2 Electrochemistry in Equilibrium

In electrochemistry an organizing criterion frequently employed is the flow of current: Experiments or - more generally - phenomena without current with the system under investigation naturally at equilibrium may be related both to the interior (bulk) of the electrolyte solution and to the electrochemical interface between electron conducting material (e.g. metal, conveniently also incorrectly called electrode) and ionically conducting electrolyte solution. Both possibilities exist also in dynamic systems, in this case the flow of electronic current in the wires, metals etc. is coupled to the flow of ions in the ionically conducting phase (electrolyte solution). Both processes and fluxes are coupled at the electrochemical interface.

In this chapter experiments without flow of current are described. Fundamental facts and relations of electrochemical and general thermodynamics, mixed phase and non-ideal thermodynamics and the relationships between electrochemical and thermodynamical data are discussed.

Experiment 2.1: The electrochemical series

Task

A standard hydrogen electrode is prepared, it is used as a reference in the determination of the standard potentials of the nickel, copper and zinc electrode. The influence of the metal ion concentration as suggested by the Nernst-equation is examined. The temperature dependence of the voltage of a copper-silver cell is measured and used for the calculation of the entropy of reaction.

Fundamentals

Between the chemical elements and their compounds substantial differences exist in their tendency of being reduced (with associated uptake of electrons) or being oxidized (with respective removal of electrons). In electrochemistry the comparison between these properties for two elements can be performed most easily by measuring a cell voltage. Comparable conditions, in this case standard ones, are established by using the elements, in particular metals (which are studied here) as electrodes in solutions containing their ions at unit activity. Because of the nonideal behavior of ions in solution this activity $a = 1\ \mathbf{M}$ is reached mostly only with concentrations considerably larger than unity $c > 1$ **M**. Between the solutions containing the hydrogen reference electrode and the metal electrode a salt bridge is employed. Cell voltage between the metal wire connector of the hydrogen electrode and the metal of the second electrode is measured with a high input impedance voltmeter. This voltage can be compared with the voltage calculated based on the cell reaction and the respective electrode reaction deduced by splitting the cell reaction. The metal whose connector is identified as plus terminal (cathode) is called nobler than the other metal, which constitutes the minus pole (anode). Taking the less noble zinc and the more noble copper as example this can be verified. Taking solutions with the respective ions at standard activity the zinc wire is the minus pole, the copper wire the plus pole. This cell is known as Daniell element (cell). Reactions are:

$$\text{Cathode (Reduction): } Cu^{2+} + 2\,e^{-} \rightarrow Cu \qquad (2.1)$$

$$\underline{\text{Anode (Oxidation): } Zn \rightarrow Zn^{2+} + 2\,e^{-}} \qquad (2.2)$$

$$\underline{\text{Cell reaction: } Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu} \qquad (2.3)$$

Comparative measurements permit establishment of a list showing metals (and more generally speaking elements and compounds) rated according to their reductive or oxidative capability. This list is called electrochemical series. These measurements are also possible with gaseous reactants. Thus a hydrogen electrode is established by bubbling hydrogen gas around an inert metal electrode (e.g. a platinum sheet) in contact with an aqueous electrolyte solution of well-defined pH-value. With proton activity $a = 1$ **M** and hydrogen pressure $p = p_0 = 1$ atm (= 101325 Pa) a standard hydrogen electrode is obtained. Measurements with this hydrogen electrode as one electrode (or half-cell) and another test electrode yield cell voltages being equivalent to the electrode potential of the test electrode because by definition the electrode potential of the standard hydrogen electrode is $E_{\mathrm{SHE}} = 0$ V. This value is equivalent to the number given in the electrochemical series.

With electrolyte solutions of other ionic activities and gas pressures (in case of gas electrodes where the gas is involved in establishing the electrode potential) different, non-standard values of the electrode potential are obtained. The relationship between activities, pressures and electrode potential is given by the Nernst-equation.

