Microscopic Kinetic and Thermodynamics
Notes of the course

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Electrochemical Energy Conversion

1.1 Introduction to electrochemistry

In this part of the course we want to put into practice the concepts obtained during the theoretical study of the kinetic inside a material and understand how to use it in practice. Our main focus will be the creation and conservation of energy inside batteries or, as chemists call them, **electrochemical cells**. Therefore, we will start with a simple introduction to the main concepts needed in this study.

The concept behind a battery is trivial in some sense, basically only three things needs to be present to have a working device: two or more electrodes, an electrolyte, and an external circuit. The idea is the one of using redox reactions between the electrodes, usually composed by metals or semiconductors, to make electron travel inside the circuit. In practice, let's imagine using two bars of Zn and Cu as electrodes putted inside a liquid, the two of them can give rise to a total cell reaction where electrons travel from Zinc to Copper as follows

$$Zn_s + Cu_l{}^{2+} \longrightarrow Zn_l{}^{2+} + Cu_s, \tag{1.1}$$
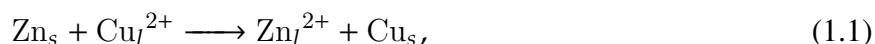
where the subscripts tell the phase in which the atom is present. Basically, what is happening is that two different reactions are performed inside the system: one where the Zinc looses two electrons giving rise to the positive ion, and one where ionic Copper takes those two electrons. Therefore, the former is an **oxidation** reaction, while the latter is a **reduction** one, generating a distinction to keep in mind.

> **Definition 1.1.1: Oxidation-Reduction**
>
> Inside an electrochemical cell the element is reducing if is gaining electrons in the process, while is oxidizing if is loosing electrons.

Also, during the course we will call the element that undergo oxidation as **anode**, while the one reducing will be the **cathode**. Still, the aim of our device is creating this reaction and using the electrons that are generated in the process. So that the point is, we connect the anode and cathode with a circuit, so that electrons will start to spontaneously flow from one to the other generating the following semi-reactions

$$Cu_l{}^{2+} + 2\,e^- \longrightarrow Cu_s, \qquad\qquad Zn_s \longrightarrow Zn_l{}^{2+} + 2\,e^-. \tag{1.2}$$

This process will so generate a current in the circuit, meaning that a voltage, called **cell potential**, is present between the two electrodes giving us energy that we can use. That is all great but as the reaction
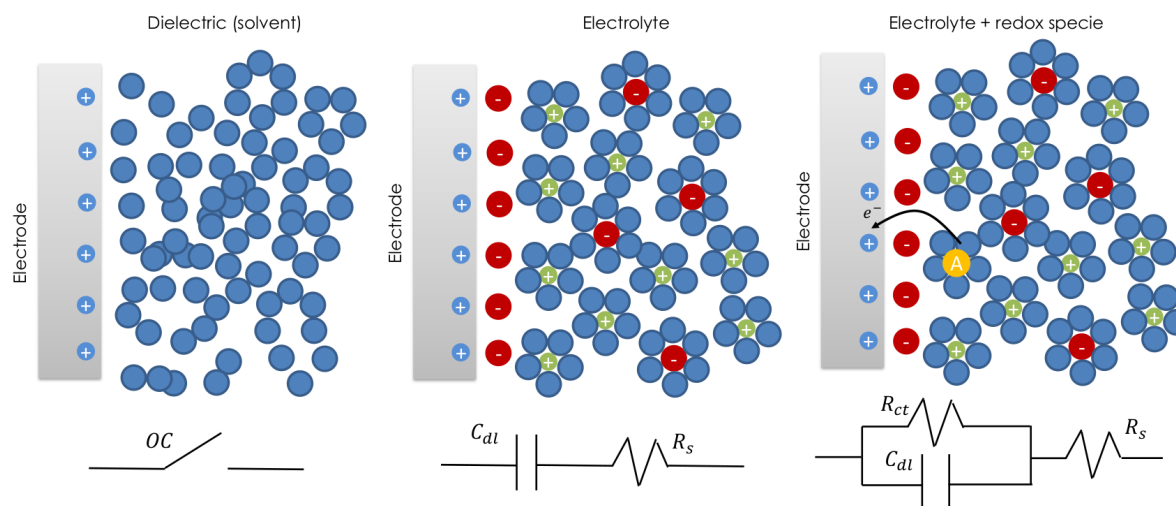
Figure 1.1: Graphical explanation of how an electrolyte works in practice, showing how the presence of ions inside it allows for the charge to move in the solution making species travel from anion to cathode making the reaction continue. Also, every step can be represented as a different circuit.

goes on the density of Zn^{2+} around the anode will reach saturation slowing down the reaction, a problem that can be easily eliminated by using the electrolyte. In fact, as we can see in Fig. (1.1), the electrolyte has the task of letting the ions generated move inside the system. For example, if a salt is present in the solution, the latter will split generating positive and negative ions which will travel to the cathode and anode respectively. That will give rise to a system that looks like a capacity, where the ions move as long as the charge around the electrodes is not compensated, but if inside the electrolyte we place also the redox species, Cu^{2+}, they will not only move to the electrodes but will react with those keeping the reaction going. For this reason the choice of the electrolyte is really important, since the diffusion properties of ions inside it will be key to the output power that we can have.

The final result that we obtain by this construction is a device that is able to generate a voltage and a current density inside the circuit attached to it. Still, the voltage and the current generated are not really as we might expect them to be. Usually, current and potential are linearly related via Hom's law, but here the relation between current density and cell potential is not, showing also the equilibrium point with no current $\mathbf{J} = 0$ at $\Delta V \neq 0$, as we can see in Fig. (1.2). Such a peculiar behavior can be described by the fact that simply the potential generated by the cell is not simply given by electrostatic interactions but a complex series of interfaces and chemical phenomena enters to play arising two questions: how to define the potential in electrochemistry, and what properties are affecting the current-potential characteristic? Both of the questions will be answered during this last part of the course, but we will try to give a simple explanation for the second one right now.

First, we should consider how inside the I-V characteristic showed in Fig. (1.2) the current density increase suddenly to then reach a plateau. That is our range to work with it, basically having a constant supply of current is exactly what we want from a battery, also if we would to go further the current will start to grow exponentially. That is due to reaching a value of the potential in the cell that is able to generate redox also inside the electrolyte oxidizing it, and is something that we want to avoid. Therefore, we will focus on the first part of the curve in the first quadrant, as showed in the figure on the right of Fig. (1.2). Inside that window we can identify two main regions to work with:

Non-Faradic. The first part where no current is present since the charge is accumulating near the electrodes as a capacitor charging. Possible presence of small capacitive current;
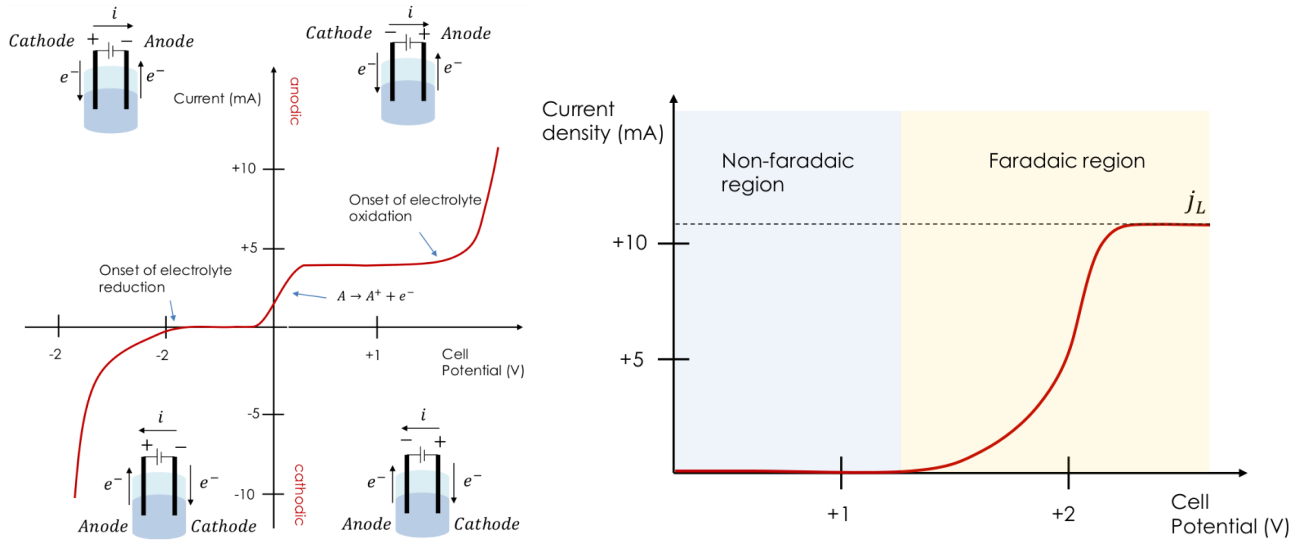
Figure 1.2: Graphics of the characteristic of a general electrochemical cell, with a close up on the first, and most important, quadrant. In the first quadrant we can see how the current will reach a plateau in the last part, that is due to the presence of diffusion inside the system that limits the speed at which the electrons can be emitted.

Faradic. The current becomes proportional to the reaction rate and starts to grow rapidly.

The latter region is the interesting one, and we can see how the first part, called **activation control**, shows an exponential growth of the current since the reaction starts and the electrons are generated with speeds proportional to the potential. Meaning that in this reagion a lot of factors, like: catalytic properties of the surface, area, adsorption, and concentration of species, are all important to the determination of the power supplied. Then, a rapid growth happens, and the constant current is reached in a situation called **mass-transport control**. The latter is a region of the graph where J is dictated by the velocity of diffusion inside the electrolyte, since the electrons goes much faster than the ionic species needed to make the reactions the numbers of electrons per unit time that pass through the circuit is limited by the flux of ions. Therefore, the current in the two regions can be described by

$$J_{ac} = nFk_{ct}c_x, \qquad\qquad J_{mt} = nFDc_b, \qquad\qquad (1.3)$$

where F is the charge inside one mole of electrons, and n the moles generated. Then, also the region in between, called **Mixed control** can be easily described using these two results since it's a mixture of the two often approximated with

$$\frac{1}{J} = \frac{1}{J_{ac}} + \frac{1}{J_{mt}}. \qquad\qquad (1.4)$$

In this way we can understand how the choice of the electrolyte is really important, since it's diffusion properties will determine the current density generated in the electrochemical window of the device.

