ELECTROCHEMISTRY
FOR PLATING
and
CORROSION ENGINEERING

By J. DEMATOS

Consulting
$\sum$
Training Courses

World Wide Plating

Contents

Contents

Introduction

The industrial applications of electrochemistry can be divided into 7 categories:

1. Electrosynthesis
2. Surface treatments (Plating)
3. Energy storage and conversion
4. Measurement and analysis
5. Environment
6. Corrosion
7. Bio electrochemistry

Introduction

1. Electrosynthesis: Production of aluminum, chlorine and caustic soda

2. Surface treatments (Plating): Deposit of one or more metals on a conductive surface or the chemical conversion of the surface

3. Energy storage and conversion: Manufacture of electrochemical generators for mobile devices (telephones, computers, music equipment) or medical devices (pacemakers, micro injectors). Today fuel cells (H2 / O2 cell) are increasingly being developed

4. Analysis and measurement: These are essentially electrochemical sensors with application in medicine

Introduction

5. Environment:
Mainly used in the treatment and purification of water

6. Corrosion:
In general, we try to fight this phenomenon, but in some cases, we try to accelerate corrosion, for example when you want to reduce the amount of material to be stored (dismantling of nuclear facilities)

7. Bioelectrochemistry:
Manufacture of biosensors for oxidation-reduction reactions in biology (transport of ions through membranes)

Introduction

Electroplating for what?

Make a deposit of a metal or alloy on another metal or composite material
Chemical modification of the metal or composite surface

To: - Improve the physical or mechanical properties of the metal or composite material
- Increase the corrosion resistance
- Modify the appearance of a part (aesthetic)

Introduction

Electroplating is present in practically all industries:

Jewelry
Electronics
Weapons
Automotive
Nuclear
Electrical equipment
Aeronautics and Aerospace
Watchmaking

Introduction

Surface treatments (plating) are based on the following subjects:

- ✓ Chemistry
- ✓ Electricity
- ✓ Electrochemistry

The basic science is electrochemistry

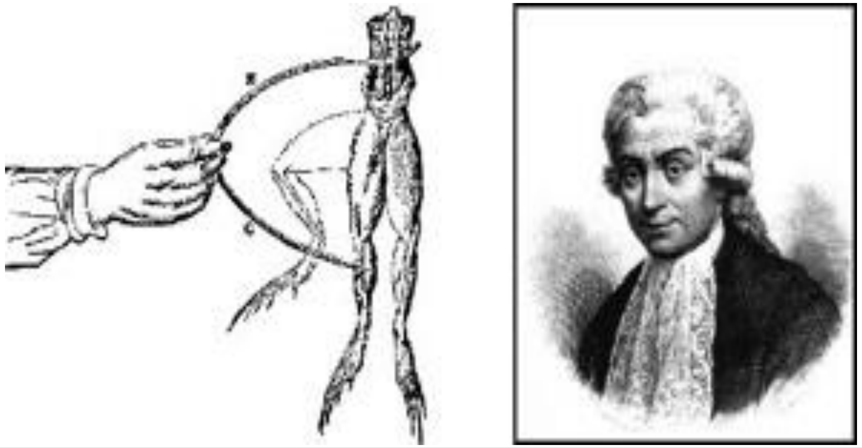
- ✓ Metallurgy
- ✓ Mechanics
- ✓ Fluid mechanics

Contents

1. A bit of History…

Electrochemistry: Branch of chemistry that describes the chemical phenomena coupled with reciprocal exchanges of electrical energy

The origins of electrochemistry come from the work of GALVANI at the end of the 18th century, and then from VOLTA at the beginning of the 19th century



Experiment of Galvani

1. A bit of History…

Volta's battery or voltaic battery (1800)

stacking of Cu and Zn discs
between soaked cloth of salty water

1. A bit of History…

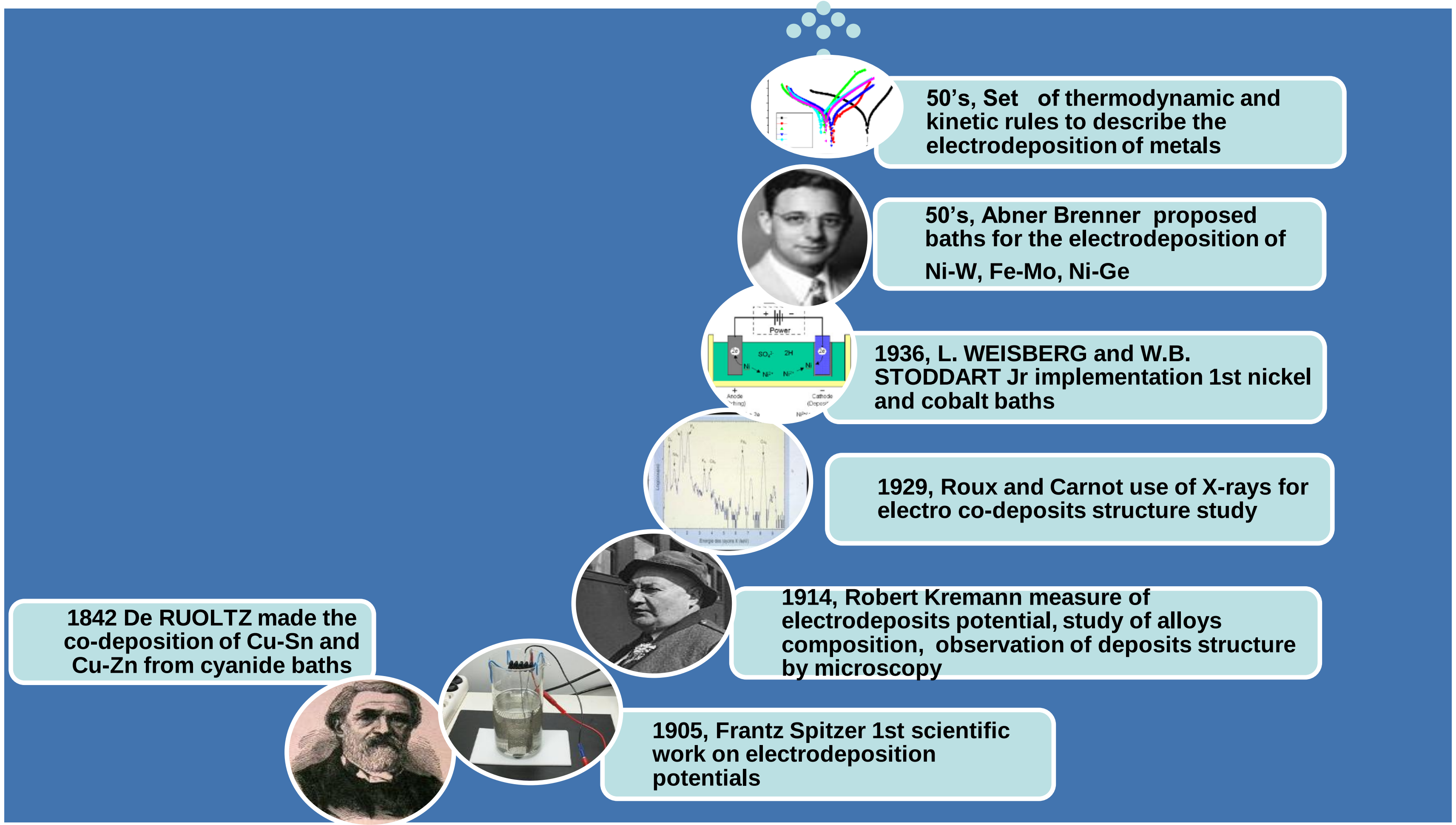
In 1925, the Japanese NAKAMURA and then in 1929, the French ROUX and COURNOT used X-rays to study the structure of electrodeposited alloys

