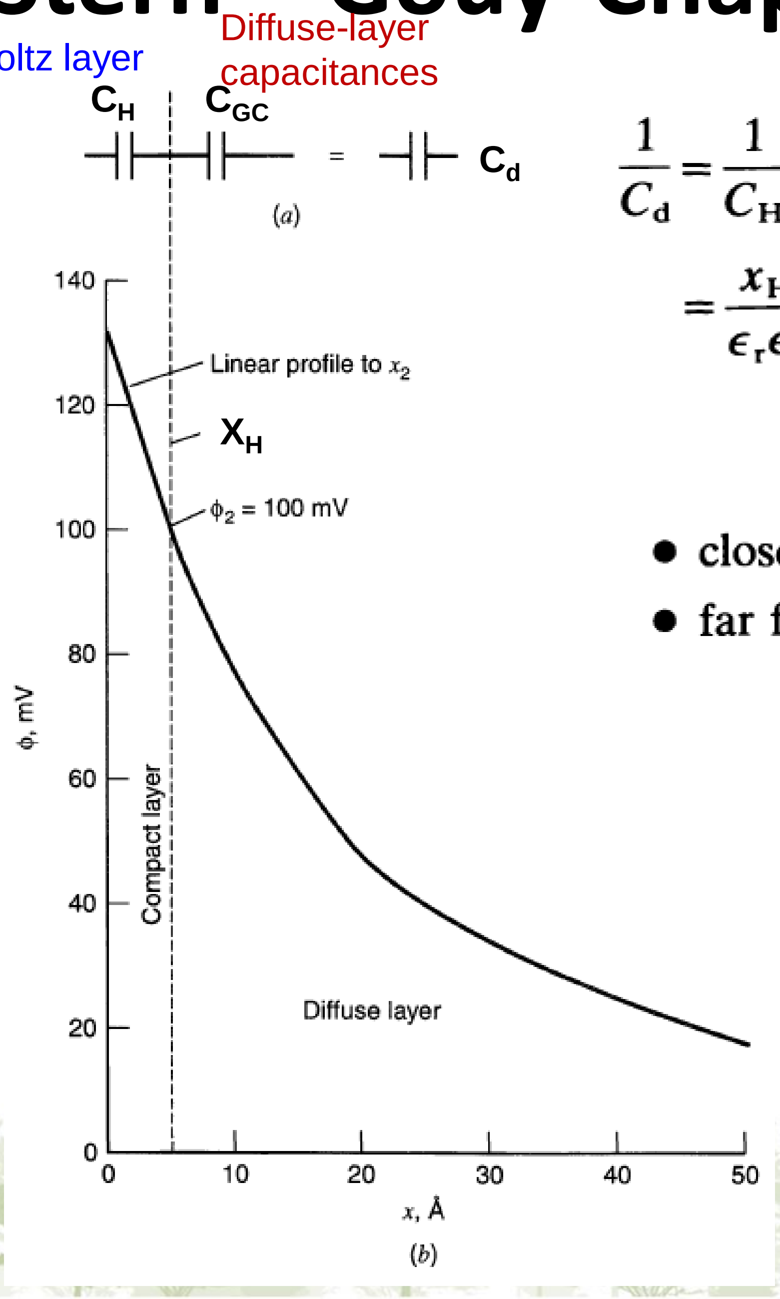
(b)



(c)

- **a) Arrangement of the ions in a compact and a diffuse layer.**
- **b) Variation of the electrostatic potential, Φ, with distance, x, from the electrode.**
- **c) Variation of C_d with potential.**