Example 1.1.1 (Lead-Acid Battery)

A good example of battery that we can look at just a moment is the Pb one, where the anode and cathode are created by bars of pure Pb and PbO_2 with an acid electrolyte. The reaction that happens inside the system are

$$Pb + SO_4{}^{2-} \longrightarrow PbSO_4 + 2\,e^-,$$
$$PbO_2 + SO_4{}^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O,$$

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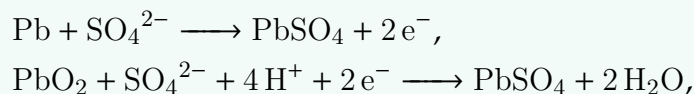
Then, imagine that we use the battery for an hour at a constant current of $20\,\text{A}$, we can compute the amount of lead needed to sustain such power supply. The charge that is transported is $Q = It$, where we know both of them having that $72\,000\,\text{C}$ is effectively transported from anode to cathode, meaning $n_e = Q/F = 0.746\,\text{mol}$. Therefore, we can compute the moles of lead needed to generate such amount of electrons by using the first semi-reaction and see how

$$n_{Pb} = n_e/2 = 0.373\,\text{mol} = 154.5\,\text{g},$$

not a small amount due to the high weight of lead. For that reason the Lithium batteries seems better, Li is lighter needing less weight for the same amount of power.

> **Note**
>
> *The most used types of electrolytes are liquid where salt is inserted in order to generate ions that can freely move inside. In this way a high mobility is achieved, but a large research is present in this field, especially to create efficient solid state electrolytes with high enough diffusivity to work nicely and also reduce the problematics related to using liquids, such as safety due to flammability. By now some solid state devices are used but since D increase with temperature are mainly used for particular application where we need to work in hot systems.*

Thermodynamics of an electrochemical cell

After this long introduction we can try to dig in the thermodynamics of the system and try to set up the basis for the discussion of specific devices. The first thing that we need to define is the concept of reversibility, which in electrochemistry is slightly different from the one we expect. The idea is that when performing an electrochemical reaction we can evaluate the value of the voltage between electrodes in the equilibrium state V_0 and then, if the reaction is **reversible**, we are able to promote either the forward and reverse reaction by applying a positive or negative bias to the system. In this sense we can give a really simple and general definition for the reversibility of a reaction as follows.

> **Definition 1.1.2: Microscopic reversibility**
>
> Infinitesimal change in a driving force causes the reaction to reverse direction.

This definition is intrinsically different from the real thermodynamic definition of reversible, but we can see how they are related somehow. In particular, a chemical reaction that is irreversible in this sense is also thermodynamically irreversible, but if is reversible is not sad to be reversible in the real sense. Still, in general all of this is thought in terms of reaction rates for reversible reactions, having that if the rate of advancing K_a and going back k_b are nearly equal is reversible, if instead $k_a \gg k_b$ than is irreversible. Basically, you only need to thing in terms of k in a reaction to say if it is reversible or not.

Knowing that we can start by thinking about the main quantities that will play a role inside the thermodynamic of the system, and since I would not like to stay here and describe one by one a series of tedious definition I will report the table given in the slides in Tab. (1.1). With the latter we can a more into the thermodynamic of the system and see how the flux that defines the direction of the reaction looks like in this context. Let's take the chemical potential of component i to write down the following

Table 1.1: Table with definition of all the types of variables we are going to use in this study and so on.

Term	Symbol	Unit	Definition	Use
Electrochemical potential	$\overline{\mu}_j^\alpha$	J/mol	partial molar Gibbs free energy of a given species j in phase α	defines criteria for equilibrium; differences in $\overline{\mu}_j^\alpha$ drive the transport, transfer, and reactivity of both charged and uncharged species
chemical potential	μ_j^α	J/mol	partial molar free energy of a given species j in phase α neglecting electrostatic contributions	differences in μ_j^α describe driving force for reactions between uncharged species and the direction of diffusive transport
electric potential	ϕ	V	electric work needed to move a test charge to a specific point in space from a reference point (often at infinite distance) divided by the value of the charge	defines direction of electron transport in metals; gradient gives electric field; used to calculate electric potential energy
electrode potential	E_{we}	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) to the working electrode	indicates oxidizing or reducing power of an electrode; related to the Fermi level of electrons in electrode
solution potential	E_{sol}	V	free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) into the bulk of a solution via a redox reaction	indicates oxidizing or reducing power of electrons involved in electrochemical redox equilibria; related to "Fermi level" of the electrons in solution and equivalent to the solution reduction potential
overpotential	η	V	generally, the difference between the applied electrode potential and the electrode potential when in equilibrium with the target electrochemical reaction	η·F gives the heat released, above that required by thermodynamics, per mole of electrons to drive an electrochemical process at a given rate; $F = 96485$ C·mol^{-1}

relation as the flux of that component

$$\mathbf{J}_i = -\left(\frac{c_i D_i}{RT}\right)\boldsymbol{\nabla}\mu_i, \tag{1.5}$$

where the chemical potential of a specie in solution will be defined as

$$\mu_i = \frac{\partial G}{\partial n_i} = \mu_i^0 + RT\ln(a_i), \qquad\qquad a_i = \gamma_i(c)c_i. \tag{1.6}$$

Basically, the potential the same as we have already seen, with the activity coefficient present. Still, this definition does not take into account the electrostatic effect presents, that we can insert by using the potential per mole in phase α called ϕ^α.

> **Definition 1.1.3: Electrochemical potential**
>
> The chemical potential of the i-th component of an electrochemical system needs to take into account also the electric potential per mole in the phase α in which is present, ϕ^α, giving
>
> $$\overline{\mu} = \mu_i + z_i F\phi^\alpha, \tag{1.7}$$
>
> where z_i is the charge number on the specie we are looking at.

That is the real potential we are going to use, so that the condition on the equilibrium of the system is given in terms of $\overline{\mu}$ and not simple μ. For this reason even if all the electrochemical potential of the species are equal still we can have differences in electrical potential, generating potential differences even at equilibrium called cell potential. Also, it's interesting to see how inside the definition of Eq. (1.7) we have how the chemical potential describe the short-range interactions while the electrical part counts for the long range since

$$\mu_i \propto r^{-6}, \qquad\qquad z_i F\phi^\alpha \propto r^{-1}. \tag{1.8}$$

Therefore, we can have one component that wins on the other in specific situations, but still the two are strictly related. In particular, the real measurable quantity is $\overline{\mu}$ it's not possible to evaluate μ or ϕ separately since the measure of a potential always imply the creation of an interface during the measurement having both in the final result.

The new definition of $\overline{\mu}$ can be put at use in a really simple way. For example, we can imagine taking a metal and apply a potential on it so that the electrochemical potential difference of the electron in two different positions of the material becomes

$$\Delta\overline{\mu}_e = \overline{\mu}_e^\alpha - \overline{\mu}_e^\beta = \mu_e^\alpha - zF\phi^\alpha - \mu_e^\beta + zF\phi^\beta = -zF\Delta\phi. \tag{1.9}$$

Where we assumed that the chemical potential of the single electron remained equal inside the metal. Using this result we can see how the flux of electron can be written as

$$\mathbf{J}_e = -\left(\frac{c_e D_e}{RT}\right)\nabla\overline{\mu}_e = zF\left(\frac{c_e D_e}{RT}\right)\nabla\phi = R\nabla\phi, \tag{1.10}$$

the Hom's law was simply found. Still, this is only a trivial application what we want to do is studying what happens when two metals touching each others in equilibrium. Where we can easily see how the following becomes true.

> **Theorem 1.1.1: Interface potential**
>
> When two metals M_1 and M_2 are in contact with each others a potential difference appear at equilibrium in the interface of the two solid phases given by
>
> $$\Delta\phi^{M_1-M_2} = \frac{\Delta\mu_e^{M_1-M_2}}{zF}. \tag{1.11}$$

Proof: That is incredibly easy, you only need to recall how the equilibrium condition in this case become $\overline{\mu}_e^{M_1} = \overline{\mu}_e^{M_2}$ so that you place them equal and obtain the result. ☺

Therefore, using the electrochemical potential is really helpful in the study of how the chemistry of the system mix with its electrical properties. For this reason it's the main quantity that we are going to study inside batteries, and we can predict cells behaviors with that.

Interface at equilibrium

To understand how the electrochemical cell works properly we need first to develop a way to study how solid liquid interface works in general, since the cell is composed by two metal electrodes inside a liquid electrolyte in general. We have already seen what happens with solid-solid interface, but now we aim to look more into the equilibrium of a reduction reaction like

$$O + ne^-(M) \rightleftharpoons R. \tag{1.12}$$

In such an equation we can easily find out the potential difference generated by the transport of electrons at equilibrium by the following important result.

> **Theorem 1.1.2: Nernst equation**
>
> The electrode potential generated by a redox reaction at equilibrium E, depend both on ambient condition and chemical properties of the system through the relation
>
> $$E = E_{O/R}^0 + \frac{RT}{nF}\ln(a_O/a_R), \tag{1.13}$$

> where $E^0_{O/R}$ is also called standard electrochemical potential.