They found no differences between the structure of the alloys obtained by electrolysis and the metallurgical alloys

An important step in 1936. L. WEISBERG and W.B. STODDART Jr implemented baths for the deposition of Ni and Co

At the end of the 50s, the American BRENNER, proposed baths that allowed the co-deposits of W, Mo, Ge and P (impossible to deposit in aqueous phase) with transition metals such as Fe, Ni and Co

1. A bit of History…



1842 De RUOLTZ made the co-deposition of Cu-Sn and Cu-Zn from cyanide baths

1905, Frantz Spitzer 1st scientific work on electrodeposition potentials

1914, Robert Kremann measure of electrodeposits potential, study of alloys composition, observation of deposits structure by microscopy

1929, Roux and Carnot use of X-rays for electro co-deposits structure study

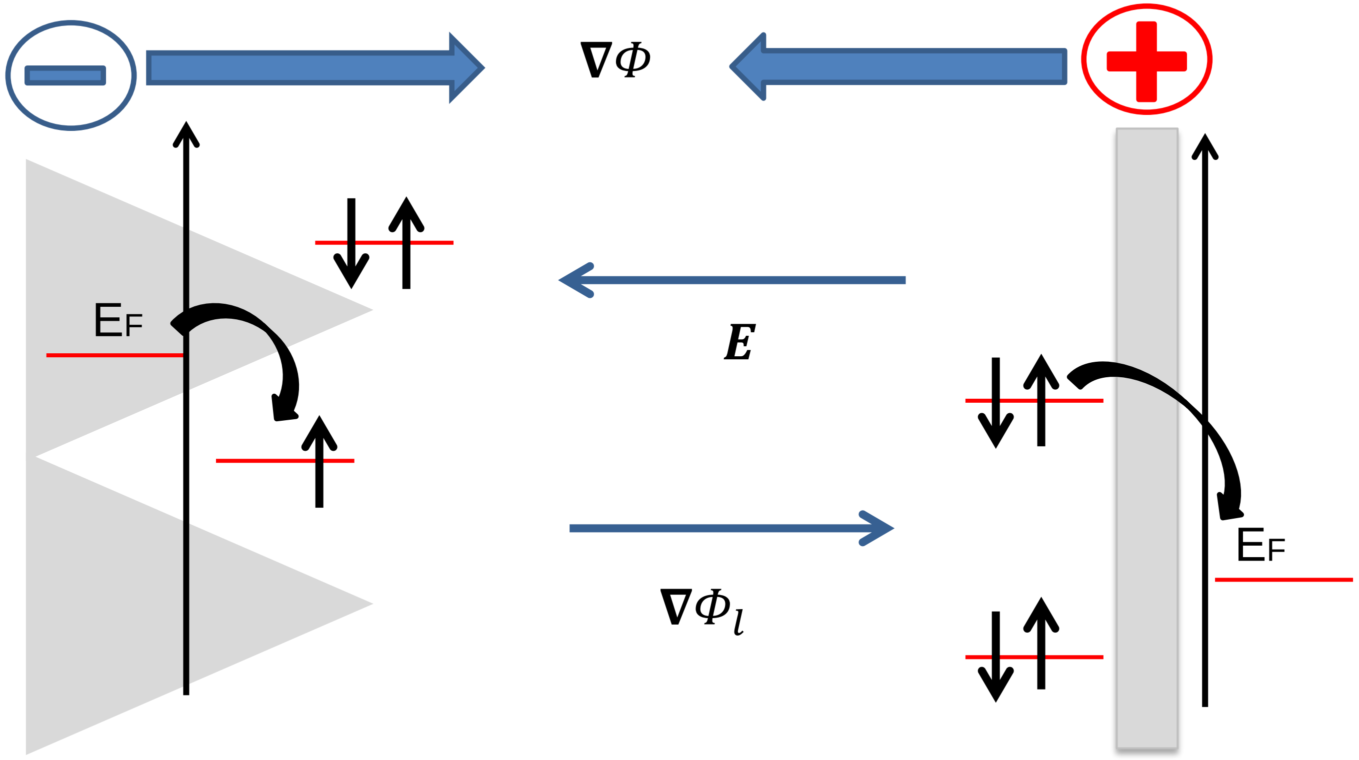
1936, L. WEISBERG and W.B. STODDART Jr implementation 1st nickel and cobalt baths

50's, Abner Brenner proposed baths for the electrodeposition of Ni-W, Fe-Mo, Ni-Ge

50's, Set of thermodynamic and kinetic rules to describe the electrodeposition of metals

