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Electrochemical separation of ^{212}Pb - ^{212}Bi mother-daughter element pairs

When studying systems with electrically charged particles, the electrical properties should always be taken into account. For example, when diffusion is investigated in an electrolyte solution where initially there is only a chemical potential difference between different points of the system, an electric potential difference will occur in the solution due to the different mobility of the ions. For this reason, even when examining this simple case, the electrochemical parameters of the system cannot be ignored.

Taking into account the electrochemical properties of the system makes the description of the phenomena quite complex, but at the same time, the different electrical parameters of the different charged parts also allow the development of analytical and separation techniques.

Ionics deals with the properties of ionic systems (electrolyte solutions, melts, and solid electrolytes). Electrodics deals with the interfacial phenomena of ionic systems, metals and metal conductors.

Separation techniques and analytical methods should also be grouped according to these two topics: the electrophoretic methods based on the transport properties of ionics and the separation processes based on the different electrode processes.

Separations based on electrode processes

The different values of the equilibrium potential of the electrode processes and the dependence of the concentration, pH, etc of this solution allows the electrical separation of the electrically charged parts in both analytical and preparative sizes. Electrolysis investigations include the preparative separation processes.

In electrolysis, chemical substance is converted in the electrolysis cell. (This can be an inorganic or an organic chemical reaction.) The electrolytic cell is a galvanic cell that is used not for power generation but for chemical conversion by connecting a source of power to the electrodes of the cell. It is distinguish internal or simple electrolysis depending on the operation of the cell by short circuiting the electrodes or conducting current from external sources. Simple electrolysis is generally performed between indifferent electrodes.

The electrochemical method of material separation is relatively simple, and at the same time the experimental conditions are well controlled, and the use of indifferent electrodes allows the material to be converted in high purity.

The basis of electrolysis

In order to induce continuous electrolysis between indifferent electrodes in an electrolyte solution, a potential difference from the external power source must be established between the electrodes. This potential difference must be greater than the decomposition voltage, that is, the electromotive force of the galvanic cell produced by electrolysis.

The current flowing between the two electrodes is defined by the relation (Eq.1.).

$$i = \frac{E'_k - E}{R} \qquad (1)$$

where E`k is the electrolytic voltage, E is the electrolytic cell battery, R is the resistance between the two electrodes. Because the resistance between two electrode metals is a function of many factors (overlay, etc.), the equation implies uncertainty and, therefore, during the investigation only one of the cell's electrode is used, the potential of which is measured against a comparative electrode. (In a series of experiments, the electrode is usually held constant - potentiostatic method.)

The electrode potential

Under potentiostatic conditions, the equilibrium electrode potential for the appropriate electrode reaction will be the decisive factor for ion deposition, which value can be calculated from the Nernst equation.

$$E = E^0 + \frac{RT}{zF} \ln a_M^{z+} \qquad (2)$$

where E is the electrode potential, E^0 is the standard electrode potential, a_M^{z+} is the ionic activity of the electrolyte solution. Often in the equation the so-called formal potentials are used:

