Diffusion based electroanalytical techniques

Diffusion

Diffusion is the natural way for a species to be transported from an area of high concentration to an area of low concentration. The concentration gradient present in the solution is at the origin of this driving force. It is an entropy−driven mass transport mechanism.

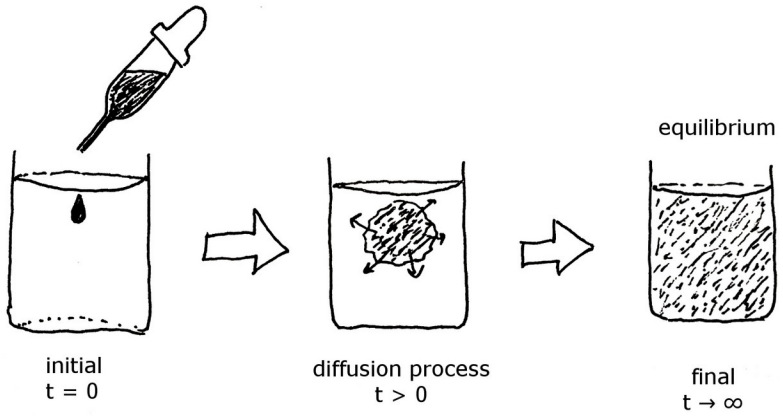

Figure 1. *Diffusion of a drop of ink in a liquid*

Likewise, when a reagent is "consumed" on the surface of an electrode, from an electrochemical reaction, the reagent in the solution diffuses towards the electrode.

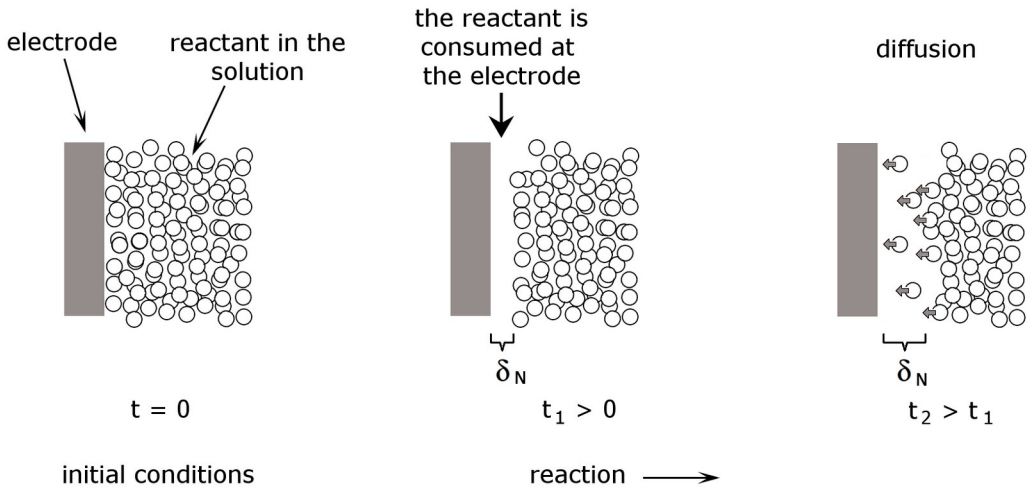

Figure 2. *Consumption following an oxidation or reduction reaction of a reactant at the surface of an electrode. δ_N = Nernst diffusion layer.*

Based on the Brownian motion of particles, Einstein finds out that the average distance traveled by a particle in a solution (x) with time can be given by the equation:

$$\overline{x^2}=2Dt \qquad (1)$$

Where D is the diffusion coefficient which corresponds to its relative speed of a species in solution.

Other possible mass transport mechanisms exist; however, we will mainly focus on diffusion.