Proof: we can start by setting the equilibrium by doing the following operation

$$\Delta \overline{\mu}_e = \overline{\mu}^s_R - (n\mu^M_e + \mu^s_O) = 0, \tag{1.14}$$

where the up scripts s and M tells us if the element is in the electrolyte solution or in the solid component. Then, by using the definition of electrochemical potential and the fact that $z_R = z_O - n$ with $z_e = -1$ we can obtain

$$z_O F(\phi^s - \phi^M) = (\mu^s_R - \mu^s_O) - n\mu^M_e, \tag{1.15}$$

where the contributions from electrostatics, chemistry of the solution and the one of the solid were divided. We can now use the fact that $\mu_i = \mu^0_i + RT \ln a_i$ to retain the following form

$$-\frac{z_O}{n}(\phi^s - \phi^M) = -\frac{\mu^{0,s}_R - \mu^{0,s}_O}{nF} + \frac{\mu^M_e}{F} + \frac{RT}{nF} \ln(a_O/a_R). \tag{1.16}$$

Here we can finish the job by defining the two main variables in the Nernst equation as follows

$$E = -\frac{z_O}{n}(\phi^s - \phi^M), \qquad E^0_{O/R} = -\frac{\mu^{0,s}_R - \mu^{0,s}_O}{nF} + \frac{\mu^M_e}{F} = -\frac{\Delta G^0}{nF}. \tag{1.17}$$

This also shows how the standard potential is also related to the form of the free energy difference. ☺

That is a powerful result, but still works only at equilibrium and understand when interfaces are at equilibrium may not be so easy. We can generally say that if the charge transfer kinetics is very fast we can be in Nernstian conditions since the superficial activity rapidly equilibrates before mass.

Now, we can imagine to level up and take into account a full cell composed by two electrodes in an electrolyte solution, so that two redox happens one for M_1 and one for M_2. Now, in order to work better with our system we are going to assume that the electrolytes solutions are separated by a porous material that allows still for charge equilibrating still avoiding the contamination of reactants. In this way the electric potential in the solution ϕ^s is constant so that by writing the $\Delta \overline{\mu}$ for both reaction and sett equilibrium we obtain Eq. (1.15) for both metals which can be summed up in order to obtain

$$-z_{O2} F(\phi^M - \phi^{M2}) = \frac{z_{O2}}{z_O}(\mu^s_R - \mu^s_O) - z_{O2}\mu^M_e - (\mu^s_{R2} - \mu^s_{O2}) + z_{O2}\mu^{M2}_e. \tag{1.18}$$

By assuming that $\mu^M_e = \mu^{M2}_e$ we can obtain a form of the potential between the electrodes, that is generated by the cell, depending on the chemical properties of the two semi-reactions present inside the cell. In particular, if we define the cell potential E_{cell} to be that potential energy difference we can transform Eq. (1.18) into

$$E_{cell} = E_{right} - E_{left}. \tag{1.19}$$

Meaning that if we know the variation of the potential at the interface for the single reactions we can compute the total one. In particular, we can also have a look at how this knowledge can be used inside in order to evaluate the free energy difference of the reaction as follows.

> ### Theorem 1.1.3: Gibbs and electrode potential
> inside an electrochemical cell the variation of free energy of the system is proportional to the electrode potential following the relation
>
> $$\Delta G = -nFE_{cell}. \tag{1.20}$$

Proof: For a generic reversible reaction in a closed system the maximum amount of work that can be extracted from the cell is $\Gamma = -W_{chem}$. If that work is extracted through heat dissipation we can say that the chemical work is equal to the electrical one, which is given by the simple relation

$$W_{el} = nFE_{cell}. \tag{1.21}$$

Which is the work done on every moving charge present, completing the result. ☺

That is great, since that tells us that if $E_{cell} > 0$ than the reaction is spontaneous. Meaning that only by looking at the components used in the cell and their reduction potentials, since the energies E are referred to the reduction reaction $\mu_R - \mu_O$, we can tell not only what E will be, but also in which direction it will point.

　　The fact that the potential is strictly related to the free energy allows us also to write down another important relation that generalize Nernst equation and probably is the real version for physicist.

> ### Theorem 1.1.4: Generalized Nernst equation
> Consider a generic reaction at equilibrium $n_{R_1} R_1 + \dots \longrightarrow n_{P_1} P_1 + \dots$ we can write down the electrode potential of the cell using
>
> $$E_{cell} = E_{cell}^0 + \frac{RT}{nF} \ln \left(\frac{\prod_i a_{R_i}}{\prod_i a_{P_i}} \right). \tag{1.22}$$

Proof: Basically we know how the change in free energy can be written up using the chemical potentials as

$$\Delta G = \sum_i n_{P_i} \mu_{P_i} - \sum_i n_{R_i} \mu_{R_i}. \tag{1.23}$$

Then we can recall the form of the chemical potential $\mu = \mu^0 + RT \ln a$ to obtain directly the final form by dividing by $-nF$. ☺

That will allow to compute the cell potential also in the case of more complex reactions, which is really important for applications. Still this formula imply that we know the values of the reduction potential of all the elements in the reaction, meaning that we need to understand how to evaluate them. The latter is not a trivial task, since if we want to evaluate the potential at an interface directly I need to insert in the system a third element, a voltmeter, which creates a new interface modifying the properties. The idea is, therefore, to place the electrode of which we want to evaluate the potential, called **working electrode** (WE), inside a cell where the other electrode is a standard reference, **reference electrode** (RE). So that, we can evaluate E_{cell} by simply measuring the one between electrodes and then obtain the final result

$$E_{WE} = E_{cell} + E_{RE}. \tag{1.24}$$

In order for such measurement to be precise we will need for the RE to possess the properties of an **ideal non-polarizable electrode**, meaning that the value of E_{RE} does not depend on the bias applied to the system. The latter usually comes from a third electrode called **counter electrode** (CE), from which a current is inserted in the circuit in order to flow from CE to WE, RE is only used for potential measurement. Therefore, to construct a good RE, that has a constant potential not varying with change in the applied current, is often composed by a metal wire in a solution containing a redox couple providing:

1 Reversible reaction with fast kinetics, allowing the use of Nernst equation;

2 Essentially constant composition;
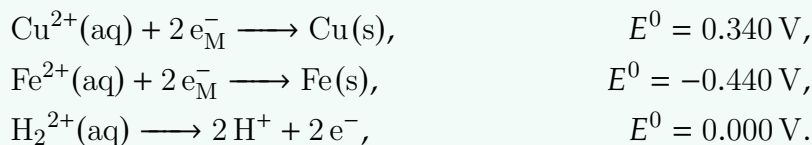
3 Ionic conduction to close the electrochemical circuit.

A good example of such reference electrodes is the hydrogen one, which is generally used as standard having a potential sett to $E^0 = 0\,\text{V}$.
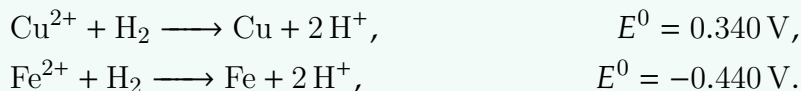
> **Note**
>
> *He also showed a particular type of diagram that can be used in order to study redox reaction called Pourbaix diagram, which simply is a phase diagram for the reduction of one electrode in the cell as a function of pH of the solution and equilibrium potential, E_{cell}.*

Example 1.1.2 (Cu/Fe-H cell)

We have made a simple example taking looking at the values of the potential generated by a Cu-H cell and a Fe-H cell. To do that you need to look at an online table and search for the semi-reaction to find out how

$$Cu^{2+}(aq) + 2\,e_M^- \longrightarrow Cu(s), \qquad\qquad E^0 = 0.340\,\text{V},$$
$$Fe^{2+}(aq) + 2\,e_M^- \longrightarrow Fe(s), \qquad\qquad E^0 = -0.440\,\text{V},$$
$$H_2^{2+}(aq) \longrightarrow 2\,H^+ + 2\,e^-, \qquad\qquad E^0 = 0.000\,\text{V}.$$

Combining them we can find out the cell potentials for the two complete electrochemical reactions as

$$Cu^{2+} + H_2 \longrightarrow Cu + 2\,H^+, \qquad\qquad E^0 = 0.340\,\text{V},$$
$$Fe^{2+} + H_2 \longrightarrow Fe + 2\,H^+, \qquad\qquad E^0 = -0.440\,\text{V}.$$

Meaning that the reduction of Copper is spontaneous, while the one of Iron requires energy since naturally it will oxidase.

1.2 Electrode's Kinetics

We will now focus on the study of the kinetics of the electrochemical reactions happening on the electrodes boundaries. In particular, we will first start searching for a way to describe the transport of charge

inside the system to then go into the mass transport phenomena. In this optics it will be quite useful to first recall some quantities that will be used inside the discussion.

Consider a general reduction reaction happening at an electrode, which can be written in the following form

$$O + ne^- \rightleftharpoons R. \tag{1.25}$$

We will describe the rates at which a reaction take place by using the flux ν of electrons' moles that travels through the electrode surface. In this way we can describe also the current density on the surface by

$$J = nF\nu, \tag{1.26}$$

where n is the number of mole of electrons involved in the reduction reaction. Also, we know how both sides of the reaction are characterized by a transition rate k_f and k_b for the forward and backward direction, respectively. Such rates can be related to the flux easily by using the components surface density $C_i(x,t)$ and focus on the density at the surface as follows

$$\nu_f = k_f C_O(0,t) = \frac{i_f}{nFA}, \qquad\qquad \nu_b = k_b C_R(0,t) = \frac{i_b}{nFA}, \tag{1.27}$$

where the surface was assumed to be at the position $x = 0$. If we connect this results we are already able to write down a form for the electrical current present in the system as

$$i = i_f - i_b = nFA[k_f C_O(0,t) - k_b C_R(0,t)]. \tag{1.28}$$

We only need to find a form for the quantities inside the equation, and that is basically what we are going to do in this section.

Nevertheless, to be ready for that we shall also recall how we already know how k can be computed by the use of transition state theory

$$k = k_0 \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right). \tag{1.29}$$

Where $\Delta G^\ddagger$ is the height of the barrier that separates the two states involved in the reaction, and the quantity κ is called transmission coefficient expressing the probability to decay from the transition state to products.