$$E = E^0 + \frac{RT}{zF} \ln C_M^{z+} \qquad (3)$$

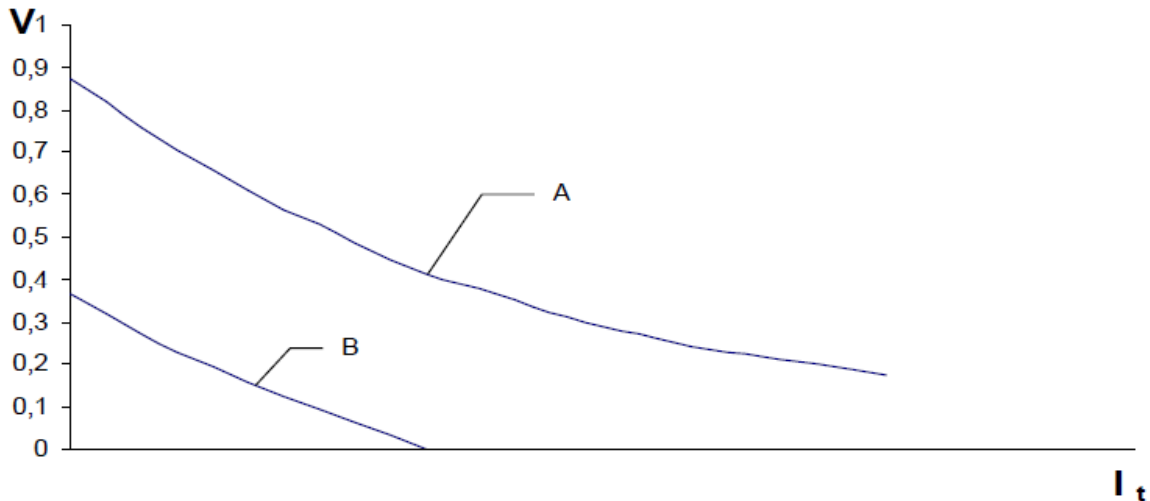which denotes that the system is formally considered as ideal behavior.

Figure 1. Current-potential curves for electrolytic separation of Ag (A) and Cu (B)

Continuous neutralization of cations occurs when the electrode potential is more negative than the equilibrium potential, in the event of a cathode overvoltage of 0.1-0.2 V, the anode process on the electrode can be ignored and vice versa: at higher anodic polarization, the cathodic process can be ignored.

Figure 1 illustrates current potential curves for the electrolytic separation of Ag and Cu. During electrolysis, the concentration of Ag^+ ion decreases, so the equilibrium potential becomes more negative.

Separation of macro and micro quantities by electrolysis

During the separation of macro quantities, electrolysis is complete when the concentration of ion species decreases below 10^{-6} mol/dm^3 in the electrolyte solution. For analytical purposes this value is the limit value.
Based on the text above, Ag and Cu can be separated by electrochemical methods.
For macro quantities, the A and B ions can be separated if inequality (4) is valid.

$$E_A^o - E_B^o > \frac{0.058}{z} \lg \frac{c_B}{c_{A\infty}} \tag{4}$$

where $C_{A\infty}$ is the concentration of A-ion at the end of electrolysis ($C_{A\infty} = 10^{-6}$ mol/dm^3), CB is the concentration of B-ions in the solution. E_A^o and E_B^o are the standard potentials for the corresponding ions.
In the case of electrochemical separation of micro quantities, the above considerations need to be supplemented. However, the isolation of radioactive isotopes in such dilute solutions is a major problem in radiochemical practice. (In addition to radiochemistry, quantification of non-radioactive trace impurities is also an important task.)
Carrier-free separation and purification of radioactive isotopes produced by different nuclear reactions or naturally occurring radioactive isotopes from their target material or from their decay series is a common but very complex task, because very small amounts of material are used. The physico-chemical properties of the range of ultra-dilute solutions cannot generally be extrapolated from known data for macro amounts.
In addition to different separation methods, such as adsorption, crystal formation, ion exchange, extraction, electrochemical processes also play an important role.
In some cases, the electrochemical separation is combined with another separation process, for example electrochromatography. The electrochemical separation of radioactive isotopes also has the advantage that the separation process can be carried out in any solution of high activity by the selection of high radiation resistant electrodes.

Experimental determination of separation potential in ultra-diluted solutions

In the range of ultra-diluted solutions, the full Nernst equation (2) must be used:

$$E = E^o + \frac{RT}{zF} \ln \frac{a_M^{z+}}{a_{MS}} \tag{5}$$

where a_{MS} is the thermodynamic activity of the separated metal on the electrode surface. In the case of separation from diluted solutions, when the amount of the separated material does not even

reach the monomolecular layer thickness on the electrode surface, the value of a_{MS} differs from the unit.