Contents

2. POTENTIAL / CURRENT DISTRIBUTION

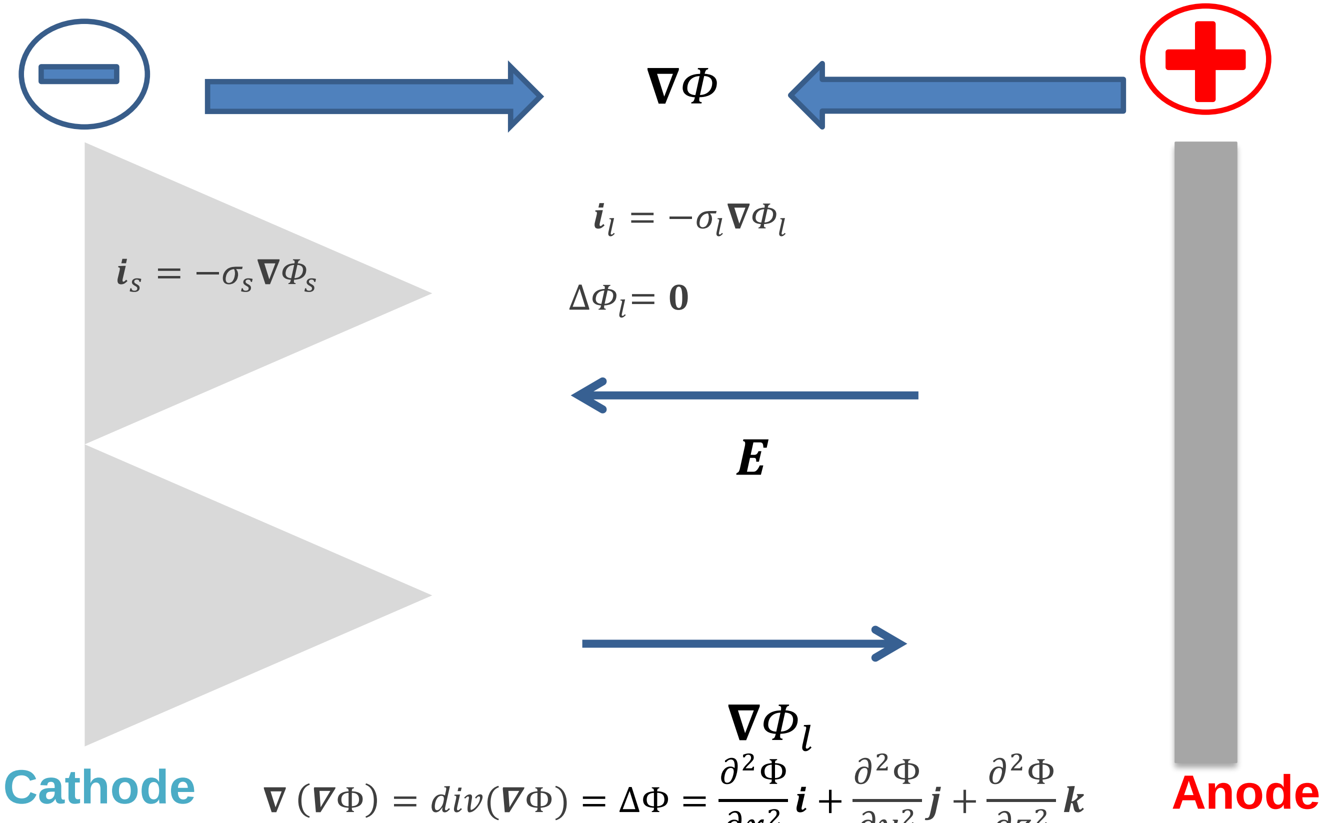


Cathode

Anode

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current primary distribution



$$\boldsymbol{\nabla}\Phi$$

$$\boldsymbol{i}_s = -\sigma_s \boldsymbol{\nabla}\Phi_s$$

$$\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla}\Phi_l$$

$$\Delta\Phi_l = \mathbf{0}$$

$$\boldsymbol{E}$$

$$\boldsymbol{\nabla}\Phi_l$$

Cathode

Anode

$$\boldsymbol{\nabla}\,(\boldsymbol{\nabla}\Phi) = div(\boldsymbol{\nabla}\Phi) = \Delta\Phi = \frac{\partial^2\Phi}{\partial x^2}\boldsymbol{i} + \frac{\partial^2\Phi}{\partial y^2}\boldsymbol{j} + \frac{\partial^2\Phi}{\partial z^2}\boldsymbol{k}$$

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi$$

$$\boldsymbol{\nabla}\Phi = \boldsymbol{i}\frac{\partial\Phi}{\partial x} + \boldsymbol{j}\frac{\partial\Phi}{\partial y} + \boldsymbol{k}\frac{\partial\Phi}{\partial z}$$

$$\boldsymbol{i} = \sigma\boldsymbol{E} = -\sigma\boldsymbol{\nabla}\Phi$$

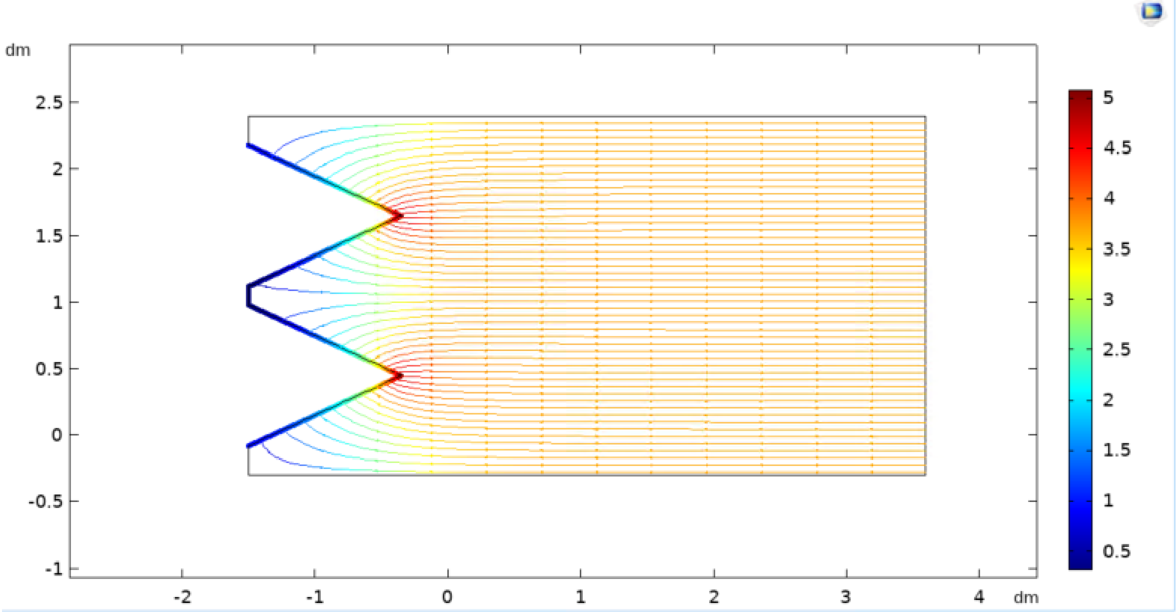
$$\boldsymbol{i}_s = -\sigma_s \boldsymbol{\nabla}\Phi_s$$

$$\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla}\Phi_l$$

$$\Delta\Phi_l = \mathbf{0}$$

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current primary distribution