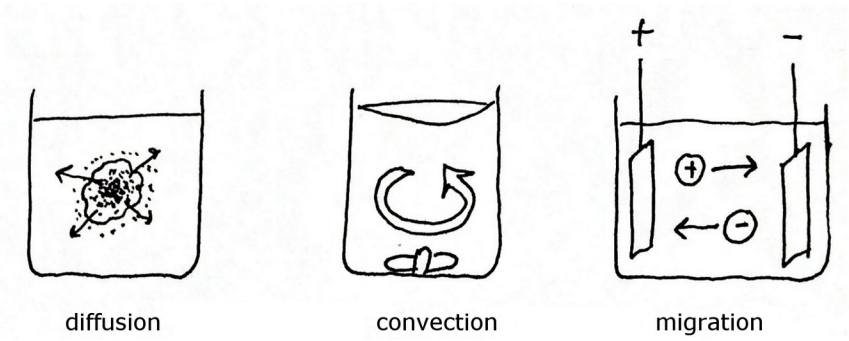

Figure 3. *Three mass transport mechanisms. Diffusion: High concentration to low concentration. Convection: The solution is stirred. Migration: Charged species (ion) are transported with the help of an electric field.*

The first Fick's Law of diffusion

Fick's law of diffusion is the common point of several electro−analytical techniques where a current limited by diffusion. Figure. 4 illustrates the concentration profile of the solution close to the surface of the electrode when the rate of the electrochemical reaction is controlled by diffusion. In this specific case, as soon as the species reaches the electrode, it is completely consumed.

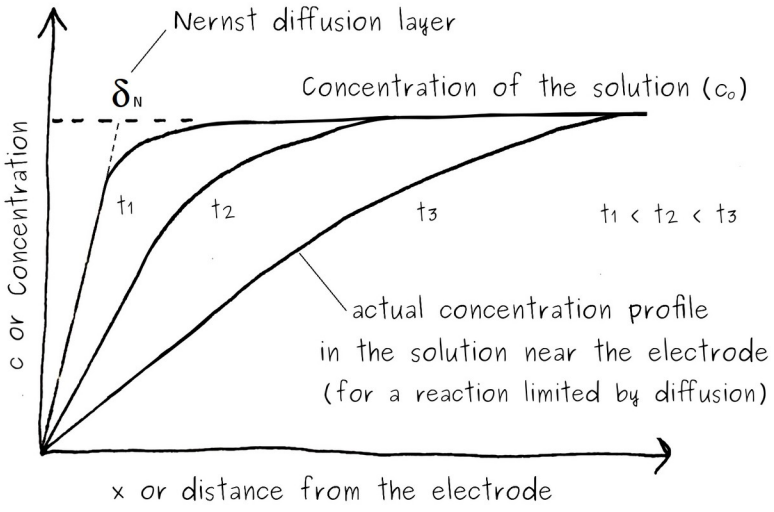

Figure 4. *Concentration profile controlled by diffusion at the surface of an electrode.*

The intensity of the mas transport of a species towards the surface is proportional to the gradient of concentration or dc/dx where c is the concentration and x is the distance from the electrode. In this case, the flow rate at the electrode corresponds to the diffusion flux (J) as described by the Fick's law of diffusion:

$$J = -D\frac{dc}{dx} \tag{2}$$

The diffusion flux is negative since, according to Fick's law, the species that diffuses are created at the electrode and it flows away from the electrode. The sign is reverse when species are consumed. The unit of the flux is the number of moles of chemical passing through a defined surface area with time ($mol.cm^{-2}.s^{-1}$). It is an indication of the intensity of the rate of diffusion.

The flux includes the diffusion constant D, which is a proportionality factor for each species that moves at random in the solution. In fact, it is a relative way to compare the speed of displacement of each species.