Butler-Volmer model

To study the kinetics of electrons in the system we start from a standard condition of equilibrium in a one-electron single step reaction, which we approximate as in Fig. (1.3). In that figure two conditions are depicted, a first one where we are in equilibrium so that the minima sits at the same height having so the same $\Delta G^\ddagger$ and therefore same rate, leading to $J = 0$. Then, we have the case where an external bias is applied and the energy of the electrons falls setting the reactants at lower potential generating a variation in the forward and backward barriers that can be estimated as follows

$$\Delta G_c^\ddagger = \Delta G_{0,c}^\ddagger - \alpha F(E - E^0), \qquad\qquad \Delta G_a^\ddagger = \Delta G_{0,a}^\ddagger + (1-\alpha)F(E - E^0).$$
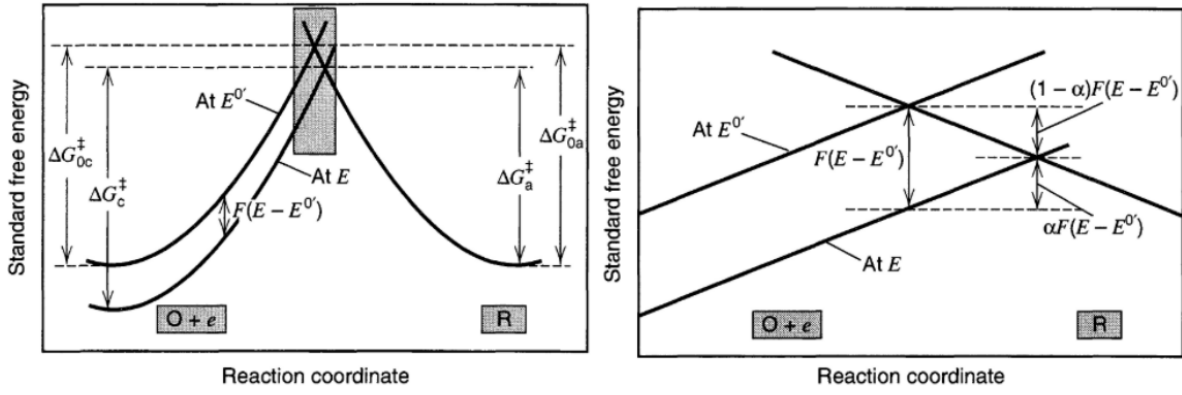
Figure 1.3: Approximation of the potential energy landscape inside a general reaction for some reaction coordinates. We are basically assuming that the reactants and products are minima in the energy and approximating the surrounding potential using second order Taylor expansion, so that the potential barrier is given by the interception of the parabolas.

Where α can be seen as an asymmetric factor, called transfer coefficient, that can range from zero to unity. Using these relations allows us to write down a form for the rates by inserting them inside Eq. (1.29) to obtain

$$k_c = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,c}^{\ddagger}}{RT}} \exp\left(-\frac{\alpha F(E - E^0)}{RT}\right),$$
(1.30)

$$k_a = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,a}^{\ddagger}}{RT}} \exp\left(-\frac{(\alpha - 1)F(E - E^0)}{RT}\right).$$
(1.31)

Knowing all of that we are able to obtain a really important result that is able to tell us the entity of the current inside our system as follows.

> **Theorem 1.2.1: Butler-Volmer equation**
>
> The current flowing through the interface of an electrode, performing a general redox reaction, inside a well stirred solution is given by the equation
>
> $$i = i_0 \left[e^{-\alpha \frac{F\eta}{RT}} - e^{-(\alpha - 1)\frac{F\eta}{RT}} \right].$$
> (1.32)
>
> Where i_0 is the equilibrium current at the cathode and anode, while η measure the bias applied as the difference between the cell potential and the standard one.

Proof: From Eq. (1.30) and Eq. (1.31) we can see how, since the system was supposed to be in equilibrium without bias, meaning $E = E^0$, the rates have the properties of $k_c(E = 0) = k_b(E = 0)$. This brings us to write down that

$$k^0 = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,c}^{\ddagger}}{RT}} = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G_{0,a}^{\ddagger}}{RT}},$$
(1.33)

which substituted back into the equation and inserted inside Eq. (1.28) gives the result

$$i = FAk^0 \left[C_O(0, t) e^{-\alpha \frac{F(E-E^0)}{RT}} - C_R(0, t) e^{-(\alpha-1)\frac{F(E-E^0)}{RT}} \right].$$
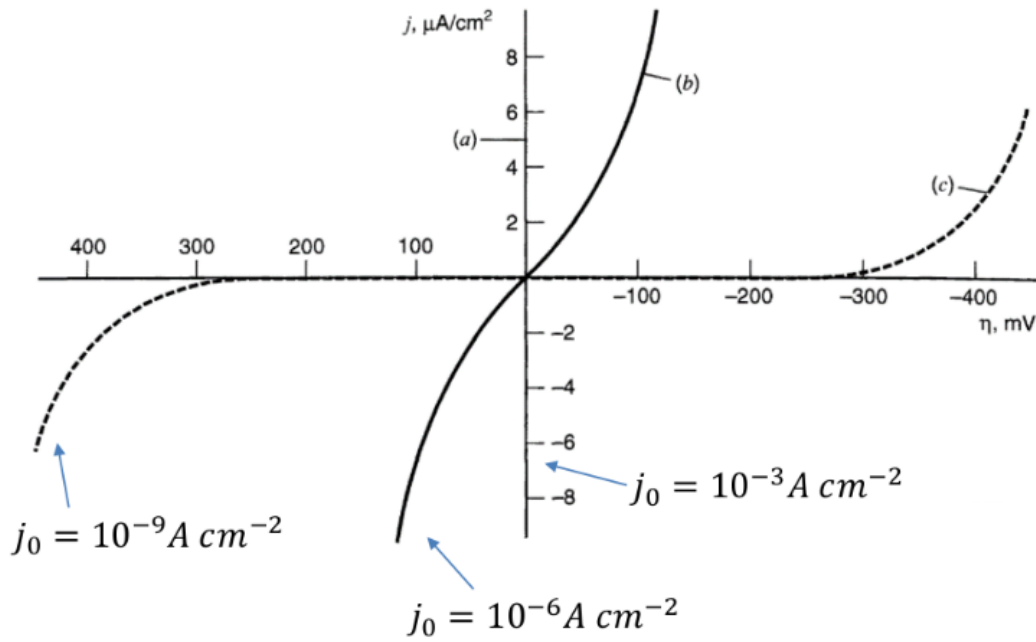(1.34)

Figure 1.4: Graphic of the net current inside the cell as a function of the overpotential for different values of the exchange current, showing how the value of i_0 gives a great contribution to the overall current.

Now, in the equilibrium we have that $i = 0$ meaning how $i_c = i_a = i_0$ taking the name of **exchange current**, which can be found out easily from previous equation. In fact, by assuming equilibrium mass transfer is much faster than charge one surface concentration in electrode is equal to bulk one $C_0(0, t) = C_{O,b}$, so that we can write down

$$i_0 = FAk^0 c_{O,b} e^{-\alpha \frac{F(E_{eq} - E^0)}{RT}}. \tag{1.35}$$

Since the system is at equilibrium we can use also Nernst equation in order to express the value of E_{eq} as a function of concentration so that we can rewrite i_0 as

$$\frac{C_{O,b}}{C_{R,b}} = \exp\left[\frac{F}{RT}(E_{eq} - E_0)\right], \qquad\qquad i_0 = FAk^0 C_O^{1-\alpha} C_R^{\alpha}. \tag{1.36}$$

Inserting it inside the previous equation of i and defining the **overpotential** η as the difference $E - E_0$

$$i = i_0 \left[\frac{C_O(0, t)}{C_{O,b}} e^{-\alpha \frac{F\eta}{RT}} - \frac{C_O(0, t)}{C_{O,b}} e^{-(1-\alpha)\frac{F\eta}{RT}}\right], \tag{1.37}$$

then in a stirred solution we also can assume that the surface concentration is equal to bulk one even out of equilibrium having that the fracions simplifies obtaining the right equation wanted. ☺

This equation is the key to understand how we can act on the variables of the system in order to boost the kinetics of the reaction. In particular, we can see how increasing both the external bias or the temperature can have huge effect on the reaction itself due to the exponential dependence. Also, one can see how the value of the exchange current posses a really important role since we can see from Fig. (1.4) how a lower i_0 gives a more **sluggish kinetics**. Where, a kinetics is more sluggish if you need a higher potential in order to obtain any net current at all inside the system.

Knowing such form for the current we can use it in order to perform some interesting computations regarding the kinetics properties. In particular, we can extract information about α and i_0 thanks to low

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and large η regime. In the former case we have that a Taylor expansion leads us to the linear form

$$i = -R_{ct}\eta, \qquad\qquad R_{ct} = \frac{i_0 F}{RT}, \qquad (1.38)$$

the resistance R_{ct} is called **charge-transfer resistance** and represent the impedance to charge transport intrinsic in the solution. Then, we can look at the case where $\eta \gg 1$, so that one of the two terms in the Butler-Volmer equation dominate so that we can easily write down

$$i = i_0 e^{-\alpha \frac{F\eta}{RT}}, \qquad\qquad \eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i. \qquad (1.39)$$

Therefore, the potential linearly depends on the logarithm of the current giving rise to the form $\eta = a + b \ln i$ also called **Tafel theory**. The two constants inside such equation can be obtained with ease in experiments allowing us to estimate the values of both α and i_0.

Mass transfer kinetics

Butler-Volmer model allowed us to see how the kinetics of the system depends also on the surface concentration at the electrodes $C_i(0, t)$, which changes over time due to mass transport inside the material. Thus, we can't limit ourselves to the simple study of charge transport but to obtain a satisfying result we shall account also for the mechanisms of migration, convection and diffusion of material that can limit the flux of ions in the cell. In order to create such a model we are going to suppose to work in Nernstian conditions, so that equilibrium is present and the potential is given by Nernst equation, and we will also assume that the reaction is governed mass transport. Meaning that the rate at which the electroactive species is brought to the surface defines the current density

$$J = nF\nu_{nt}, \qquad (1.40)$$

where ν_{nt} is the flux of matter inside the electrolyte. Nevertheless, that is only the beginning of the model what we need to do now is to find out a more precise way to describe it.