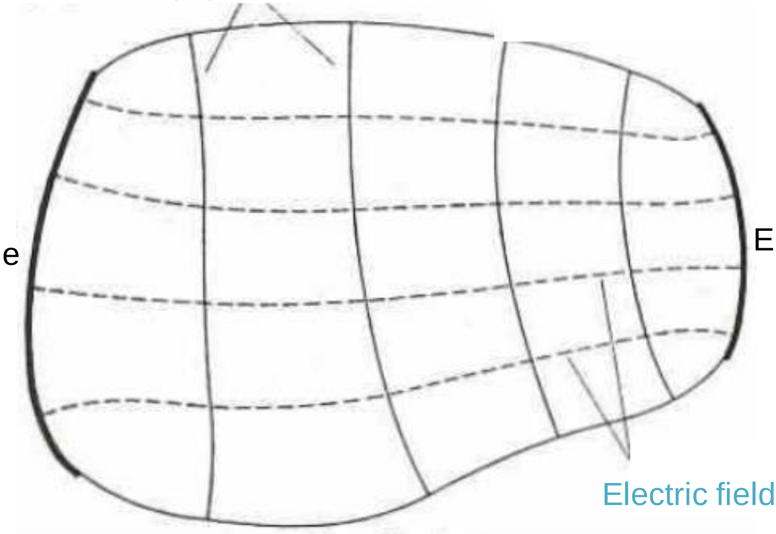


Numerical Simulation of the Electric Field

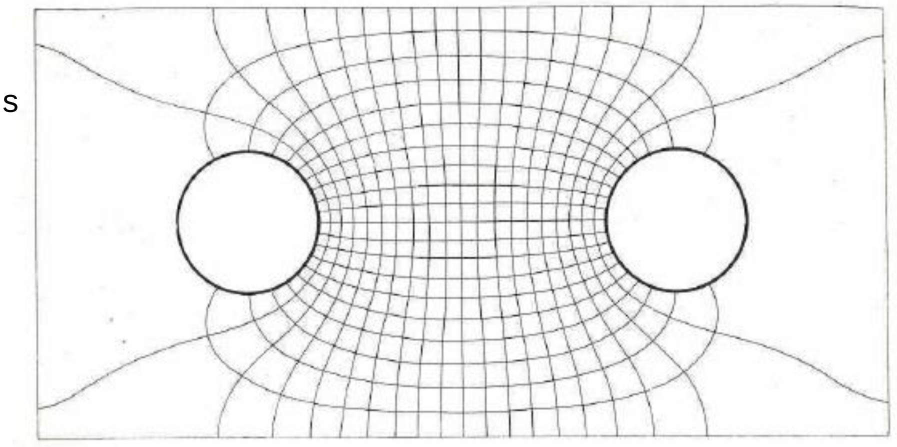
Comsol Multiphysics® Software
By Guillaume Mourre, Septembre 2021

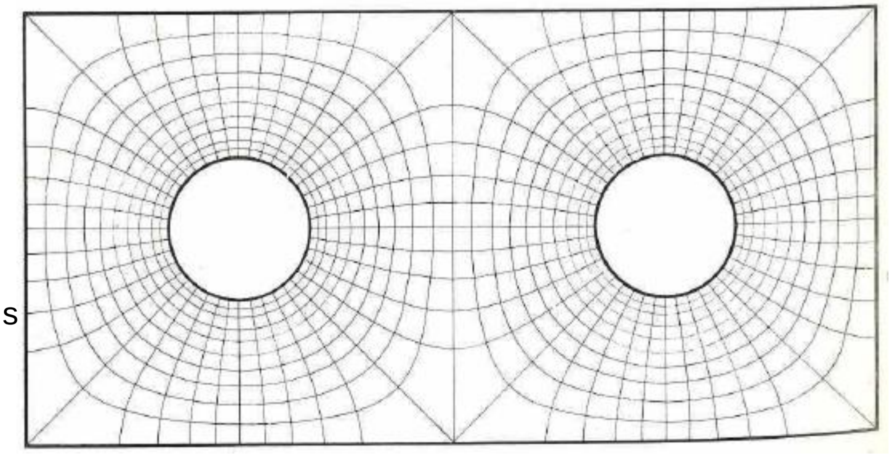
2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current primary distribution



tank with insulating walls





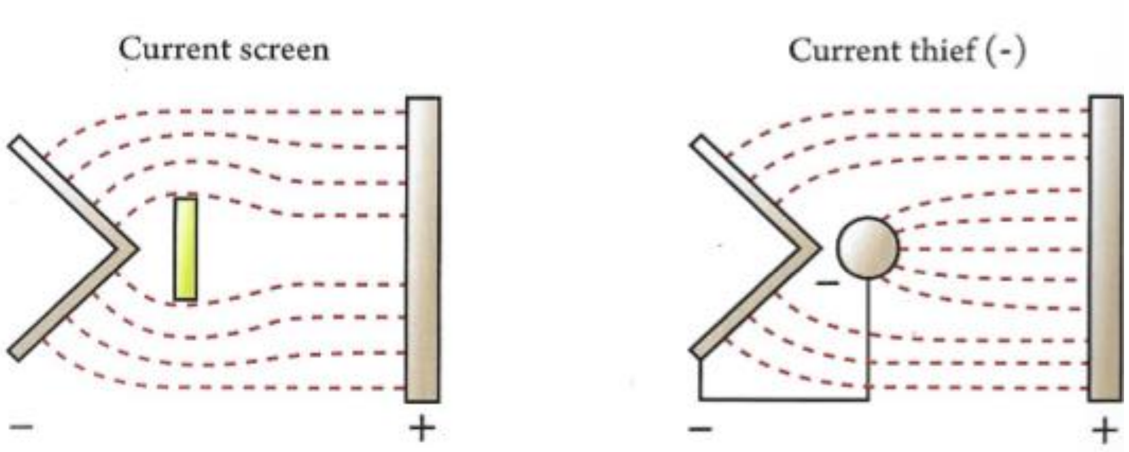
tank with conductive walls

Robert H. Rousselot, Répartition du Potentiel et du Courant dans les Electrolytes, Dunod, 1959

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current primary distribution

Practical applications:



Per Møller and Lars Pleth Nielsen, Advanced Surface Technology, Volume 1, Publisher: M&N, 2013