The thermodynamic activity of the separated substance from the solid phase cannot be determined theoretically. Therefore, for each separation process, the potential for separation of the respective ion species should be determined experimentally.
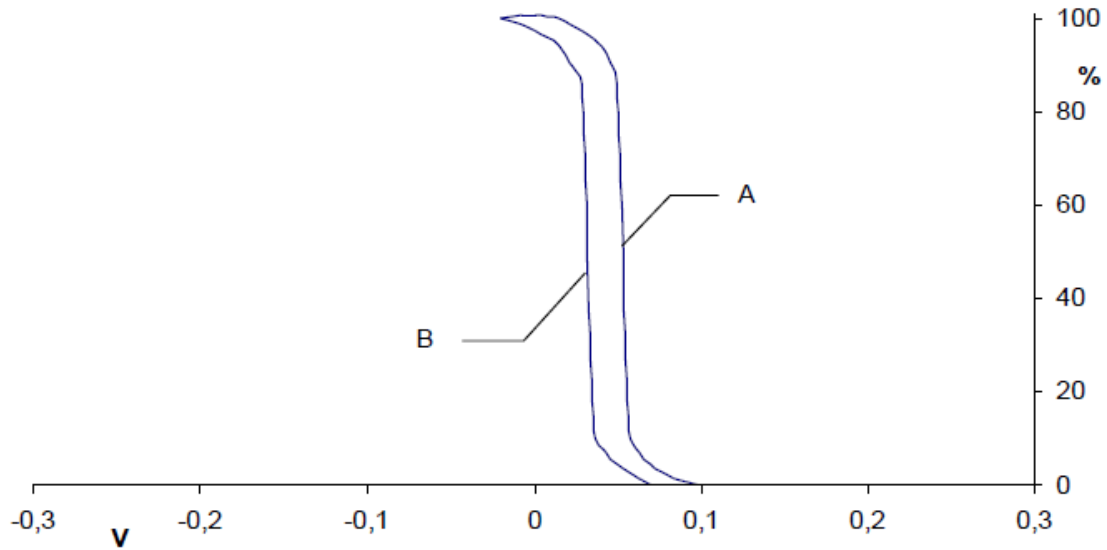

Figure 2 Rate curve of electrolytic separation of Bi on mercury A: 10^{-10} mol/dm^3
B: 10^{-6} mol/dm^3 Bi^{3+} ion solution

The other, also potenciostatic method is used to electrolyze at a given potential until the solution/electrode equilibrium is reached. The critical detachment potential is determined from the equilibrium quantity potential (Fig.2). The two curves should give approximately the same result.

Determining Ek value for separated ions the possibility of separation can be easily determined and the degree of purity can be calculated.

The principle electrical connection of the potentiostatic experimental method is shown in Figure 3.