The cell voltage is related to the Gibbs energy of the cell reaction according to

$$\Delta G_R = -z \cdot F \cdot U_0 \tag{2.4}$$

Using the partial derivative of the Gibbs equation assuming a constant (i.e. temperature-independent) value of the reaction enthalpy ΔH_R in the studied range of temperatures

$$(\partial \Delta G_R / \partial T)_p = (\partial \Delta H_R / \partial T)_p - (\partial T \Delta S_R / \partial T)_p \tag{2.5}$$

yields

$$(\partial \Delta G_R / \partial T)_p = -\Delta S_R \tag{2.6}$$

The reaction entropy can now be calculated from measurements of the temperature coefficient of the cell voltage:

$$(\partial U_0 / \partial T)_p \cdot z \cdot F = \Delta S_R \tag{2.7}$$

Execution

Chemicals and instruments

Aqueous solution of $CuSO_4$, 1 **M**
Aqueous solution of $ZnSO_4$, 1 **M**
Aqueous solution of $NiSO_4$, 1 **M**
Aqueous solution of $AgNO_3$, 1 **M**
Aqueous solution of HCl, 1.25 **M** (the proton activity is approx. 1 **M**)
Salt bridge filled with 1 **M** KNO_3[1]
Silver, copper, nickel, platinum and zinc electrodes (wires, sheets)
High input impedance voltmeter
Thermostat
Hydrogen gas

Setup

The metal salt solutions are filled into beakers; the metal electrodes are cleaned with abrasive paper, rinsed with water and immersed in the respective solutions. Connection between two beakers is made with the salt bridge; the beakers are exchanged with careful rinse of the salt bridge.

Procedure

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[1] Filling the salt bridge with a solution of KCl is not recommended because chloride ions adsorb specifically on most metals, they may cause corrosion.

The voltage between the two metal terminals is measured with the various possible combinations of electrodes. In addition the cell voltage of the metal electrodes vs. the hydrogen electrode is measured.

The zinc sulfate solution is diluted to 0.1 **M** and 0.01 **M**; the measurements vs. the hydrogen electrode are repeated.

Using the cell Ag/$AgNO_3$-solution/salt bridge/$CuSO_4$ solution/ copper the cell voltage as a function of temperature in the range 20 °C < T < 80 °C is measured[1].

Evaluation

The obtained values are listed as in the electrochemical series; they are compared to literature data. Values obtained with zinc sulphate solutions of various concentrations are examined using he Nernst equation.

Measurement of the cell voltage of the copper-silver-cell in an easily accessable range of temperatures results in data as displayed for a typical experiment below (next page). Conceivable causes of deviations between obtained numbers and expected ones are differences in temperature between he interior of he cell and the thermostat bath. The calculated value[2] for room temperature RT is U_0 = 0.469 V the experimentally observed one is U_0 = 0.454 V. To identify sources of this difference he potentials of both electrodes can be measured versus a reference electrode. With a saturated calomel electrode he results are: $E_{\mathrm{Cu\ vs.\ SCE}} = 0.322$ V and $E_{\mathrm{Zn\ vs.\ SCE}} = 0.775$ V. Obviously the deviation is caused by a non-ideal behavior of the copper electrode.

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[1] Measurements of the temperature coefficient of the Daniell cell seem to be a more attractive way to obtain reaction entropy because thermodynamic data for this cell reaction are well known. The very small reaction entropy of this reaction has already induced earlier researcher to assume, that the Daniell cell provides a way for complete conversion of the reaction enthalpy into useful work. The copper electrode tends to formation of poorly defined surface oxide layers especially when exposed to corrosive environments. The amphoteric nature of the zinc electrode adds further uncertainty making this cell a less attractive candidate.