2. POTENTIAL / CURRENT DISTRIBUTION

➢ The potential and the current primary distribution

❖ **Physical Laws:**

In the electrolyte and at the electrodes surface ➔ Ohm's Law

➔ $\boldsymbol{i}_s = -\sigma_s \boldsymbol{\nabla}\Phi_s$ $\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla}\Phi_l$

Conservative flux ➔ Laplace Equation in the bulk solution: $\Delta\Phi_l = \mathbf{0}$

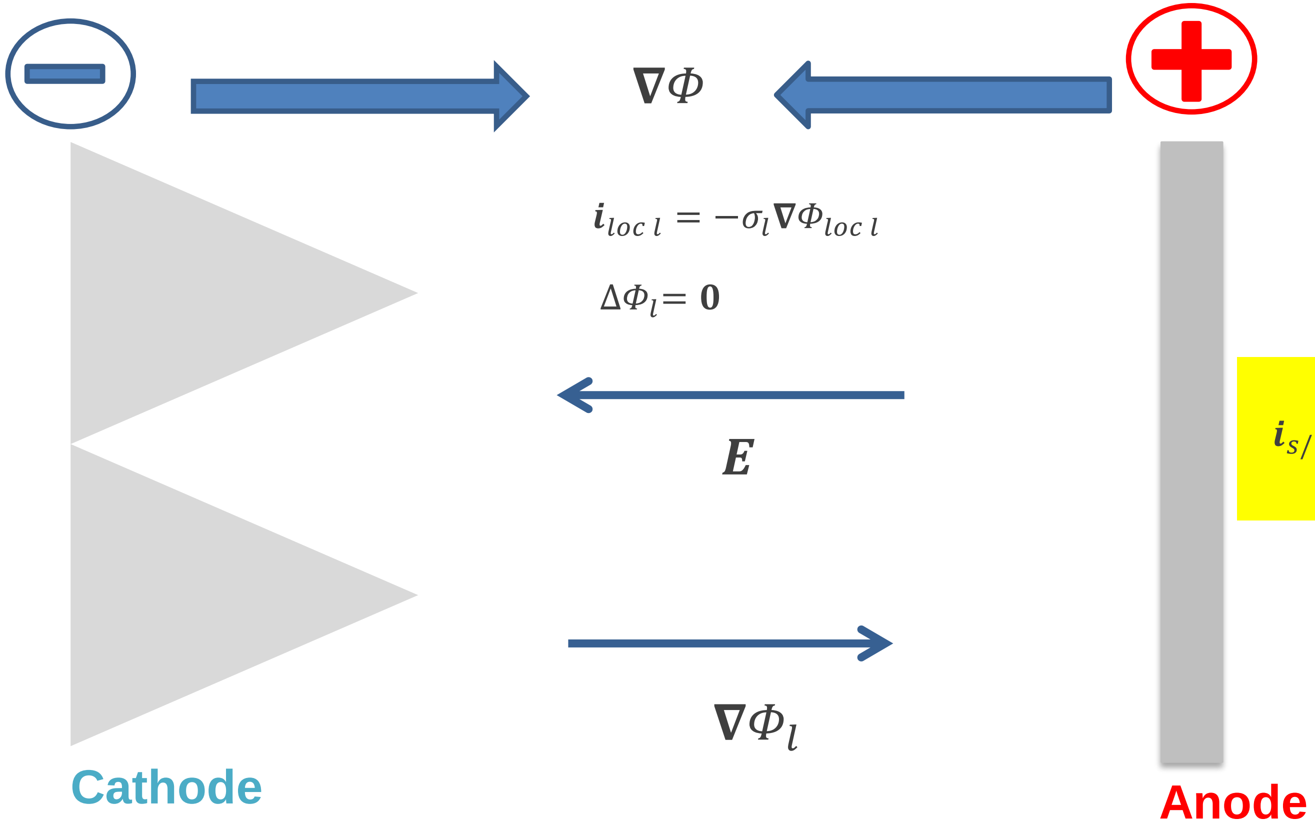
❖ **No overpotential at the electrodes** ➔ $\eta(i) = 0$ ➔ $\Phi_s - \Phi_l = E_{eq}$

❖ **No concentration gradients** ➔ $\boldsymbol{\nabla} C = 0$

Consequences: The peak and edge effects are amplified and the throwing power is near 0

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current secondary distribution



$$\boldsymbol{i}_{loc\ l} = -\sigma_l \boldsymbol{\nabla}\Phi_{loc\ l}$$

$$\Delta\Phi_l = \mathbf{0}$$

$$\boldsymbol{i}_{s/l} = -i_0 \exp\left(-\frac{\alpha n F}{RT}\,\eta(i)_c\right)$$

$$\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla}\Phi_l$$

$$\Delta\Phi_l = \mathbf{0}$$

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current secondary distribution

❖ **Physical Laws:**

Butler-Volmer at the cathode:

➔ $\boldsymbol{i}_s = -\sigma_s \boldsymbol{\nabla} \Phi_s$

Ohm’s Law in the electrolyte ➔ $\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla} \Phi_l$

Conservative flux in the bulk of the electrolyte ➔ Laplace Equation: $\Delta \Phi_l = \mathbf{0}$

❖ **This type of distribution takes into account the conditions of the primary distribution**