Stern = Gouy-Chapman-Stern Model

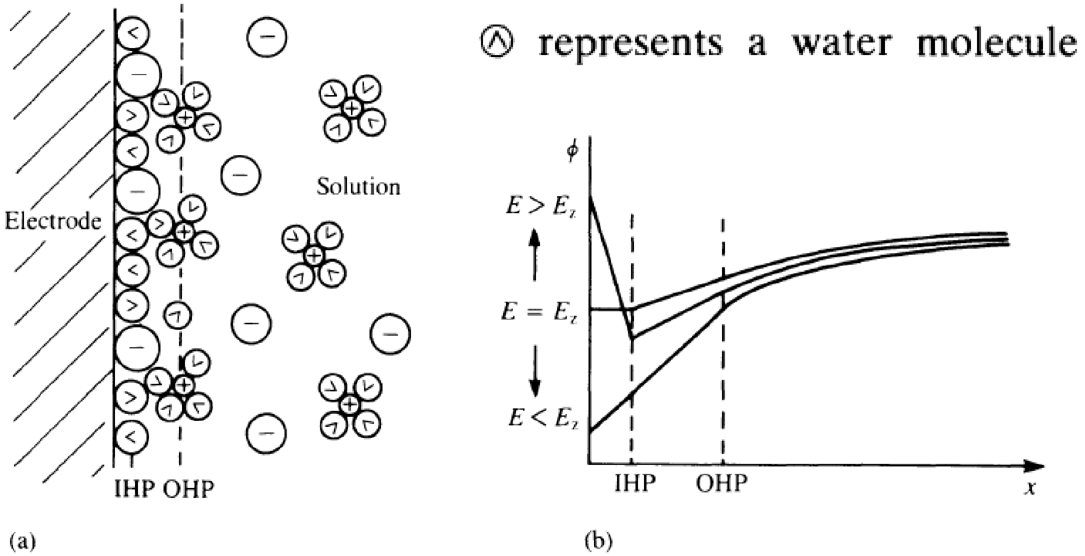


$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

$$= \frac{x_H}{\epsilon_r\epsilon_0} + \frac{1}{(2\epsilon_r\epsilon_0 z^2 e^2 n_i^0/k_B T)^{1/2}\cosh(ze\phi_{\Delta,0}/2k_B T)}$$

- close to E_z, $C_H \gg C_{GC}$ and so $C_d \sim C_{GC}$
- far from E_z, $C_H \ll C_{GC}$ and $C_d \sim C_H$

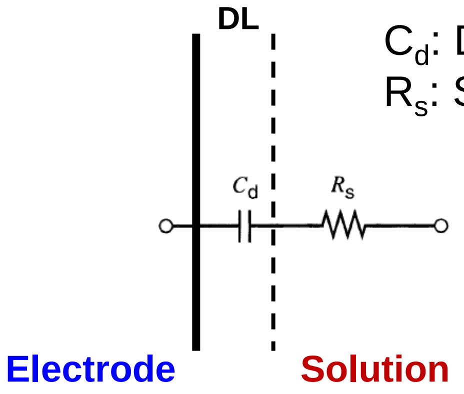
DL Model IV: Grahame



- **IHP (Inner Helmholtz plane)**
  - A specifically adsorbed ion loses its solvation, approaching closer to the electrode surface—besides this it can have the same charge as the electrode or the opposite charge, but the bonding is strong. the solvent molecules form its first solvation layer; the IHP is the plane that passes through the centre of these dipoles and specifically adsorbed ions.
- **OHP (Outer Helmholtz plane)**
  - In a similar fashion, OHP refers to adsorption of solvated ions that could be identified with a second solvation layer. Outside this comes the diffuse layer.

Ideal Polarized Electrode: Only Non-Faradaic Process

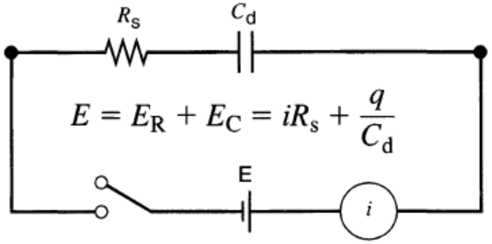
The current for charging the DL capacitance drops to 37% of its initial value at *t* = *τ*, and to 5% of its initial value at *t* = *3τ*.



C_d: Double-layer capacitance
R_s: Solution Resistance

RC series problem!