Expected D values: 10^{-6} $cm^2.s^{-1}$ < D (aqueous) <10^{-4} $cm^2.s^{-1}$

Table 1. Diffusion constant of some species in water at 25 °C (and other solutions)

species	D (10^{-5} $cm^2.s^{-1}$)	species	D (10^{-5} $cm^2.s^{-1}$)
H^+	9.31	Li^+	1.03
OH^-	5.27	$Fe(CN_6)^{3-}$	0.980
O_2(aq)	2.42	CO_3^{2-}	0.955
I^-	2.045	Pb^{2+}	0.945
Cl^-	2.03	Hg^{2+}	0.913
Br^-	2.010	Ba^{2+}	0.848
NH_4^+	1.98	Cu^{2+}	0.733
K^+	1.96	Zn^{2+}	0.715
NO_3^-	1.9	Mg^{2+}	0.705
CH_3OH	1.8	PO_4^{3-}	0.612
Ag^+	1.648	Fe^{3+}	0.604
$C_{12}H_{22}O_{11}$ sucrose	1.6	H_2O	0.52
F^-	1.46	Species	D ($cm^2.s^{-1}$)
Na^+	1.33	O_2 in air	0.176
HCH_3COO	1.2	H_2 in Fe (at 10 °C)	0.00017
SO_4^{2-}	1.065	Al in Cu	1.9×10^{-30}

Sources: *https://www.aqion.de/site/194*
Materials and Structures/Materiaux et Constructions, Vol. 36, April 2003, pp 156–165

note: D(H^+) value is abnormally high for a small cation since it uses the Grotthuss diffusion mechanism.

The diffusion coefficient is a constant, present in all equations for electroanalytical analysis based on diffusion, i.e. voltammetry, chronoamperometry, polarography, etc.

Unlike coulometry where all the reactants must be consumed, a chronoamperometry analysis consumes only a fraction of the active species in solution. Therefore, the initial concentration or C_o remains unchanged even after several analysis. C_o is used to indicate the concentration of a species away from the electrode where its remains constant throughout the analysis.

Since the flux J is an indication of the intensity of the flow rate of the species toward the electrode AND that the current is limited by diffusion then:

$$i_{diffusion} \propto J$$

Knowing that the flow rate is proportional to the concentration gradient $\Delta C/\Delta x$ (Figure 4) then:

$\Delta C = C_o - 0$ since all the chemical is consumed at the surface of the electrode ($C_{surface} = 0$).

$\Delta x = \delta_N$:the Nernst diffusion layer.

In this case, the current corresponding to the diffusion is given by:.

$$i_{diffusion} = \text{constant} \times D\frac{C_o}{\delta_N}$$

Finally, the diffusion current associated to the electrochemical consumption of a charged species is:

$$i_{diffusion} = nFD\frac{C_o}{\delta_N} \qquad (3)$$

Exercise.

If $Cu^{2+}(aq)$ is completely consumed at an electrode (reduction) where its concentration in the solution is c = 1.0 mmol/L, calculate the size of the Nernst diffusion layer when $i_{diffusion}$ = 2.5 μA/cm^2 .
The diffusion coefficient D(Cu^{2+}) = 0.733×10^{-5} cm^2/s.

Solution:

$$i_{diffusion} = nFD\frac{C_o}{\delta_N} \quad \Longrightarrow \quad \delta_N = nFD\frac{C_o}{i_{diffusion}}$$

$$\delta_N = (2e^-/\text{mol } Cu^{2+})(96485 \text{ A.s/mole } e^-)(0.733\times10^{-5}\text{cm}^2/\text{s})\frac{(1.0\times10^{-3}\text{mol/L})\times(1\text{L}/1000\text{cm}^3)}{2.5\times10^{-6}\text{A/cm}^2}$$

δ_N = 0.566 cm.

Chronoamperometry

Chronoamperometry is a dynamic electroanalytical technique since it involves the flow of current. Unlike potentiometry, the precise knowledge of the potential of the working electrode is not essential (however desirable) to perform the analysis. This technique relies on a precise measurement of the current flowing through a cell with time. A potential change triggers a reaction to a point where all the active species at the surface of the electrode is consumed. Then, the only "mechanism" responsible for the current flow is the diffusion of the species towards the electrode.