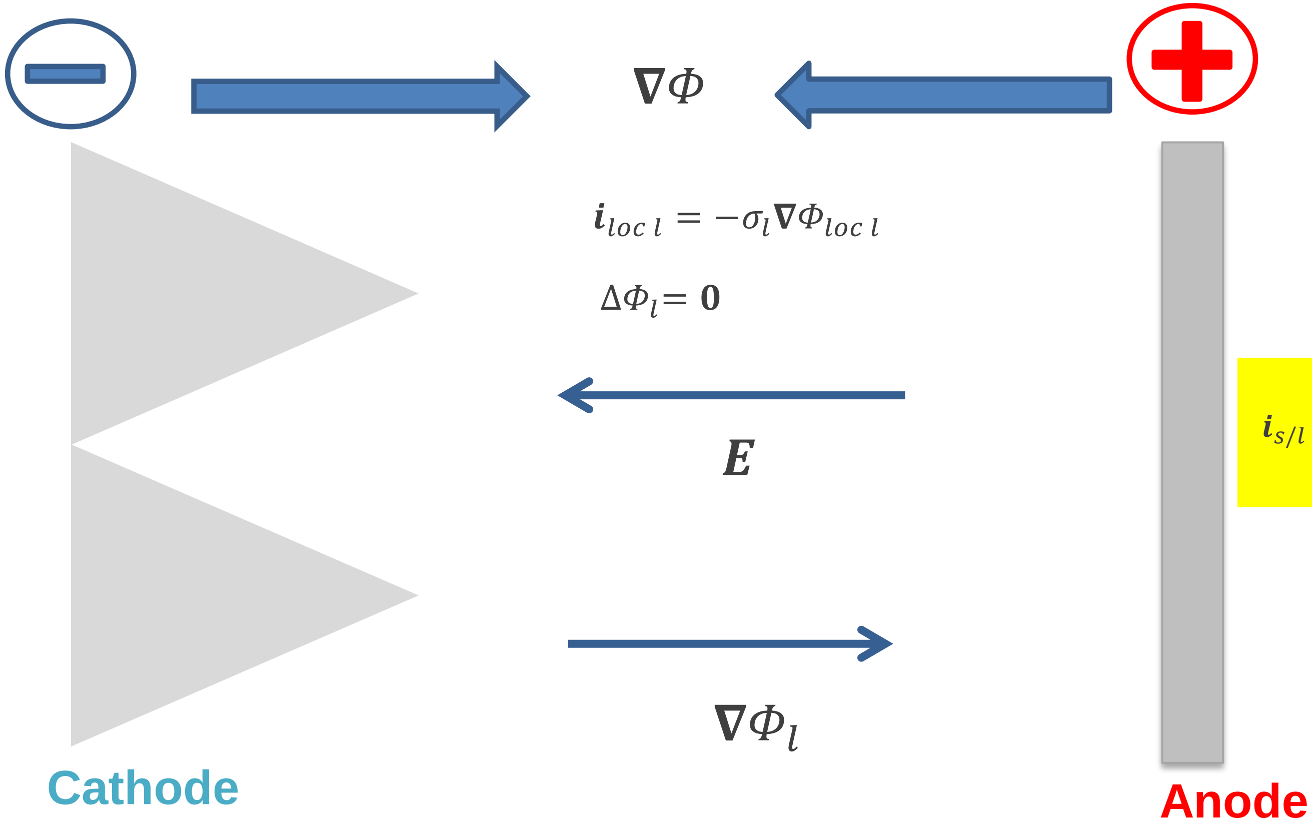
❖ **Transfer overpotential at the electrodes** $\eta(i)_{act} \neq 0$ ➔ $\Phi_s - \Phi_l - E_{eq} = \eta(i)_{act}$

❖ **No concentration gradients** ➔ $\boldsymbol{\nabla} C = 0$

Consequences: The peak and edge effects are damped and the throwing power is slightly improved but remains close to 0

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current tertiary distribution



$$\nabla\Phi$$

$$i_{loc\ l} = -\sigma_l \nabla\Phi_{loc\ l}$$

$$\Delta\Phi_l = 0$$

$$\boldsymbol{E}$$

$$\nabla\Phi_l$$

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi$$

$$\boldsymbol{i} = \sigma\boldsymbol{E} = -\boldsymbol{\nabla\Phi}$$

$$\boldsymbol{i}_{s/l} = -i_0 \frac{C_{Ox_{s/l}}}{C_{Ox_l}} \exp\left(-\frac{\alpha nF}{RT}\,\eta(i)_c\right)$$

$$\boldsymbol{i}_l = -\sigma_l \nabla\Phi_l$$

$$\Delta\Phi_l = \boldsymbol{0}$$

2. POTENTIAL / CURRENT DISTRIBUTION

- The potential and the current tertiary distribution

❖ **Physical Laws:**

Butler-Volmer at the electrodes:

➔ $$i_{s/l} = -i_0 \frac{C_{ox_{s/l}}}{C_{ox_l}} \exp\left(-\frac{\alpha nF}{RT}\,\eta(i)_c\right)$$

Ohm’s Law in the electrolyte ➔ $\boldsymbol{i}_l = -\sigma_l \boldsymbol{\nabla} \Phi_l$

Conservative flux in the bulk of the electrolyte ➔ Laplace Equation: $\Delta\Phi_l = \mathbf{0}$

❖ **This type of distribution takes into account the conditions of the primary & the secondary distribution**

❖ **Transfer overpotential at the electrodes** $\eta(i)_{act} \neq 0$ ➔ $\Phi_s - \Phi_l - E_{eq} = \eta(i)_{act}$

❖ **Overpotential diffusion** ➔ $\nabla C \neq \mathbf{0}$

Consequences: the peak and edge effects are dampened more than for secondary distribution and the throwing power is significantly improved
Thicknesses distribution is less important than for secondary distribution

2. POTENTIAL / CURRENT DISTRIBUTION

In summary

- **The potential and the current primary distribution**:
  - Only the geometry factor accounts for the potential and the current distribution
  - No reaction is considered at the electrodes/solution interface
  - The peak and edge effects are amplified and the throwing power is near 0
- **The potential and the current secondary distribution:**
  - Accounts the conditions of the primary distribution
  - Transfer overpotential ➔ Butler Volmer
  - No concentration gradient
  - The peak and edge effects are damped and the throwing power is slightly improved but remains close to 0

2. POTENTIAL / CURRENT DISTRIBUTION

In summary

- **The potential and the current tertiary distribution**:
  - Accounts the conditions of the primary & secondary distribution
  - There is a concentration gradient ➔ diffusion
  - The peak and edge effects are dampened more than for secondary distribution and the throwing power is significantly improved Thicknesses distribution is less important than for secondary distribution

- Secondary distribution: $i = -i_0[\exp(b_c\,\eta(i)_c]$; b_c<0 B.V. with $\boldsymbol{\nabla} C = \mathbf{0}$

- Tertiary distribution: $i = -i_0\left(\frac{C_{s/l}}{C_l}\right)[\exp(b_c\,\eta(i)_c]$; b_c<0 B.V. with $\boldsymbol{\nabla} C \neq \mathbf{0}$

2. POTENTIAL / CURRENT DISTRIBUTION

Evaluation of the current distribution:

$$\boldsymbol{W_a = \frac{d\eta}{di}\,\frac{\sigma}{L}}$$

High value of W_a ➔ secondary distribution
Higher value of W_a ➔ tertiary distribution

W_a near 0 ➔ primary distribution

W_a: The Wagner's number (dimensionless)

$\frac{d\eta}{di}$: slope of the polarization curve (= polarization resistance) ($\Omega\ m^2$)