Potential Step



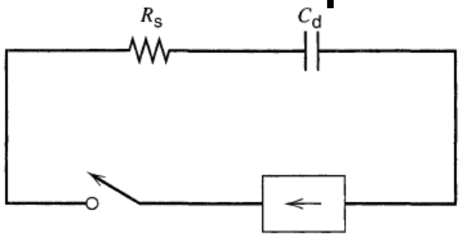
$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

$$\boxed{i = \frac{E}{R_s} e^{-t/R_sC_d}}$$

Time constant, $\tau = R_sC_d$

E_R vs. time, E_C vs. time and i vs t?

Current Step

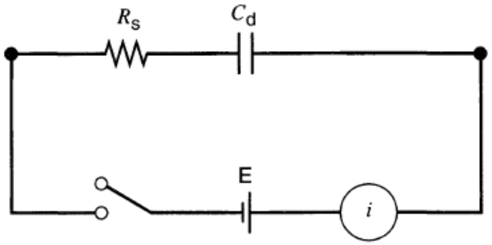


Constant current source

$$E = iR_s + \frac{i}{C_d}\int_0^t dt$$

$$\boxed{E = i(R_s + t/C_d)}$$

Potential Sweep



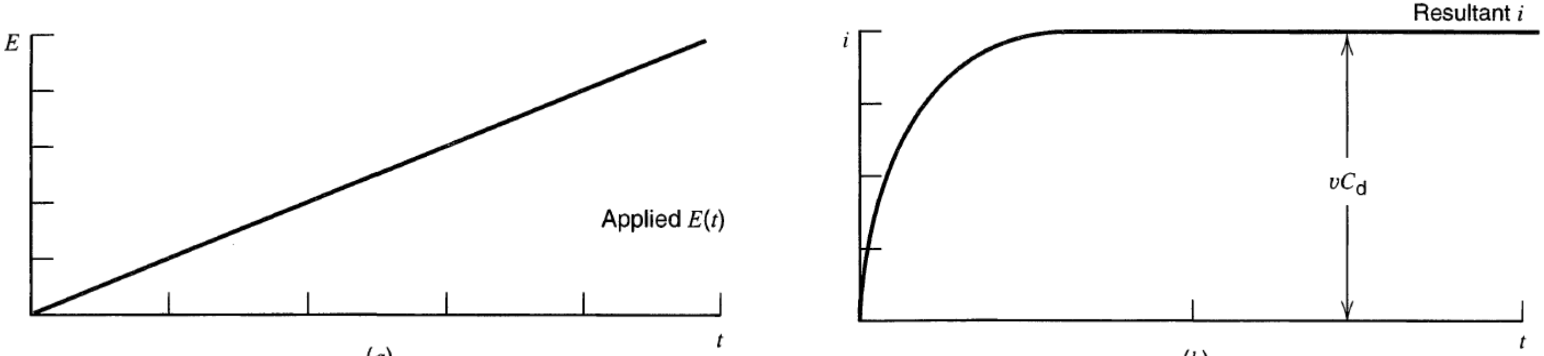
$$E = vt \quad \text{sweep rate } v$$

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

$$vt = R_s(dq/dt) + q/C_d$$

If $q = 0$ at $t = 0$,

$$\boxed{i = vC_d\,[1 - \exp(-t/R_sC_d)]}$$



(*a*) (*b*)