[2] Activity coefficients are $\gamma_{\mathrm{CuSO_4}} = 0.047$ and $\gamma_{\mathrm{AgNO_3}} = 0.4$

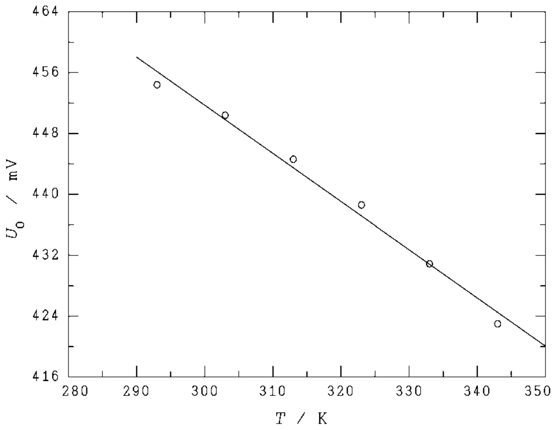

Fig. 2.1: Temperature dependence of the cell voltage of a copper-silver-cell

Using the temperature coefficient calculated from the plot $\partial U_0/\partial T$ = – 0.63 mV K^{-1} a reaction entropy ΔS = – 121 J·K^{-1}·mol^{-1} can be calculated. The value calculated from thermodynamic data (Atkins) is ΔS = – 193 J·K^{-1}·mol^{-1}.

Questions

- Can an electrode be established with an insulator instead of a metal?
- Is the answer valid also for semiconductors (e.g. silicon)?

Experiment 2.2: Standard electrode potentials and the mean activity coefficient

Task

1: By measuring the cell voltage of the galvanic cell Ag/AgCl/ HCl/H_2/Pt the

a: standard electrode potential of the silver chloride electrode

b: the mean activity coefficient of HCl in aqueous solutions

shall be determined.

2: The electrode potential of the silver ion electrode and the Fe^{2+}/Fe^{3+}-redox electrode shall be measured as a function of concentration.

Fundamentals

The electrode potential is by definition the voltage measured between the electrode under investigation and a standard hydrogen electrode. If both electrodes are in standard state (i.e. unity activities of all species controlling the electrode potential and room temperature) the electrode potential is a standard potential. Experimental determination of standard potentials yields activities calculated with he Nernst equation; this in turn provides access to several thermodynamic data (e.g. equilibrium constants, activity constants).

In this experiment particular attention must be paid to measurement of voltages at zero current and without diffusion potentials. High input impedance voltmeters are recommended, in addition calibrations vs. a Weston element is recommended.

Diffusion potentials can be avoided completely only, when both the hydrogen electrode and the electrode under study are immersed in the same electrolyte solution (cell without transfer; EC:96). When the electrolyte solutions in the electrodes differs salt bridges should be used filled with electrolyte solutions of salts with equal mobility of anions and cations like eg. KCl or KNO_3.

The use of a hydrogen electrode is somewhat inconvenient because permanent purging of the platinum electrode with a stream of hydrogen gas is necessary. Thus other electrodes with a stable, reproducible and well-defined electrode potential are frequently used instead. Particularly popular are calomel and silver chloride electrodes. Their electrode potential depends on the concentration of KCl employed as electrolyte (electrodes of a second kind) he respective values are tabulated (Landolt-Börnstein, 6th edition, volume II, section 7).

The relationship between electrode potential (always in equilibrium in his chapter) and activities of the species involved in he electrode reaction is given by the Nernst equation:

$$E = E_0 + ((R \cdot T)/(n \cdot F)) \cdot \ln \prod_i a_i^{\nu_i} \qquad (2.8)$$

The product of activities $\prod_i a_i^{\nu_i}$ equals the equilibrium constant of the electrode reaction. Activities of solid phases are 1; the same applies to gases at standard pressure. Accordingly he following relationships can be derived for the electrodes studied here:

a) Ag/Ag^+-Electrode

$$\mathrm{Ag} \leftrightarrows \mathrm{Ag}^+ + \mathrm{e}^- \qquad (2.9)$$[1]

$$E_0(\mathrm{Ag/Ag}^+) = E_{00}(\mathrm{Ag/Ag}^+)+((R\cdot T)/F)\cdot\ln\, a_{\mathrm{Ag}^+} \tag{2.10}$$

b) $\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}$-Electrode

$$\mathrm{Fe}^{2+} \leftrightarrows \mathrm{Fe}^{3+} + \mathrm{e}^- \tag{2.11}$$

$$E_0(\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+})=E_{00}(\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+})+(R\cdot T)/F)\cdot\ln(\,a_{\mathrm{Fe}^{3+}}\,/\,a_{\mathrm{Fe}^{2+}}\,) \tag{2.12}$$