σ: Conductivity of the solution ($S\ m^{-1}$)

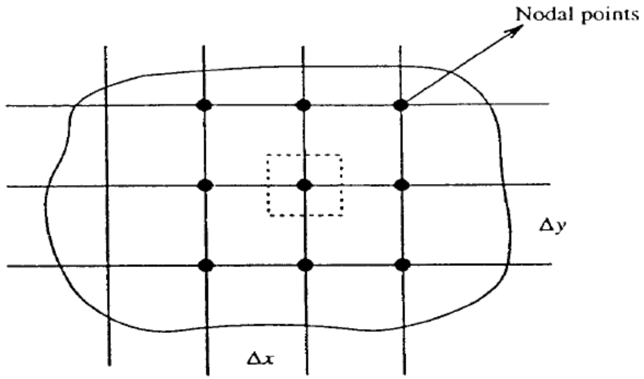
L: Caracteristic length (m)

Contents

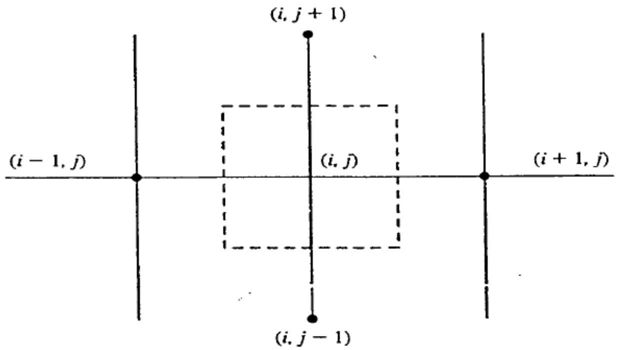
3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

- Laplace Equation is a second order partial differential equation (PDE)
  - ✓ Electricity, fluid flow, and steady heat conduction
  - ✓ The finite Difference Method ➔ express a differential equation in terms of systems of equations and linear algebra

FDM: discretize the PDE by replacing the partial derivatives with their approximations

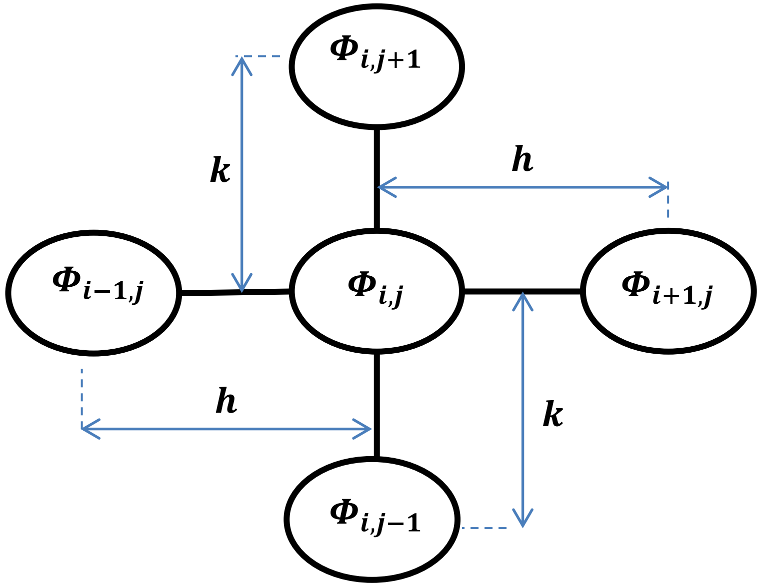


Finite differencing along x and y



5-point stencil for Laplace equation

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION



$$\frac{\partial^2\Phi}{\partial x^2} = \frac{\frac{\partial\Phi}{\partial x}_{|FD} - \frac{\partial\Phi}{\partial x}_{|BD}}{h}$$

$$\frac{\partial^2\Phi}{\partial x^2} = \frac{\frac{\Phi_{i+1,j}-\Phi_{i,j}}{h} - \frac{\Phi_{i,j}-\Phi_{i-1,j}}{h}}{h}$$

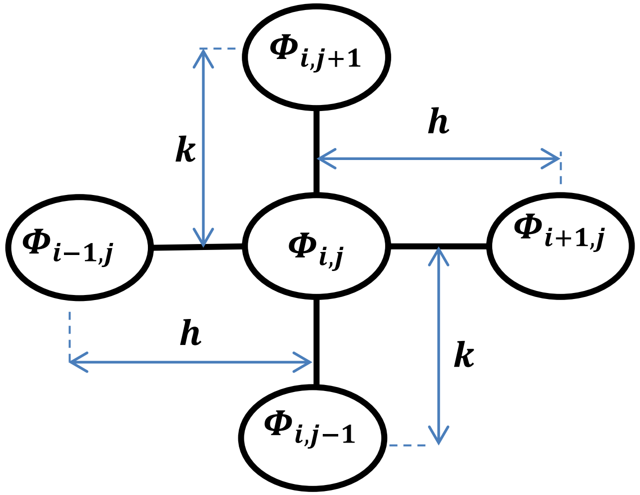
$$\frac{\partial^2\Phi}{\partial x^2} = \frac{\Phi_{i+1,j}+\Phi_{i-1,j}-2\Phi_{i,j}}{h^2}$$

$$\frac{\partial^2\Phi}{\partial y^2} = \frac{\Phi_{i,j+1}+\Phi_{i,j-1}-2\Phi_{i,j}}{k^2}$$

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

- Laplace Equation (2D space):

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$$



$$\frac{\Phi_{i+1,j} + \Phi_{i-1,j} - 2\Phi_{i,j}}{h^2} + \frac{\Phi_{i,j+1} + \Phi_{i,j-1} - 2\Phi_{i,j}}{k^2} = 0$$

$For: \ h = k$

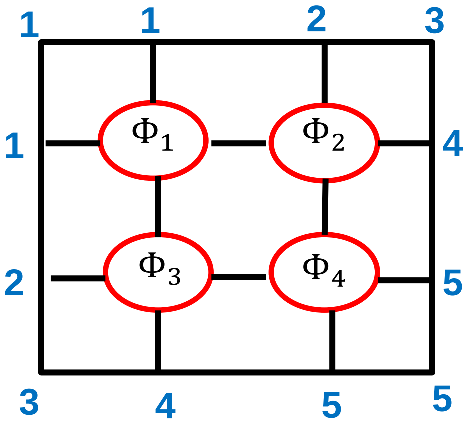
$$\frac{\Phi_{i+1,j} + \Phi_{i-1,j} + \Phi_{i,j+1} + \Phi_{i,j-1} - 4\Phi_{i,j}}{h^2} = 0$$