Consider a solution containing 1.0 mol/L $FeCl_2(aq)$ in which a platinum working electrode and an auxiliary electrode are added. As long as the potential of the platinum electrode is much less than the reversible potential of the iron(II) oxidation, no current is recorded.

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^- \qquad E° = 0.77 \text{ V vs. NHE}$$

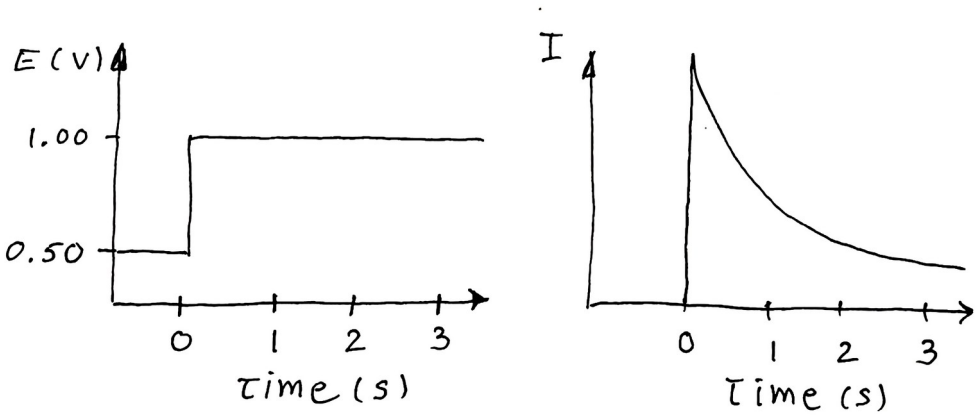

Figure 5. *Voltage imposed to an electrode vs. a NHE reference electrode (left) with the corresponding current response (right) for the system $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$.*

However, if the potential changes drastically to a potential more anodic than 0.77 V vs. NHE, then all the Fe^{2+} at the surface of the electrode will be consumed. In this case, the recorded current is mainly sustained by the diffusion process of the ions toward the electrode

In this case, the behavior of the current with time is described by the Cottrell equation.

$$i(t) = \frac{nFAC_\circ\sqrt{D}}{\sqrt{\pi t}} \tag{3}$$

n = mole of electron exchanged / mole chemical

F = Faraday constant (96485 C.mole e^-)

t = time (s)

C_o = concentration of the species in the solution (mol.cm^{-3})

A = Surface area of the electrode (cm^2)

D = Diffusion constant ($cm^2.s^{-1}$)

i = Current at the time t (A)

The current measured depends on several parameters. However, if the same setup is used with solutions of different concentrations, a calibration curve can be made to find the unknown concentration of a species. This technique is also useful to calculate the diffusion coefficient of a species or even to evaluate the quality of a polishing process of a metal since the surface area can be measured by chronoamperometry as shown by figure 6.