c) H_2-Electrode

$$\mathrm{H}_2 \leftrightarrows 2\ \mathrm{H}^+ + 2\ \mathrm{e}^- \tag{2.13}$$

$$E_0(\mathrm{H}_2) = E_{00}(\mathrm{H}_2) + ((R\cdot T)/(2\cdot F))\cdot\ln(\,a^2_{\mathrm{H}^+}\,/\,p_{\mathrm{H}_2}\,) \tag{2.14}$$

$$= E_{00}(\mathrm{H}_2) + ((R\cdot T)/(F))\cdot\ln(\,a_{\mathrm{H}^+}\,/\,p^{1/2}_{\mathrm{H}_2}\,) \tag{2.15}$$

or at $p_{\mathrm{H}_2} = p_0$ and $E_{00}(\mathrm{H}_2) = 0$ V

$$E_0(\mathrm{H}_2) = ((R\cdot T)/F)\cdot\ln a_{\mathrm{H}^+} \tag{2.16}$$

d) Ag/AgCl-Electrode

$$\mathrm{Ag} + \mathrm{Cl}^- \leftrightarrows \mathrm{AgCl} + \mathrm{e}^- \tag{2.17}$$

$$E_0(\mathrm{Ag/AgCl}) = E_{00}(\mathrm{Ag/AgCl})+((R\cdot T)/F)\cdot\ln(a_{\mathrm{AgCl}}/a_{\mathrm{Ag}}\cdot a_{\mathrm{Cl}^-})) \tag{2.18}$$

$$E_0(\mathrm{Ag/AgCl}) = E_{00}(\mathrm{Ag/AgCl})–((R\cdot T)/F)\cdot\ln a_{\mathrm{Cl}^-} \tag{2.19}$$

Standard electrode potentials are needed for calculations of activity coefficients based on electrode potential measurements. He following procedure is applied:

1. Measurement of equilibrium cell voltage at various concentrations of ionic species
2. Extrapolation of data to $c = 0$ **M** ($\gamma = 1$) based on Debye-Hückel theory.

As an example the cell

$$\mathrm{Ag/AgCl/\ HCl/H_2/Pt} \tag{2.20}$$

With the cell reaction

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[1] For better visibility subscripts denoted in description of an electrode are written in line here.

$$\mathrm{AgCl} + \tfrac{1}{2}\,\mathrm{H_2} \leftrightarrows \mathrm{Ag} + \mathrm{H^+} + \mathrm{Cl^-} \tag{2.21}$$

The cell voltage U_0 is given by

$$U_0 = E_0(\mathrm{Ag(AgCl)} - E_0(\mathrm{H_2}) \tag{2.22}$$

$$= E_{00}(\mathrm{Ag/AgCl}) - ((R\cdot T)/F)\cdot \ln a_{\mathrm{Cl^-}} - ((R\cdot T)/F)\cdot \ln a_{\mathrm{H^+}} \tag{2.23}$$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((R\cdot T)/F)\cdot(\ln a_{\mathrm{Cl^-}} + \ln a_{\mathrm{H^+}}) \tag{2.24}$$

With $a^2_{\mathrm{HCl}} = a_{\mathrm{H^+}} \cdot a_{\mathrm{Cl^-}}$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((R\cdot T)/F)\cdot \ln a^2_{\mathrm{HCl}} \tag{2.25}$$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((2\cdot R\cdot T)/F)\cdot \ln a_{\mathrm{HCl}} \tag{2.26}$$

and $a_{\mathrm{HCl}} = c_{\mathrm{HCl}}\cdot\gamma_{\mathrm{HCl}}$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((2\cdot R\cdot T)/F)\cdot \ln(c_{\mathrm{HCl}}\cdot\gamma_{\mathrm{HCl}}) \tag{2.27}$$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((2\cdot R\cdot T)/F)\cdot \ln c_{\mathrm{HCl}} - ((2\cdot R\cdot T)/F)\cdot \ln \gamma_{\mathrm{HCl}} \tag{2.28}$$