The best way to model the flux of particle we can use a general form given by the sum of the contribution given by the three main processes mentioned before

$$\nu_i(x) = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial \Phi}{\partial x} + c_i v(x). \qquad (1.41)$$

Where we have, in order, diffusion, migration and convection contribution, and v represent the velocity of the solution in a certain point. Obviously such an equation is really complex, therefore we usually need to simplify it by setting ourselves in a situation where one or two contributions can be neglected such as:

Diffusion. Introducing stirring;

Migration. Addition of a concentrated supporting electrolyte;

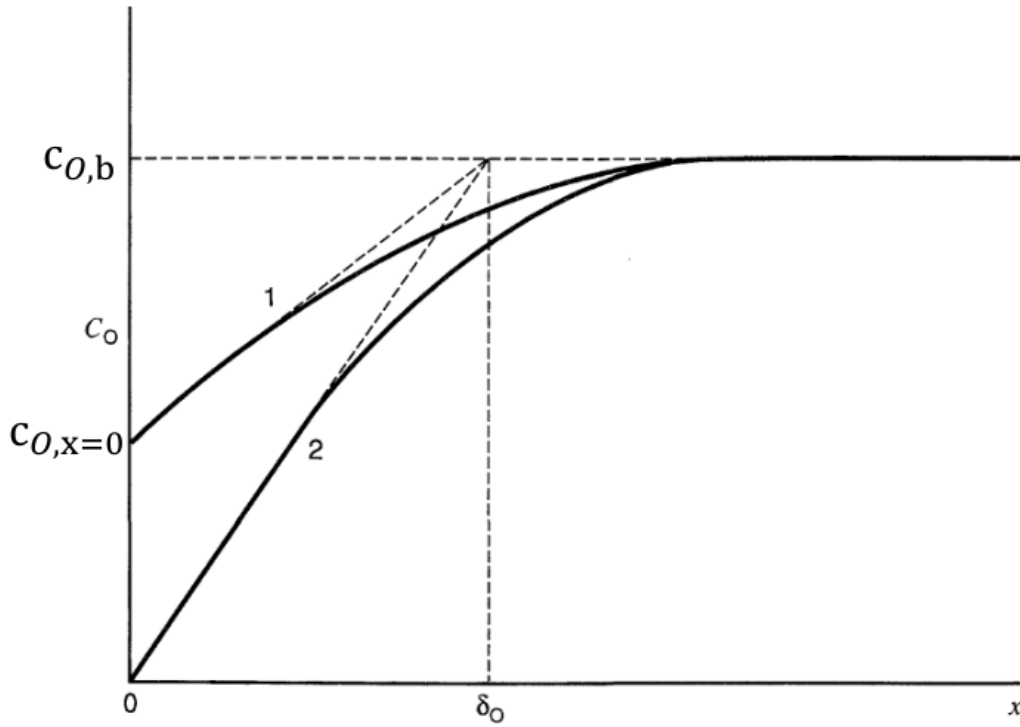**Convection.** Avoiding vibrations or stirring.

Figure 1.5: Representation of the concentration gradient approximation to understand what δ effectively looks like and how the concentration is.

Therefore, we can choose to use one or more trick in order to eliminate the related processes. Thus, we are going to imagine to work in a diffusion limited process so that v_i is defined simply by Fick's first law and the current density becomes

$$J = nFv_d = nFD \left.\frac{dC_O}{dx}\right|_{x=0}. \tag{1.42}$$

Where the derivative is evaluated at the interface and in a stirred solution we can assume that the bulk concentration is stable in the middle of the solution, meaning that C_O is constant at $C_{O,b}$ for x large enough. In this way we can approximate the derivative simply as a difference of the kind

$$J \approx nFD \frac{C_{O,b} - C_O(x=0)}{\delta}, \tag{1.43}$$

where δ is a constant that needs to be tuned in order to optimize the approximation called **Nernst Diffusion Layer thickness** and can be seen in Fig. (1.5). From that we can see how the diffusion is quicker the smaller δ is or the more negative the potential becomes. Still, it's quite difficult to know the value of δ so that it's value is usually combined with the diffusivity defining the **mass-transfer coefficient** $m_i = D_i/\delta_i$. This relation can be used in order to describe the limiting behavior that the mass transport has on the kinetics of the reaction by seeing the following result.

> **Theorem 1.2.2: Limiting current**
>
> Inside an electrochemical cell where mass transport is driven by diffusion the system posses a limiting current given by
>
> $$J_L = nFm_OC_{O,b}. \tag{1.44}$$

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Proof: Since electrons travels at higher speeds respect to diffusion of ions in the solution, the rate of the reaction is limited for high value of the overpotential by the maximum flux of ions possible in the electrolyte. In particular, we have seen how Eq. (1.43) gives a way to estimate the rates inside the system for both O and R transfer, where the latter can be expressed by changing the constants and remembering how the electrode is positioned on the right and the solution on the left, so you need to invert the concentrations

$$J = nFm_R(C_{R,x=0} - C_{R,b}).$$ (1.45)

In both equations we can see how the maximum possible value that we can obtain is when the density of element on the surface of the electrode is zero, $C_{O,x=0} = 0$. That is the maximum flux that we can obtain, giving rise also to the maximum possible current inside the system. ☺

This relation can also be used in order to rewrite the concentrations of the elements in the solution in a simpler way. In particular, if you use the previous relation alongside with the form of the limiting current we can obtain that

$$C_O(x = 0) = \frac{J_L - J}{nFm_O}, \qquad\qquad \frac{C_O(x = 0)}{C_{O,b}} = 1 - \frac{J}{J_L},$$ (1.46)

which will be really useful in further descriptions. In particular, using such relations one can see how a value for the cell potential can be found out by assuming how the initial concentration of reduced specie is zero $C_{R,b} = 0$. This assumption inserted inside Eq. (1.45) allows us to obtain $C_{R,x=0} = J/nFm_R$ which inserted inside Nernst equation, alongside with Eq. (1.46), to obtain

$$E = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{J_L - J}{J} \right).$$ (1.47)

Such equation shows interesting behavior since all the quantities inside it are easy to evaluate experimentally, still only works if at the start of the reaction only one element is present in the solution. Nevertheless, we can see how at a certain value of the current $J = J_L/2$ the equation simplifies a lot, having

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R},$$ (1.48)

which value is often taken equal to E^0 since $m_O/m_R \approx 1$ in most of the cases. Therefore, that value is often used in order to rewrite the total equation substituting it, giving the final general form of the equation

$$E = E_{1/2} + \frac{RT}{nF} \ln \left(\frac{J_L - J}{J} \right).$$ (1.49)

In reality is possible to describe a model also for the case where both reduced and oxidized species are present inside the solution at time zero. In that case is important to take into account that two different limiting currents are present inside the material, one in the cathodic and one in the anodic direction as

$$J_{L,c} = nFm_O C_{O,b}, \qquad\qquad J_{L,a} = -nFm_R C_{R,b}.$$ (1.50)

Which comes out from the same theory used previously to find Eq. (1.44), meaning that the relations Eq. (1.46) are valid also for C_R. In this way we can substitute everything inside the Nernst equation to gain the final general result

$$E = E^0 - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{J_{L,c} - J}{J - J_{L,a}} \right).$$ (1.51)

This is a more general result that can be used, which also posses a peculiar property. In fact, is possible to see by this equation how the potential at equilibrium, $J = 0$, gives out exactly Nernst equation $E^0 + RT \ln(C_{O,b}/C_{R,b})/nF$.

All of this theory is great but is only an approximation frozen in time to estimate the limiting current. In reality, the value of J_L can change overtime due to changes in the concentration of the species inside the solution, but more importantly by the variation of the concentration gradient inside it due to diffusion processes. In particular, we can describe such a process by using the following result.

> **Theorem 1.2.3: Cottrell equation**
>
> If the reaction is Nernstian the limit current density decreases with time, following the equation
>
> $$J_L = nFC_{O,b}\sqrt{\frac{D}{\pi t}}. \tag{1.52}$$

Proof: If the reaction is Nernstian, the concentration at the electrode surface immediately adjusts to the equilibrium value, but its gradient slowly shifts due to diffusion. The thickness of the Nernst diffusion layer is then time-dependent

$$\delta(t) = \sqrt{\pi D t}, \tag{1.53}$$

which can be substituted inside Eq. (1.43) to obtain the result. Inside it, we assume $C_{O,b}$ is constant in time since if the solution is stirred it gets homogeneous in the bulk really quickly, the problem is only the gradient at the boundary. ☺

> **Note**
>
> *As it was sad the presence of convection allows us to assume $C_{O,b}$ constant over time inside Eq. (1.52), but it also generates one other thing. Basically, since the bulk concentration is homogeneous, the presence of convection is also limiting the diffusion in decreasing the gradient, meaning that when it is flattened to a certain point it can go any further since it needs to change the part of solution that has constant concentration thanks to convection. For this reason, in presence of convection $J_L(t)$ will not decrease indefinitely with time, but will reach a plateau.*

Microscopic theories for charge transfer

So far so good, nevertheless all the theory described right now are of a phenomenological type, focussing on describing the phenomena using a series of constant that we need to compute experimentally, like k^0 or α. Now we want to relax such condition creating a more fundamental model for charge transfer inside the solution that can limit the number of constant that we are using. Thus, we are going to describe a famous model called **Marcus model** which is able to find a form of the transition rate dependent only on one phenomenological constant that can be also modelled via first principles.

We are interested in study the exchange of one electron from the electrode, so a metal, to the oxidation molecule inside the solution. The latter, is going to be modelled as a metallic sphere with a certain dipole and dielectric constant, which can interact with the electrode in two main ways: **outer sphere**, where the molecule is separated from the surface by a layer of solvent so that the e^- needs to travel by tunneling effect, or **inner sphere**, where a strong interaction is present so that the molecule is close to the surface leading to the exchange. We are not going to pick one of the two cases, since both

will be described by the model, as we will see, which simply focus on the transfer of the charge making the following four assumptions:

Isoenergetic process. the electron must move from an initial state (on the electrode or in the reductant, R) to a receiving state (in species O or on the electrode) of the same energy;

Franck-Condon. Basically no change in the atomic configuration happens, meaning that the nuclei remains still since electronic processes are much faster respect to atomic ones;

Fixed position. The reactant O has fixed position with respect to the electrode;

Quadratic G. Standard free energies of O and R, G_O and G_R, depend quadratically on the reaction coordinate, q.

Keeping in mind such approximations we are able to find out a general way to write down the transition rate for the reaction in general as follows.