In potenciostatic measurement, the potential of the working electrode (M) is kept electronically constant to reference electrode (R) with the potentiostat (P). The desired voltage between R and M is setted by the potentiometer (1. and 2.).
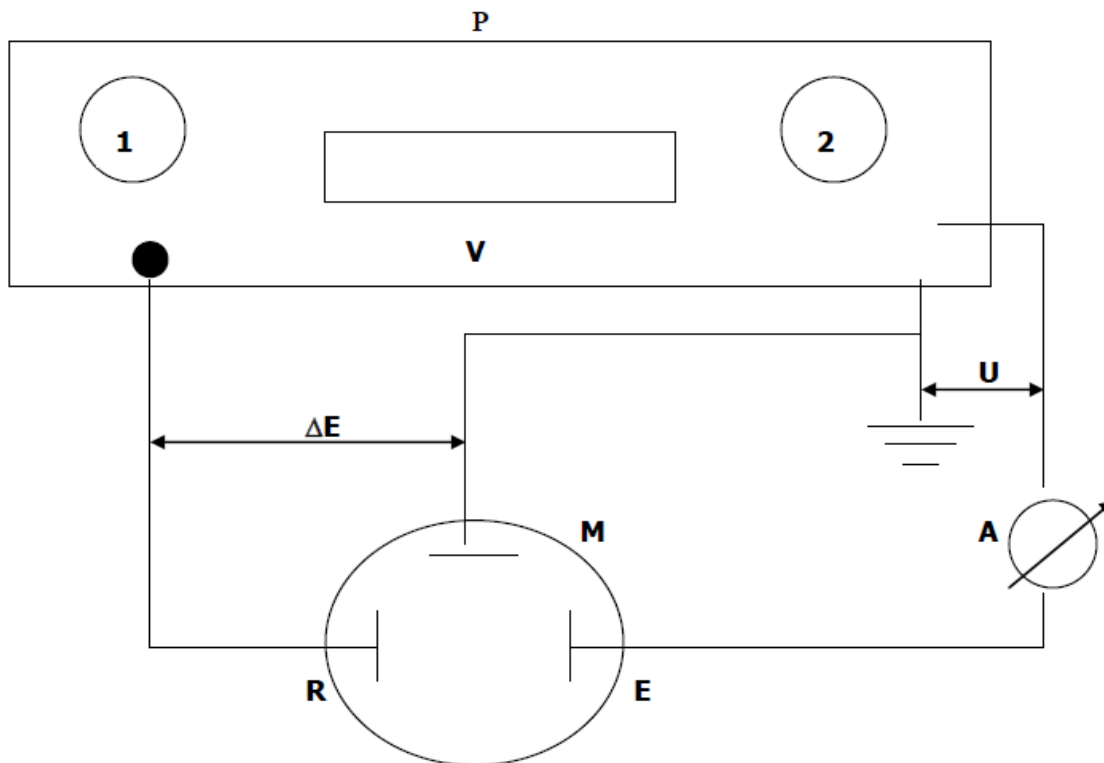
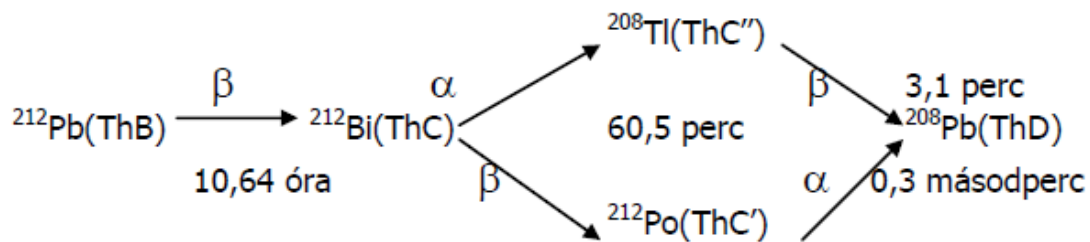Figure 3. Determining the detachment potential by potenciostatic method

The voltage connection between M-E electrodes in the electrolytic cell is indicated by the instrument (V) and the flow of the current is shown by the ammeter (A). The principle function of the potentiostat is that when the voltage between M and R electrode is different from the adjusted ΔE, this difference occurs as an error signal. This error signal controls the output voltage (U) of the potenciostat by proper electronic amplification to return the desired voltage (ΔE) between electrode R and M. As a result, the potential of the working electrode will be relatively constant (ΔE) to the reference electrode.

In the case of diluted solutions the ammeter shows current conductive salts in the solution, since the concentration of radioactive isotopes is an order of magnitude lower. The transmission number of radioactive ions in the system is close to zero and they are practically not involved in conducting current.

The task of purification related to the production of radioactive isotopes is to obtain the appropriate isotope from a mixture of radioactive isotopes of various elements. Often, this purification task means that the mother-daughter pairs needs to be separated as in the case of ^{90}Sr-^{90}Y, ^{140}Ba-^{140}La, ^{212}Pb-^{212}Bi.

During the laboratory practice such a mother-daughter pairs (^{212}Pb-^{212}Bi) will be separated which can also be considered for other similar systems.