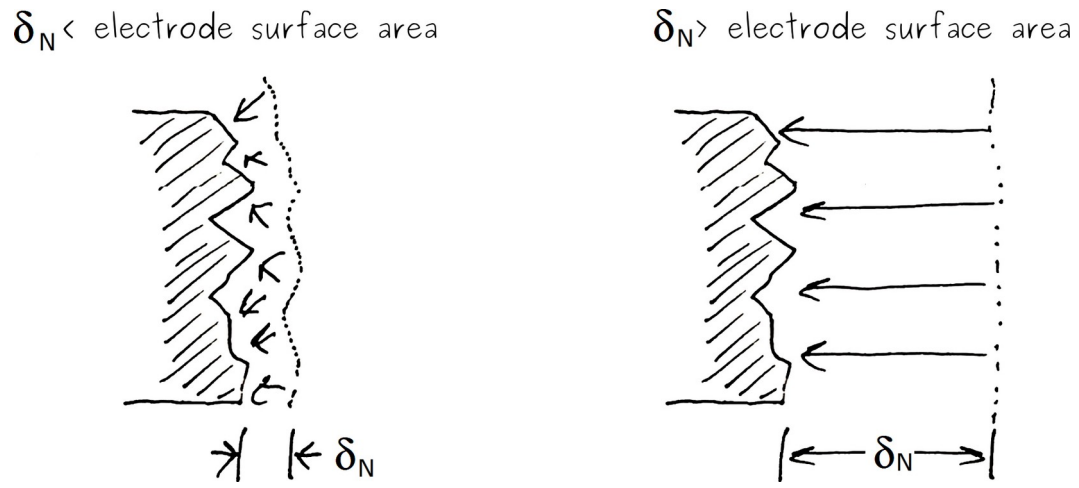

Figure 6. *The surface area of an electrode could be larger than its geometrical dimension according to the length of the Nernst diffusion layer (δ_N). With a short time analysis, the surface imperfection becomes apparent.*

Example:

An electrode with a geometric area of 0.100 cm^2 was polished. Calculate the actual area of this electrode from the following chronoamperometric analysis:

The current for the reduction of a 5.00 mM ferricyanide ion solution is 211 µA after 0.500 s at 25.0 °C. The reduction of ferricyanide to ferrocyanide is a reversible 1 electron process.

Solution: Finding the surface area of the electrode with the Cottrell equation.

From table 1, the diffusion coefficient at 25 °C of the ferricyanide ion is 9.80×10^{-6} $cm^2.s^{-1}$.

Cottrell equation $$i(t)=\frac{nFAC_\circ\sqrt{D}}{\sqrt{\pi t}} \quad \Rightarrow \quad A=\frac{i\sqrt{\pi t}}{nFC^\circ\sqrt{D}}$$

$$A=\frac{(211\times10^{-6}\text{A})\sqrt{(3.1416)(0.50\text{s})}}{(1\,\text{mol}e^-/\text{mol})(96485\,\text{A.s/mol}e^-)(5.00\times10^{-3}\text{mol/1000 cm}^3)\sqrt{9.80\times10^{-6}\text{cm}^2.\text{s}^{-1}}}$$

A(actual) = 0.175 cm^2

The electrode has an actual area 75% larger than its apparent physical dimension due to its rough surface created by the poor quality of the polishing process.

Verification of the validity of the Cottrell equation

The Cottrell equation assumes that the species are reaching the electrode using only a linear diffusion mechanism. However, as the analysis progresses, the Nernst diffusion layer (d) increases. Consequently, a different type of diffusion appears: radial or spherical diffusion.

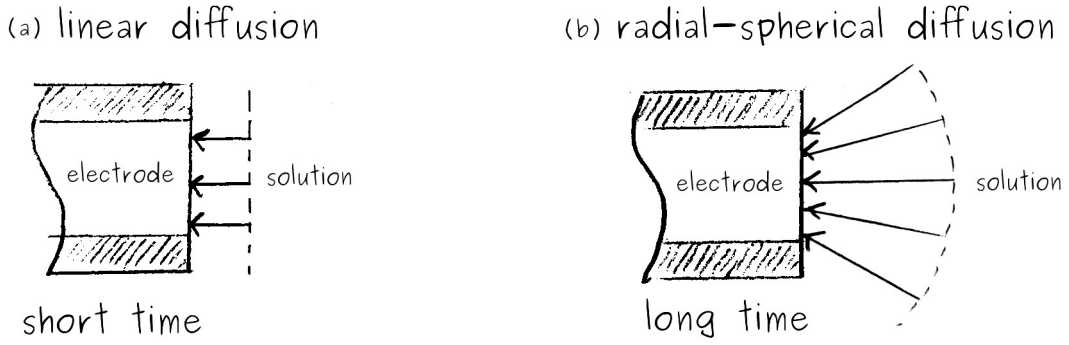

Figure 7. *Different diffusion profile (a – linear, b – spherical) present at an electrode with time.*

In this type of diffusion, the Cottrell equation is no longer valid and a correction factor for the spherical diffusion must be introduced. Therefore, it is essential to verify the extent of the validity of the equation before using it.