Theorem 1.2.4: Marcus result

Inside an electrochemical cell where the four conditions before mentioned are satisfied, the transition rate for the charge transfer process is given by

$$k = \kappa Z \exp\left[-\frac{\lambda}{4RT}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2\right], \tag{1.54}$$

where κ is usually taken as 1, Z is a function of an electrostatic and collisional term, and λ is the so-called reorganization energy accounting for both inner and outer interactions.

Proof: the free energy is approximated to a quadratic form, therefore we can write down

$$G_O(q) = \frac{k}{2}(q - q_O)^2, \qquad\qquad G_R(q) = \frac{k}{2}(q - q_R)^2 + \Delta G^0, \tag{1.55}$$

where k is a proportionality constant and ΔG^0 is the usual potential bias $F(E - E^0)$. Having both this values we can put them in a system and find out the point where the two curves intersect giving rise to the approximated transition state. Such a computation gives rise to the result

$$q^{\ddagger} = \frac{q_R + q_O}{2} + \frac{\Delta G^0}{k(q_R - q_O)}, \tag{1.56}$$

which can be used in order to evaluate the potential barrier for the oxidation process as $G_O(q^{\ddagger}) - G_O(q_O)$ which gives rise to

$$\Delta G^{\ddagger} = \frac{k(q_R - q_O)^2}{8}\left[1 + \frac{2\Delta G^0}{k(q_R - q_O)^2}\right]^2 = \frac{\lambda}{4}\left[1 + \frac{\Delta G^0}{\lambda}\right]^2. \tag{1.57}$$

Therefore, we have a form for the potential barrier which depends on the form of the reorganization energy. The latter can be evaluated by taking into account the inner and outer components' contribution
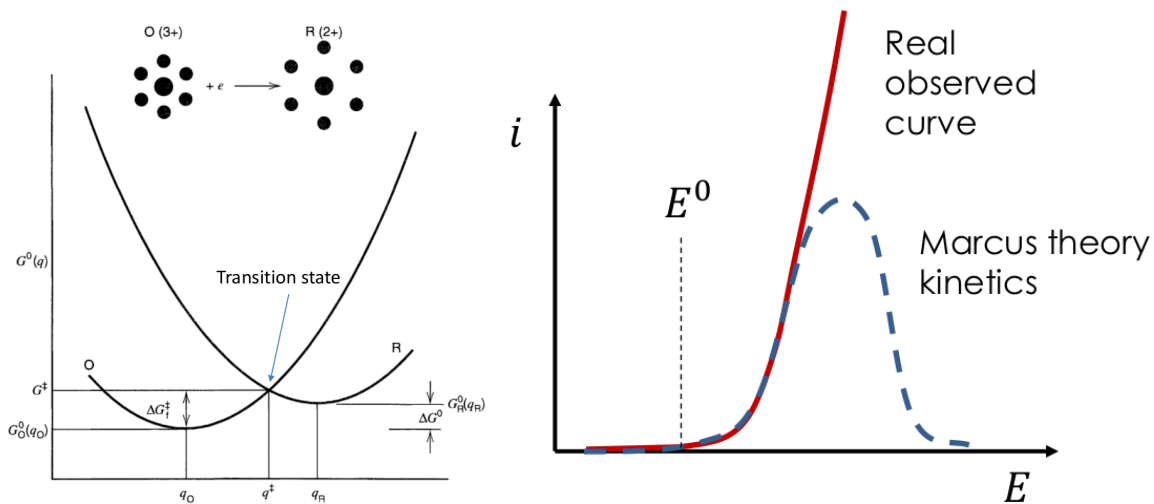
Figure 1.6: Representation of the energy landscape of the reaction in the Marcus approximation, on the left, and the graph of the result model obtained versus the experimental result, on the right.

to the reorganization of the species O and the solvent $\lambda = \lambda_i + \lambda_o$. Both of them can be modelled, the latter is given by the sum of normal vibration modes of reactants

$$\lambda_i = \sum_j \frac{k_j}{2}(q_{O,j} - q_{R,j})^2. \tag{1.58}$$

The latter, instead, is computed by calculating the ion-solvent electrostatic interaction for reactant and products, assuming the solvent as a dielectric continuum and the reactant a sphere of radius a_O

$$\lambda_o = \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{a_O} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right). \tag{1.59}$$

Where R is twice the distance of molecule and surface of electrode, while the dielectric constants are the one of the molecule and of the electrode. Knowing this we can insert that value inside the known form of the transition rate in order to obtain the wanted relation. ☺

This model is really great, showing how depending on the ratio $\Delta G^0/\lambda$ the reaction will actually change its velocity. In particular, we can see how for biases so that $\Delta G^0 < -\lambda$ we got $k \propto \Delta G^0$ reaching a maximum in $\Delta G^0 = -\lambda$ and then having $k \propto 1/\Delta G^0$ for higher values. This is a really strange behavior since experimentally the so-called **inverted region** is not seen, as we increase the potential the reaction speeds up and that was the reason because the model took some time to be accepted by the community. The reason why this happens are basically two: the first is that **O are not still**, basically as E is increase the molecule interact more with the electrode lowering the distance R and so increasing λ, and **More levels are involved**, the model we have described assumed that the electron transferred is taken from the higher level inside the electrode, the Fermi level, that is true only in practice since as we increase the potential the electrons in lower levels can be exited and transferred too.

    This theory can be in principle expanded in order to account better for such effect in a higher approximation by using the **Gerischer-Marcus model**. The latter uses the assumption that electrons are able to jump only from one occupied state into an unoccupied isoenergetic state, where the occupied state for a reduction is inside the metal electrode and the unoccupied is on species R in the solution, while for oxidation is the contrary. In this way the information we need in order to describe the evolution of
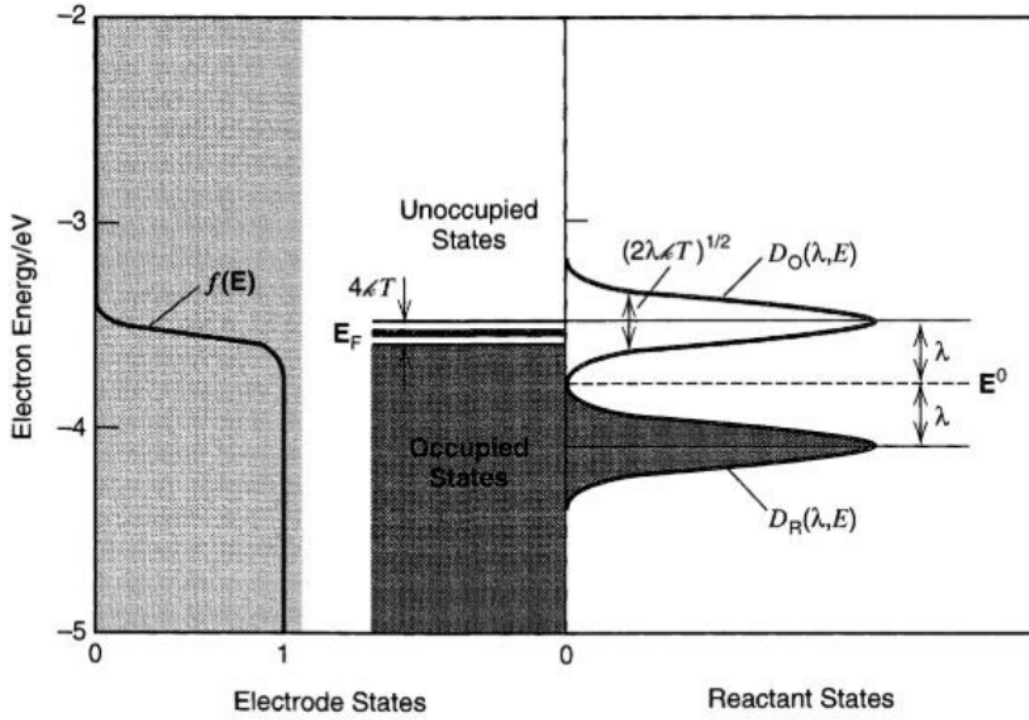
Figure 1.7: Example graph of the density of state of a metal near the concentration of the species energies, showing how the O states are able to overlap with occupied states, meaning that the integral for k_f is not zero allowing for the reaction to happen.

the reaction are contained inside the DOS of the metal and of the reactant. In particular, in this case it's better to express the density of states inside the solution using a concentration of type $D_R(\lambda, E)dE$, giving the concentration of species R in the solution in the energy range $[E, E + dE]$. We expect such concentration to be somehow proportional to the surface concentration of R on the electrode, so that we will assume the possibility to rewrite it as

$$D_R(\lambda, E) = N_A C_R(0, t) W_R(\lambda, E), \qquad \int_{\mathbb{R}} W_R(\lambda, E)dE = 1. \qquad (1.60)$$

Where the function $W_R(\lambda, E)$ can be thought of a probability density distribution of having the specie at that specific energy under the influence of that reorganization energy. Knowing this it's possible to obtain a result to describe the transitions rates for the oxidation and reduction reaction in terms of such functions as follows.

> **Theorem 1.2.5: Transition rates**
>
> The transition rates inside the Gerischer-Marcus model can be computed as the following integrals
>
> $$k_f = v \int_{\mathbb{R}} \varepsilon_{red}(E) W_O(\lambda, E) f(E) \rho(E) dE, \quad k_b = v \int_{\mathbb{R}} \varepsilon_{ox}(E) W_R(\lambda, E)[1 - f(E)] \rho(E) dE. \qquad (1.61)$$
>
> Where ε_{ox} and ε_{red} are proportionality functions involving the tunneling probability and precursor equilibrium constants. Also, $\rho(E)$ and $f(E)$ are DOS and Fermi function of the metal.