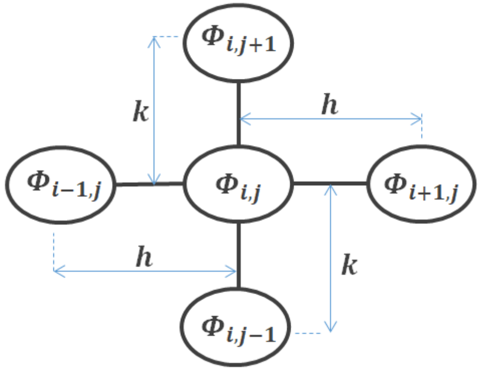
$$\Phi_{i,j} = \frac{1}{4}(\Phi_{i+1,j} + \Phi_{i-1,j} + \Phi_{i,j+1} + \Phi_{i,j-1})$$

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

Solve: $\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0$

For boundary values shown in figure:





$$\Phi_{i,j} = \frac{1}{4}(\Phi_{i+1,j} + \Phi_{i-1,j} + \Phi_{i,j+1} + \Phi_{i,j-1})$$

For Φ_1, $\Phi_1 = \frac{1}{4}(\Phi_2 + 1 + 1 + \Phi_3)$ 1

For Φ_2, $\Phi_2 = \frac{1}{4}(4 + \Phi_1 + 2 + \Phi_4)$ 2

For Φ_3, $\Phi_3 = \frac{1}{4}(\Phi_4 + 2 + \Phi_1 + 4)$ 3

For Φ_4, $\Phi_4 = \frac{1}{4}(5 + \Phi_3 + \Phi_2 + 5)$ 4

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

Solution: $$\Phi_{i,j} = \frac{1}{4}(\Phi_{i+1,j} + \Phi_{i-1,j} + \Phi_{i,j+1} + \Phi_{i,j-1})$$

$$\Phi_1 = \frac{1}{4}(\Phi_2 + 1 + 1 + \Phi_3) \quad 1$$

$$\Phi_2 = \frac{1}{4}(4 + \Phi_1 + 2 + \Phi_4) \quad 2$$

$$\Phi_3 = \frac{1}{4}(\Phi_4 + 2 + \Phi_1 + 4) \quad 3$$

$$\Phi_4 = \frac{1}{4}(5 + \Phi_3 + \Phi_2 + 5) \quad 4$$

Using GAUSS SEIDAL Method

Iteration #1: taking initial values as

$$\boldsymbol{\Phi_1 = \Phi_2 = \Phi_3 = \Phi_4 = 0}$$

$$\Phi_1 = \frac{1}{4}(\Phi_2 + 1 + 1 + \Phi_3) = \frac{1}{4}(0 + 1 + 1 + 0) = 0.5$$

$$\boldsymbol{\Phi_1 = 0.5\,;\ \Phi_4 = 0}$$

$$\Phi_2 = \frac{1}{4}(4 + 0.5 + 2 + 0) = 1.625$$

$$\Phi_3 = \frac{1}{4}(0 + 2 + 0.5 + 4) = 1.625$$

$$\Phi_4 = \frac{1}{4}(5 + 1.625 + 1.625 + 5) = 3.3125$$

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

Iteration #2: taking initial values as

$\boldsymbol{\Phi_1 = 0.5\ ;\ \Phi_2 = 1.625\ ;\ \Phi_3 = 1.625\ ;\ \Phi_4 = 3.3125}$

$$\Phi_1 = \frac{1}{4}(\Phi_2 + 1 + 1 + \Phi_3) = 1.3125$$

$$take \quad \Phi_1 = 1.3125\ and\ \Phi_4 = 3.3125$$

$$\Phi_2 = \frac{1}{4}(4 + 1.3125 + 2 + 3.3125) = 2.6562$$

$$take \quad \Phi_1 = 1.3125\ and\ \Phi_4 = 3.3125$$

$$\Phi_3 = \frac{1}{4}(3.3125 + 2 + 1.3125 + 4) = 2.6562$$

$$take \quad \Phi_3 = 2.6562\ and\ \Phi_2 = 2.6562$$

$$\Phi_4 = \frac{1}{4}(5 + \Phi_3 + \Phi_2 + 5) = \frac{1}{4}(5 + 2.6562 + 2.6562 + 5) = 3.8281$$

3. NUMERICAL RESOLUTION OF THE LAPLACE EQUATION

$$\Phi_1 = \frac{1}{4}(\mathit{\Phi}_2 + 1 + 1 + \mathit{\Phi}_3)$$

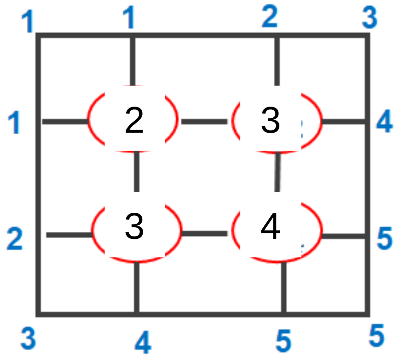
$$\Phi_2 = \frac{1}{4}(4 + \mathit{\Phi}_1 + 2 + \mathit{\Phi}_4)$$

$$\Phi_3 = \frac{1}{4}(\mathit{\Phi}_4 + 2 + \mathit{\Phi}_1 + 4)$$

$$\Phi_4 = \frac{1}{4}(5 + \mathit{\Phi}_3 + \mathit{\Phi}_2 + 5)$$

Relative error:

$$\frac{\Phi^{new} - \Phi^{old}}{\Phi^{new}}$$



Itr. No.	$\boldsymbol{\Phi_1}$	$\boldsymbol{\Phi_2}$	$\boldsymbol{\Phi_3}$	$\boldsymbol{\Phi_4}$	Maxi. Error
1	0.5	1.6250	1.6250	3.3125	-
2	1.3125	2.6562	2.6562	3.8281	0.6190
3	1.8281	2.9141	2.9141	3.9570	0.2821
4	1.9570	2.9785	2.9785	3.9893	0.0659
5	1.9893	2.9946	2.9946	3.9973	0.0162
6	1.9973	2.9987	2.9987	3.9993	0.040
7	1.9993	2.9997	2.9997	3.9998	0.0010
8	1.9998	2.9999	2.9999	4.0000	0.003
9	2.0000	3.0000	3.0000	4.0000	0.0001

Thank you for your attention

www.worldwideplating.com

Consulting
∑
Training Courses

World Wide Plating