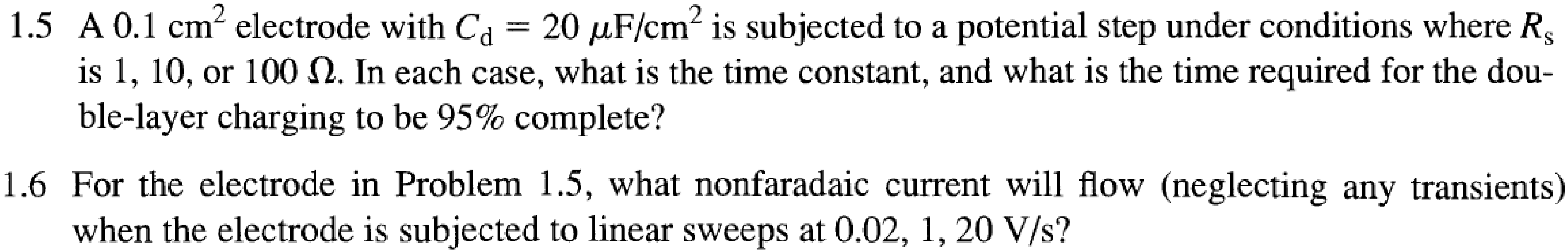
Example

The ideal polarized electrode is charged in the electrochemical cell, which the solution resistance and double-layer capacitance are 10 Ω and 20 μF. How long does the charged current drops to 5% of its initial value?

$$\tau = R \times C = 10 \times 20 \times 10^{-6} = 2 \times 10^{-4}\,s$$

$$5\% \Rightarrow 3\tau = 3 \times 2 \times 10^{-4} = 6 \times 10^{-4}\,s = 600\,\mu s$$

Example



1.5 A 0.1 cm^2 electrode with $C_d = 20\ \mu\text{F/cm}^2$ is subjected to a potential step under conditions where R_s is 1, 10, or 100 Ω. In each case, what is the time constant, and what is the time required for the double-layer charging to be 95% complete?

1.6 For the electrode in Problem 1.5, what nonfaradaic current will flow (neglecting any transients) when the electrode is subjected to linear sweeps at 0.02, 1, 20 V/s?

Problem 1.5

for 1 Ω

$$\tau = R \times C = 1 \times 20 \times 10^{-6} \times 0.1 = 2 \times 10^{-6}\, s$$

$$5\% \Rightarrow 3\tau = 3 \times 2 \times 10^{-6} = 6 \times 10^{-6}\, s = 6\ \mu\text{s}$$

Problem 1.6

for 0.02 V/s

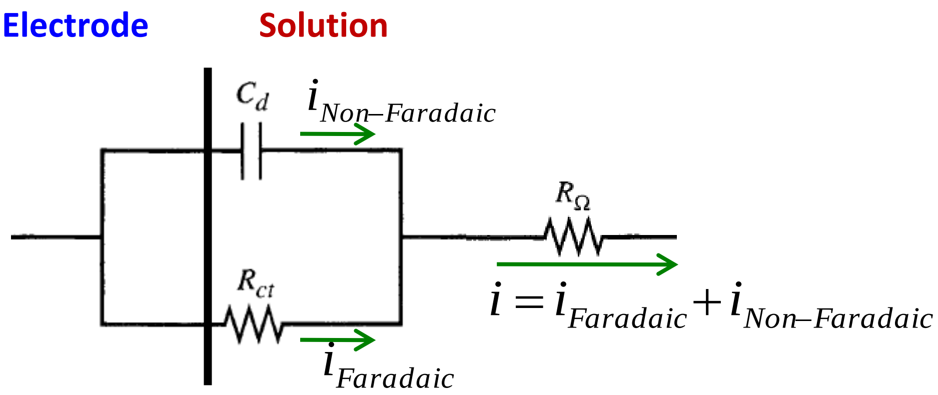
$$i = \upsilon C_d \left(1 - \frac{E}{R_\Omega} e^{-\frac{t}{R_s C_d}}\right), \text{at steady state}, i = \upsilon C_d$$

$$i = 0.02 \times 20 \times 10^{-6} \times 0.1 = 4 \times 10^{-8}\ \text{A}$$

Practical Electrode Process

= Faradic Process + Non-Faradic process

$$i = i_{Faradaic} + i_{Non\text{–}Faradaic}$$



Charged by constant potential,

for short time:

$$i_{Non\text{–}Faradaic} = \frac{E}{R_\Omega} e^{-\frac{t}{R_s C_d}}$$

for long time:

$$i_{Faradaic} = \frac{E}{R_\Omega + R_{ct}}$$

i vs. time curve?

Most of time, Faradaic current >> Non-Faradaic current.
However, non-Faradaic current cannot be ignored in some cases, e.g. porous electrode, high-speed potential sweep, high dielectric constant solvent.