Using such results we are able to evaluate the transition rate in a general way, we only need to find out

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a way to model the probability density W. Such a task can be done by using once again the Marcus theory, which allows us to obtain the following forms

$$W_O(\lambda, E) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\left(E - E^0 - \lambda\right)^2}{4\lambda k_B T}\right],$$
(1.62)

$$W_R(\lambda, E) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\left(E - E^0 + \lambda\right)^2}{4\lambda k_B T}\right].$$
(1.63)

Such results show also how the states of O and R species have peaks of densities specular to each others and the transition rates increase as such peaks come closer to point of high density of states inside the metal, as we can see in Fig. (1.7). Therefore, based on the value of λ and of the Fermi energy, E_f, we are able to change the overlap of the states increasing k_f or k_b as we want. In fact, the value of E_f can be changed by an external bias, shifting it up and down the levels along with the direction of the reaction, as we have already seen previously.

> **Note**
>
> *Such a theory is particular good in order to describe the effect of using electrodes made of semiconductor, since their behavior can be easily described by the simple use of a density of state with a gap in the middle.*

1.3 Non-Faradic processes and Electrical Double Layer

So far we have described the evolution of the kinetics inside the solution inside a Faradic regime, still the system needs first to traverse a non-Faradic one where the double layer near the electrode gets created. Such a double layer is important to take into account inside experimental application since its presence can be seen as the adding of a condensator with capacity C_{dl} inside the circuit that the cell form, generating an **equivalent circuit** (EQ). Therefore, what we aim to do is to model such a generation to find out an equation for C_{dl}, and to do this we are going to quickly describe three different type of models with increasing degrees of complexity:

Helmholtz theory. Assume the layer as a parallel plate capacitor with a constant surface density of charge proportional to the excess charge on the metal;

Gouy-Chapman model. Still a rigid charge surface is present, but gets screened by a cloud of oppositely charged ions in the solution;

Stern model. Combination of the two models having one or the other depending on the distance from the surface.

Helmholtz theory

Inside such a simple model, which can be seen graphically in Fig. (1.8), the capacity can be evaluated really easily since we know how the excess charge density on the metal is proportional to the external
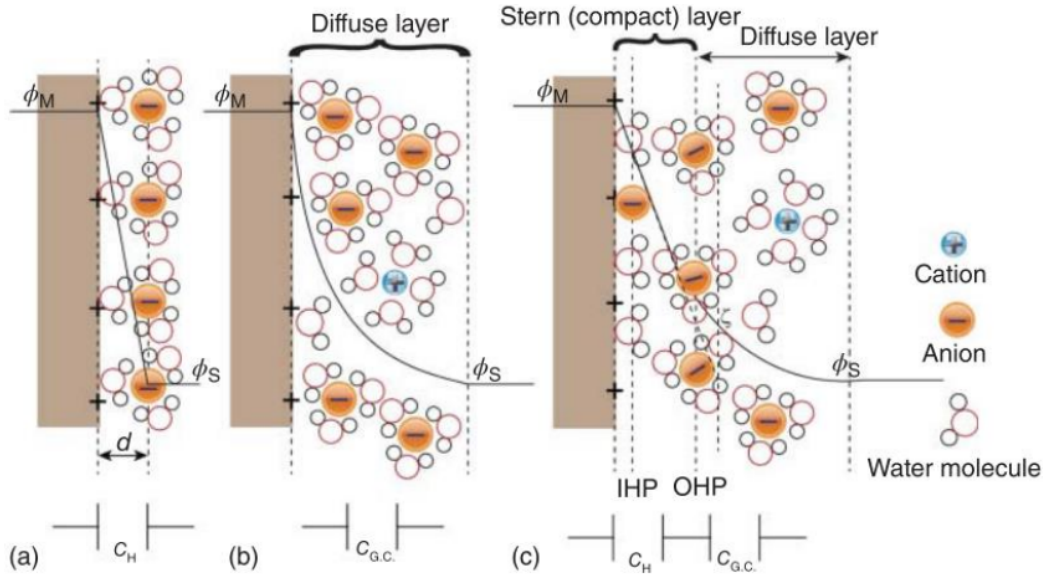
Figure 1.8: Graphical representation of the three models for the double layer, showing also how the potential changes inside it in the three cases.

field E, having so that also the surface charge σ on the capacitor has the same property. In this way we can write down the capacity in the following way

$$C_{dl} = \frac{\partial \sigma}{\partial E} = \frac{\epsilon_o \epsilon_r}{d},$$

(1.64)

where ϵ_i is the dielectric constant of the specie and d the width of the layer, called **Helmholtz layer**. Such a model is really simple, but posses also a lot of problems in general: predicts a **linear potential drop**, since the potential inside a capacitor is proportional to position, the **capacity not dependent on bias or charge**, and therefore also independent on concentration of electrolyte, and **overestimate the capacity**, with general values of $340\,\mu\text{F}$ versus real values of $16\,\mu\text{F}$.

Such complication may let the reader think that this is a useless model but is rather not. In particular, if we have large potentials we effectivelly have the C_{dl} has a really low dependence on potential and charge variations, leaving the model as a good simple choice that can be adopted.

Gouy-Chapman diffuse double layer

The concentration of the oppositely charged ions (q^S) decreasing with distance from the surface since they are acted upon by two forces: electrostatic attraction by q^M, and random thermal motion. Inside such a situation a thermodynamic study of the system can be done to see how the equilibrium distribution of the ions can be expressed in terms of potential using Boltzmann statistic that takes the following form

$$C_i(x) = C_{i,b} \exp\left(-\frac{z_i F}{RT}\phi_x\right),$$

(1.65)

where ϕ_i is the potential at distance x from the surface, which we can see in Fig. (1.8) has a rapid decay on a longer space respect to the Helmholtz theory due to the screening given by the opposite ions diffusing near the layer. That can be evaluated thanks to the Poisson equation that can be integrated by

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finding a form for the charge density, which can be done in the following way

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\epsilon_r \epsilon_0}, \qquad\qquad \rho(x) = F \sum_i z_i C_i(x). \qquad (1.66)$$

Using the previous relation for C_i and setting some boundaries conditions, such as $\phi(d) = \phi_S$ and $\phi(0) = \phi_M$, that equation can be numerically integrated to find out the wanted form of the potential. Nevertheless, it's also possible to obtain an analytic result for the charge density at the interface of the metal thanks to Gauss theorem as follows

$$q^M = -\epsilon_r \epsilon_0 \left(\frac{\partial \phi}{\partial x}\right)_{x=0} = \sqrt{8RT\epsilon_r \epsilon_0 C_b} \sinh\left(\frac{|z|F}{2RT}\phi_0\right), \qquad (1.67)$$

where ϕ_0 is referring to the potential at the surface. Now, we have the surface density as a function of the potential, meaning that we can write down a form for the capacity simply taking the derivative

$$C_{G.C.} = \frac{\partial q^M}{\partial \phi_0} = |z|F\sqrt{\frac{\epsilon_r \epsilon_0}{RT}C_b} \cosh\left(\frac{|z|F}{RT}\phi_0\right), \qquad (1.68)$$

which is function that shows a minimum for the case where $\phi_0 = \phi_S$ that, for reasons, is equal to the situation where $q^M = 0$. That point is called **potential of zero charge** (PZC) and it's value is

$$C_{G.C.}(PZC) = |z|F\sqrt{\frac{\epsilon_r \epsilon_0}{RT}C_b}. \qquad (1.69)$$

This is obviously a better model since is able to predict how the capacity depends on the potential applied, but still has some problems: **High concentration** range not well-predicted, where ion-ion interactions become important and cannot be neglected, ϵ_r **constant**, while it is strongly changing in the near proximity of the electrode surface, and **ions are treated as point charges** neglecting volume and approximating the charge at the surface.

Stern model

The idea of this model is to combine the two seen before by assuming that two layers are present inside the system basically: a first one composed by the electrode and the **Inner Helmoltz Plane** (IHP), where solvent and ions are specifically adsorbed to the electrode, then another between IHP and an **Outer Helmholtz Plane** (OHP), where the nearest solvated ions are non-specifically absorbed interacting via electrostatic forces. Along with such division the model assumes also that after the OHP starts the **Diffuse Layer** forming the part where the concentration is dropping exponentially with the distance as in the previous model. In this situation we can model the capacity of the double layer as the one of a system with two capacitors in series generating

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{G.C.}}, \qquad (1.70)$$

basically combining the good parts of both models. Still, we have some problems with such an estimation: The solvent is also acting as a dielectric, partially shielding the charges and modifying the Helmholtz layer thickness, which we are not counting, The surface of the electrode is also hydrated to some extent, that I don't know what it means, and the degree of hydration is different between ions, still no idea. Seems that the point is that C_{dl} experimentally depends on the concentration of the electrolyte and this model is not able to capture that, but I'm not sure.

To evaluate the capacity we can do a lot of things, first we always need to take into account that when we evaluate quantities inside a cell we always need to use a reference electrode to study the one we are interested in. Such electrode will so generate another interface to take into account, but usually the capacity of such electrode interface is much higher and in series respect the one of the double layer, so that the total equivalent capacity inside the equivalent circuit is $C_T \approx C_{dl}$. Taken that into account we have that the system we are dealing with is simply an RC circuit, since we have the intrinsic resistance of the solution, R_S, and the capacity of the double layer at work. Therefore, we can apply the known results for the current inside such a circuit to describe how the current flows inside it

$$i = \frac{E}{R_S}e^{-\frac{t}{R_S C_{dl}}}. \tag{1.71}$$

That is the solution for a constant potential, and shows how at the start a current is present, but is lowered quickly in time reaching the non-Faradic regime as expected where no current is present in the circuit, and after the double layer is charged the Faradic current, if present, can start flowing. Already here the data can be fitted with this result in order to obtain the value of C_{dl}, but we can do better by using a potential that vary in time as $E = vt$, so that the solution to the circuit becomes

$$i = vC_{dl}\left[1 - e^{-\frac{t}{R_S C_{dl}}}\right], \tag{1.72}$$

in this way we only need to evaluate the current when the system has reached the regime having a much more accurate measure.