The ^{212}Pb (ThB) decay series is the following:

The change in the activity of mother element over time:

$$A_1(t) = A_{1,0}\, e^{-\lambda_1 t}$$

(5)

In the case of the daughter element:

$$A_2(t) = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_{1,0} e^{-\lambda_1 t}\left[1 - e^{-(\lambda_2 - \lambda_1)t}\right] + A_{2,0} e^{-\lambda_2 t}$$

(6)

Meaning of abbreviations in equations:

$A_{1,0} = \lambda_1 N_{1,0}$ the activity of mother element in the beginning of the measurement (t=0)

$A_{2,0} = \lambda_2 N_{2,0}$ the activity of daughter element in the beginning of the measurement (t=0)

$A_1(t) = \lambda_1 N_1$ the activity of mother element in t time

$A_2(t) = \lambda_2 N_2$ the activity of daughter element in t time

λ_1 decay constant of mother element

λ_2 decay constant of daughter element

N number of radioactive nucleus

If t>10 hours then the equation for $A_2(t)$ takes the following value:

$$A_2(t) = A_{1,0}\frac{\lambda_2}{\lambda_2 - \lambda_1} e^{-\lambda_2 t}$$

(7)

i.e. the decay rate of daughter element is proportional to the decay rate of mother element. Thus, the amount of mother element can be determined from these measurements. (ThC' and ThC" have much shorter life and the equilibrium reaches sooner than in case of ^{212}Bi.)

If the mixture of ^{212}Bb and ^{212}Bi is electrolyzed and the alpha radiation of separated amount is measured, then the activity is determined by the amount of ^{212}Bi. The only alpha emitter is ^{212}Bi and ^{212}Po as it can be seen in the decay series. During the measurement the ^{212}Po has a very short half-life so it is constantly in equilibrium with the mother element.

1. If only the ^{212}Bi is separated during electrolysis, equation (6) is as follows:

$$A_2(t) = A_{2,0}\, e^{-\lambda_2 t} \tag{8}$$

i.e. the alpha activity over time is measured in the sample and is extrapolated to the end of the electrolysis (t = 0) than the amount of Bi separated is received.

2. If ^{212}Pb will also be separated with ^{212}Bi than equation (6) should be used in full shape, and after 10 hours the sample activity can be measured and extrapolated to the end of the electrolysis (t = 0) than the amount of separated lead can be obtained.

When the critical detachment potential of ^{212}Pb is examined the radioactivity of the sample on the electrode is measured always in the latter way (after 10 hours of waiting).

The separation factor can be calculated as follows:

$$\alpha = \frac{N_{Bi}}{N_{Pb}} = \frac{\lambda_1 A_{2,0}}{\lambda_2 A_{1,0}} \tag{9}$$

$A_{1,0}$ and $A_{2,0}$ can be determined from equations (6-8).

It is not possible to wait 10 hours during laboratory practice so the process as it is follows: Alpha activity is measured on the electrode for an hour as it is follows: for the first 10 minutes in every minute then every 10 minutes (thus, all together you will have 15 measurement data after an hour).
The evaluation will be carried out using the so-called 'Scientist' computer program.

Task

The aim is to determine the separation factors and the critical detachment potential of Bi^{3+}-ion from carrier free solution of $^{212}Pb^{2+}$-$^{212}Bi^{3+}$.
Add 25 cm^3 0.1 mol/dm^3 HNO$_3$ solution containing $^{212}Pb^{2+}$ and $^{212}Bi^{3+}$-ions in carrier free concentration into the electrolysis cell. The radioactive ions are evenly distributed throughout in the stock solution by preparing the solution in time. Electrolysis is continued for a period of time at each sample and cathode potential (0, -25, -50, -75, -100, -150 mV saturated calomel electrode).
At the end of electrolysis measurement begins again and the change in the electrode alpha activity is measured over time. Samples should be measured under the same geometric conditions (with the help of special sample holder).
The evaluation will be carried out using the so-called 'Scientist' computer program. Which will help to determine the $A_{1,2}$ than ^{212}Bi amount and the separation factors can be calculated.
It can be seen from the practice that Bi and Pb can be separated and quantitatively calculated from ultra-diluted solutions (c <10-15 mol/dm^3), knowing the appropriate electrochemical properties.

Test questions:

1. Write down the Nernst equation and name the abbreviations!
2. Write down the law of radioactive decay, name the abbreviations (with units of measure), and explain why it is fist-order kinetics!

3. Describe the kinetics of mother-daughter pairs in radioactive equilibrium, what is the condition of transient equilibrium?
4. Basics of electrolysis.
5. Draw and explain the theoretical scheme of the experimental equipment.