A simple way to determine the time period over which the Cottrell equation is valid, is to plot the chronoamperometric curve differently: I vs. (time)$^{-½}$

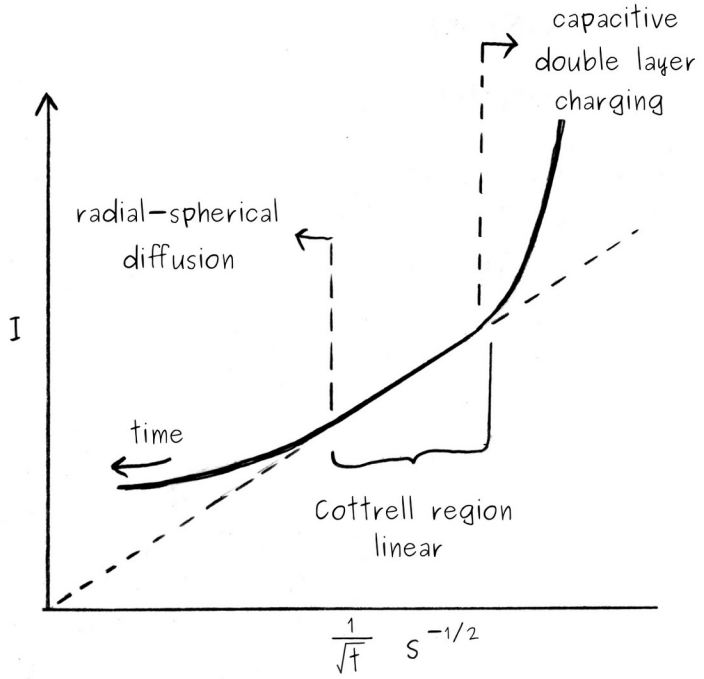

Figure 8. *Determination of the period of time over which the Cottrell equation is valid.*

In Figure 8, the slope of the graph (linear region) includes all constant values of the Cottrell equation

$$\text{slope} \quad \text{or} \quad \frac{\Delta(I)}{\Delta(t^{-½})} = \frac{nFAC_{\circ}\sqrt{D}}{\sqrt{\pi}}$$

At the beginning of the analysis (very short time), the current includes the capacitive double−layer current of the electrode. On the other when the time of the analysis is longer, radial and spherical diffusion arise in combination with natural convection. By measuring the current at the time where the Cottrell equation is respected, one has access to several parameters like the active surface area of the electrode, the diffusion coefficient or the concentration of an active species in a solution.

Migration

When a charge particle is placed between two electrodes with a difference of potential, the presence of the electric field induces a force on the particle which increases its motion in solution. It is the principle of the electrophoresis process separation. Depending on the electrical charge of the species, migration can increase or slow down its diffusion speed towards an electrode.

Migration applies to all species carrying a charge (ion, nucleic acid, proteins, etc.). However, for a chronoamperometric analysis it must be eliminated. To minimize the migration effect, a "supporting electrolyte" is added in large amounts (e.g. KCl, $NaNO_3$). In this case, if the concentration of the species studied is less than 1% of that of the supporting electrolyte, the migration effect can be neglected.

Conditions to obtain a current that is consistent with the Cottrell equation

- The electroactive species is consumed to completion at the electrode (no accumulation)
- Using a polished electrode with a large surface area.
- Short time analysis (diffusion layer ≪ size of the electrode).
- No stirring of the solution or temperature gradient.
- Setup free of vibration, therefore no convection.
- Analysis of species with low diffusion coefficient to minimize any radial−spherical diffusion.
- Addition of a supporting electrolyte to minimize migration (also increase the conductivity).

Diffusion analysis using a small electrode. The case of an ultramicroelectrode.

On an ultramicroelectrode (δ_N » electrode size), mass transport is based on a spherical diffusion mechanism since the thickness of the Nernst diffusion layer is more important than the size of the electrode.