Now, in a simple case one would assume that this behavior will not affect the current in the non-Faradic region, but that is not true. In particular, if we have a potential sweep the capacitve current is present also in the Faradic region having that the total one is $i = i_F + i_c$, but also the potential inside the solution will be changed by the drop due to the double layer which will influence both transition rate k and exchange current i_0 in a phenomenon called **Frumkin effect**. Such a variation can be accounted for by saying that the potential variation is given by $\phi^M - \phi^S - \phi$, where the last term is given by the double layer properties, and so the transition rate is changed as

$$k_{0,t} = k_0 e^{-(\alpha-z)\frac{F\phi}{RT}}. \tag{1.73}$$

In the case where there is an absence of specific absorption, so that the molecule will only reach the OHP with a lower potential due to the effect of IHP so that $\phi = \phi^{OHP}$ that can be computed, since the interaction is only electrostatic, and we can compute it. Nevertheless, when specific absorption is present ϕ^{OHP} can't be known without info on the specific interaction that is present, leaving us without analytic solution.

> **Note**
>
> *The value of C_{dl} gives us also interesting information on the geometry of the surface, since we know how the capacity is a property that depends on geometry. Basically we can compare it with a reference value C_S for the same element perfectly flat, so that the quantity $ECSA = C_{dl}/C_S$ is able to give a qualitative estimate of how rough the surface of the electrode is.*
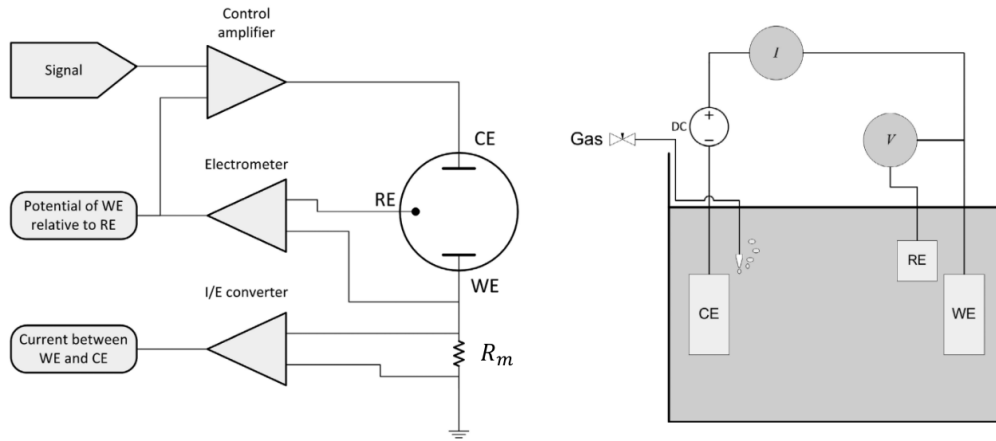
Figure 1.9: Graphical representation of the working device used in this particular method, both in the circuit part and the implementation of the cell.

1.4 Experimental methods

Potential step method

This is a way to evaluate the current potential characteristic of a cell by using a particular apparatus called **potentiostat** or **galvanostat**. The idea is to add into the cell a third electrode along with the reference and working one, called **counter electrode** (CE), in order to prevent potential variations due to current flowing through the RE. Still, the potential of the cell is evaluated by the difference in potential of the RE and WE, but the other one allows us to control such a potential along with the current that is circulating inside the cell. In particular, we can have a look at Fig. (1.9) to see effectively how the setup works, basically you have the electrometer that evaluates $E_{WE} - E_{RE}$ and passes that value to the control amplifier that controls if that potential is equal to the signal value that we want and generates a current in the CE in order to lower or increase the potential of the cell accordingly. In this way we are able to control the cell potential while monitoring the current that is passing through it using the I/E converter part of the circuit, therefore collecting the I vs E characteristic.

Inside a general experiment of this type usually one applies a potential E_1 where Faradic processes are not occurring so that no current basically flows inside the circuit. Then, the potential is increased to E_2 inside the Faradic region allowing for the system to reach the mass-limited current regime with J_L that decrease over time due the Nernst layer becoming thicker. We can so monitor the evolution of the current over time setting the $t = 0$ moment as the one where we switch from E_1 to E_2 so that we expect an evolution of the current of the type

$$E(t) = \begin{cases} E_1 & t_i < t < 0 \\ E_2 & t > 0 \end{cases}, \qquad i(t) = \begin{cases} \frac{E}{R_S} e^{-\frac{|t|}{R_S C_{dl}}} & t_i < t < 0 \\ nFAC_{O,b}\sqrt{\frac{D_O}{\pi t}} & t > 0 \end{cases}. \qquad (1.74)$$

Where before the switch the current is the one of the RC circuit, while in the Faradic region is the equation of the limiting current. In this way we can decide a time τ at which we are going to collect the current for a certain potential E_2 and then after collecting $i(\tau)$ for several values we can reconstruct the characteristic in order to fit it with the Butler-Volmer model

$$i = i_0 \left[e^{-\alpha \frac{F\eta}{RT}} - e^{-(\alpha-1)\frac{F\eta}{RT}} \right], \qquad (1.75)$$

25

which can give information about α or i_0.

Another possibility is to perform a **Linear sweep** where the potential is changed over time not in a stepped way but using $E = E_i - vt$ so that we can control $i(E)$ in time so that we obtain several regions that allows us to have information:

$E \ll E^0$: mainly non-Faradic current due to charging of double layer;

$E \sim E^0$: reduction starts, thus $C_{O,x=0}$ decrease while $C_{R,x=0}$ increase;

$E = E^{peak}$: the reactant is fully consumed at the surface and mass-transfer reaches a maximum rate due to the maximum concentration gradient;

$E > E^{peak}$: the depletion layer starts to increase, therefore the current decrease, stabilizing to a current depending on the steady state thickness.

If we assume Nernstian conditions the current-potential relation can be solved analytically in order to obtain the energy of the peak and the current as

$$E^{peak} = E_{1/2} - 1.109\frac{RT}{nF}, \qquad\qquad i^{peak} = (2.69 \times 10^5)AC_{O,b}\sqrt{n^3 D_O v}, \qquad (1.76)$$

allowing to find out information on both number of electrons involved in the reaction, n, and diffusion coefficient, D_O. Nevertheless, in this case the evaluation has a complication due to the presence of a resistance inside the solution, R_{cell}, that generate an internal drop of potential proportional to the current so that we shall account for it as

$$E_{cell} = E_{WE} - E_{CE} - iR_S. \qquad (1.77)$$

Therefore, a correction needs to be added to the measurements, and we need also to be careful since Faradic and non-Faradic components of the current are summed in the final result so that remembering how $i_F \propto \sqrt{v}$ at LSV peak and $i_c \propto v$ if the scanning rate, v, is too high the i_c will dominate on i_F having so a lower peak difficult to see. Another problem is that if we have a precision, sett by the scanning rate, comparable with the bias $i_{tot}R_u$ the sweep will not be truly linear and the curve will flatten for more negative values of E not allowing us to identify the peak. Thus, we need to carfully tune v, also because having how $i^{peak} \propto \sqrt{v}$ we have that higher the scan rate the more E^{peak} will be shifted being a function of v as well.

The last way we have seen in order to experimentally study the evolution of the cell potential was the **cyclic voltammetry**, the idea is to perform two linear sweep right one after the other in opposite directions. In particular, you want to increase the potential reaching the LSV to then quickly turn back and return to the starting one. This can be seen in Fig. (1.10) where we can see how the concentration gradient changes inside the material and turns back during the process, still not becoming the initial one due to slowness of diffusion. Still, in this data we can see both peaks for both forward and backward reactions inside the system giving us information on both peaks positions that allows us to evaluate the formal potential

$$E_{pc} - E_{pa} = E_{1/2} \approx E^0. \qquad (1.78)$$

Then we can also give an estimate of the reversibility of the reaction by evaluating the ratio i_{pa}/i_{pc} related to the reaction rate ones, and also to the electrochemical reversibility, which is proportional to ΔE_p having that in particular the following is true

$$\Delta E_p^{rev} = 2.3\frac{RT}{nF}, \qquad\qquad \Delta E_p^{non-rev} > 2.3\frac{RT}{nF}. \qquad (1.79)$$
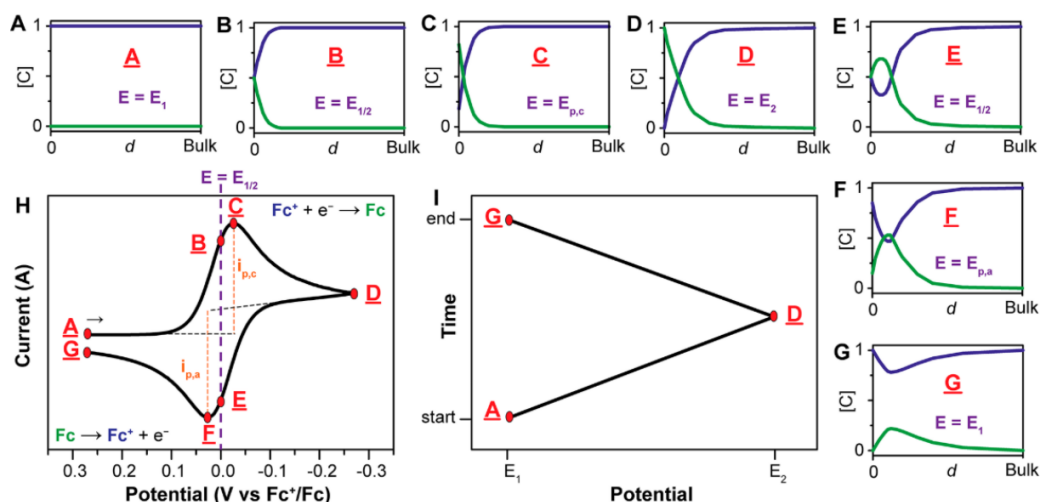
Figure 1.10: Representation of the potential, current and concentration inside a cyclic voltammetry experiment showing how the final form of the caratteristic is a loop like form that is influenced by the slowness of diffusion in order to perfectly return to the initial point.

To make an example of how this works one can take a reaction of the following type

$$O + e^- \rightleftharpoons R \longrightarrow Z, \tag{1.80}$$

where the first is reversible while the second not. The form of the CV cycle is highly dependent on the rate, k_c, of the second reaction: if is small is like nothing happens and the cycle is normal, but if it's high the reaction is not fully able to come back and the back process curve flattens out. This also allows to evaluate a so-called **reversibility parameter** α that is not sad how to compute it really, but I will trust the prof on words.