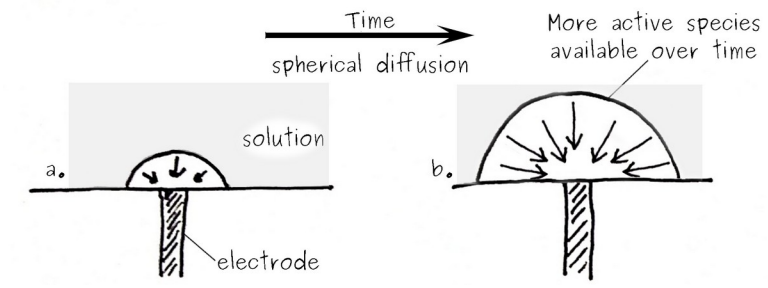

Figure 9. *Spherical progression of the Nernst diffusion layer on an ultramicroelectrode.*

Thus, as the experiment progresses, the decrease in the concentration of the species at the electrode is equally compensated by an increase in the number of species available due to spherical mass transport (Figure 9). Consequently, the current is constant with time ($i_{steady\ state}$) which is, for a disk electrode:

$$i_{steady\ state} = 4\ n\ F\ D\ C_o\ r \qquad \text{(r is the radius of the ultramicroelectrode disk)} \qquad (4)$$

All the problems are at 25 °C

You may need to use the values from table 1 to solve some problems.

1. You had performed a chronoamperometric analysis for 15 s with an average current of 12.0 µA. If your 250. mL solution contains 5.00 mM ferricyanide ion, what percent of the sample present in the solution was consumed by this analysis. The reduction reaction is one electron/mole ferricyanide. (*note: This is a coulometric calculation to illustrate the amount of reactant consumed in a chronoamperometric measurement*).

2. You did a chronoamperometric analysis of I^-(aq) *c* = 0.050 M, reaction: $2I^- \rightarrow I_2 + 2e^-$.
   The current measured after 5.0 s was 1.38 mA on an electrode of A = 0.25 cm^2. Calculate the iodide diffusion coefficient.

3. You had performed the reduction of Ag^+ on a silver electrode (A = 1.079 cm^2) in an aqueous solution at 25 °C. You plot the chronoamperogram I vs. $(time)^{-½}$ to find the linear part of the plot (as shown by Figure 8). The slope of this part of the graph is 11.2 $mA.s^{-½}$. Calculate the concentration (mol/L) of Ag^+ in the solution.

4. What concentration of Fe^{3+} should you add to a solution to obtain, a chronoamperometric analysis with a reduction current of 5.00 mA after 10.0 s.
   The surface area of the electrode is 2.54 cm^2 and the reduced species formed is Fe^{2+}.

5. A chronoamperometry analysis is performed to reduce the manganese permanganate ion MnO_4^-. The following conditions are used (or obtained) for this analysis:
   $c(MnO_4^-)$ = 0.500 mM, $D(MnO_4^-) = 1.632\times10^{-5}$ cm^2/s, $A_{electrode}$ = 1.0 cm^2,
   $I_{measured}$ = 185 µA at t = 8.80 s.
   What is the oxidation state of the manganese ion produced?

6. A disk ultramicroelectrode is used to find the diffusion coefficient of Pb^{2+}. A solution of 2.34×10^{-3} M of $Pb(NO_3)_2$ is reduced by a platinum microdisk of 25.0 µm. A steady state current 21.3 nA is obtained. Calculate the diffusion coefficient of Pb^{2+}(aq) note: the reaction is $Pb^{2+} + 2e^- \longrightarrow Pb(s)$

Answers

1– 1.5×10^{-4} % (no effective change of the concentration of the solution)

2– 2.05×10^{-5} $cm^2.s^{-1}$

3– 0.0470 mol/L

4– 0.0465 mol/L

5– Mn^{2+}

6– 9.43×10^{-6} $cm^2.s^{-1}$