and according to Debye-Hückel theory $\ln \gamma_\pm = -\,0.037\, c^{1/2}$

$$U_0 - E_{00}(\mathrm{Ag/AgCl}) = -((2\cdot R\cdot T)/F)\cdot \ln c_{\mathrm{HCl}} + ((2\cdot R\cdot T)/F)\cdot 0.037\, c^{1/2} \tag{2.29}$$

$$U_0 + ((2\cdot R\cdot T)/F)\cdot \ln c_{\mathrm{HCl}} = E_{00}(\mathrm{Ag/AgCl}) + ((2\cdot R\cdot T)/F)\cdot 0.037\, c^{1/2} \tag*{(2.29)}$$

Plotting $(U_0 + ((2\cdot R\cdot T)/F)\cdot \ln c_{\mathrm{HCl}})$ versus $c^{1/2}$ yields the standard electrode potential $E_{00}(\mathrm{Ag/AgCl})$ as the y-axis intersection.

Execution

Chemicals and instruments

Diluted nitric acid (1:1)
Aqueous solution of $AgNO_3$, 0.1 **M**
Aqueous solution of KNO_3, 0.1 **M**
Aqueous solution of $FeCl_3$, 0.01 **M**
Aqueous solution of $FeSO_4$, 0.1 **M**
Aqueous solution of $FeSO_4$, 0.01 **M**
Aqueous solution of HCl, 3 **M**, in automatic burettes
Galvanic cell with H_2- and Ag/AgCl-electrode
Hydrogen supply (tank, pressure reducer, needle valve)
Nitrogen supply (tank, pressure reducer, needle valve)
High input impedance voltmeter
Galvanometer (sensitive ammeter)

Weston cell
Silver electrode
Platinum electrode
Calomel electrode
10 measurement flasks 100 ml

1. Standard potential and mean activity coefficient

Setup

The setup of the galvanic cell is shown below:

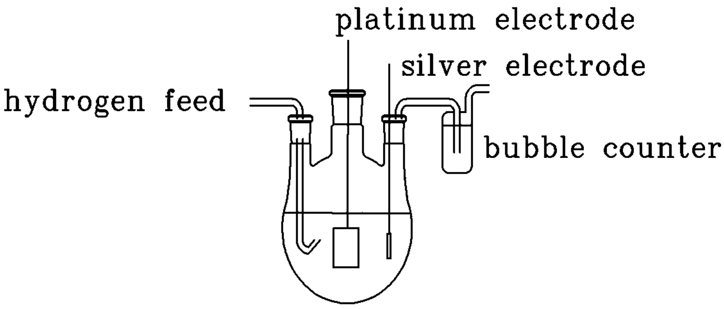

Fig. 2.2: The galvanic cell for determination of a standard potential

Procedure

- By diluting the stock solution of 3 **M** HCl the following solutions (10 ml each) are prepared: 2; 1; 0.5; 0.1; 0.05; 0.01; 0.005; 0.001 and 0.0005 **M**.
- The galvanic is filled with one of he solutions starting with the most dilute one; hydrogen flow is adjusted to about 2 bubbles per second.
- The voltmeter is calibrated (if necessary) with the Weston-cell.
- Because of the logarithmic relationship between activity and electrode potential determination of the equilibrium potential must be performed with great care. Cell voltages must be constant within 0.1 mV before recording.

Evaluation

The standard potential of the Ag/AgCl-electrode is determined graphically according to eq. (2.30). Fig. 2.3 shows a typical result:

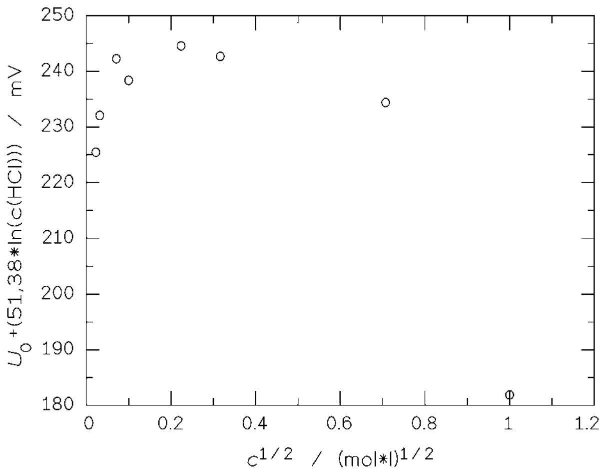

Fig. 2.3: Plot used for the graphic determination of the standard electrode potential of the Ag/AgCl-electrode

Extrapolation using the cell voltages measured at small concentrations (at higher concentrations deviations are too large) yields a value of E_{00} =0.225 V the literature value is E_{00} =0.222 V.

Using this result activities a and activity coefficients γ of HCl can be calculated according to

$$U_0 = E_{00}(\mathrm{Ag/AgCl}) - ((2 \cdot R \cdot T)/F) \cdot \ln a_{\mathrm{HCl}} \qquad (2.31)$$

With the data displayed values of γ ranging from 0.904 at the lowest and 5 at the highest concentration are calculated.

2. Determination of electrode potentials

Setup

The silver electrode is formed by a silver wire dipping into an aqueous solution of $AgNO_3$. The saturated calomel electrode serving as the second (and reference) electrode is connected to the silver electrode via a salt bridge filled with an aqueous solution of 0.1 **M** KNO_3.[1]

A platinum electrode dipping into the solution containing both Fe^{2+} and Fe^{3+} ions establishes a redox electrode. The saturated calomel reference electrode can be dipped directly into this solution.

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[1] Contamination of the silver nitrate solution with chloride ions must be avoided; the porous plug of the calomel electrode may get plugged with silver chloride.

The reference electrode is always connected to the “low” or “mass”/”ground” input of the voltmeter I order to get voltages and potentials with proper sign.

Execution

Ag/Ag^+-Electrode

Diluted aqueous solutions (25 ml each) of $AgNO_3$ with concentrations of 0.05; 0.02; 0.01; 0.005; 0.002 and 0.001 **M** are prepared by diluting of the stock solution. The silver wire is cleaned with diluted nitric acid, carefully rinsed and dipped into he silver nitrate solutions. Voltages are measured with a high input impedance voltmeter versus the saturated calomel electrode connected to the silver electrode with the salt bridge starting with the most diluted solution.

Fe^{2+}/Fe^{3+}-electrode

25 ml of a 0.01 **M** solution of $FeCl_3$ are placed in the cell vessel and purged with nitrogen. Subsequently 0.5; 1; 5; 10 and 20 ml of the 0.01 **M** aqueous solution of $FeSO_4$ are added; after every addition the solution is mixed with a brief nitrogen purge, the voltage versus the saturated calomel reference electrode is measured after switching off the purge. In order to obtain low ratios of c_{ox}/c_{red} the procedure is repeated starting with 25 ml of a 0.1 **M** solution of $FeCl_3$ and subsequent additions of 2.5; 5; 10 and 25 ml of a 0.1 **M** aqueous solution of $FeSO_4$.

Evaluation

From the measured cell voltages the electrode potentials are calculated they are plotted vs $\lg c_{Ag^+}$ or $\lg(c_{Fe^{3+}} / c_{Fe^{2+}})$. The slope of the curves is determined, extrapolation to lg $c = 0$ is done to determine the respective standard electrode potentials. Taking into account the potential of the saturated calomel electrode the standard potential of he silver electrode is determined $E_{00} = 0.81$ V. The literature value is $E_{00} = 0.799$ V. A typical lot of the measured cell voltage is displayed in Fig. 2.4 (next page).

Questions

Explain the term “mean activity coefficient”

Describe the calculation of mean activity coefficients according to the Debye-Hückel theory.

Explain the term “cell without transference”

Why do you need cells without transference for exact determination of standard electrode potentials?

Discuss the error caused by variations of hydrogen pressure (ambient atmospheric pressure).

Which systematic error must be taken into account when using he method described here?

Describe the design of the Weston cell. Why does it guarantee a constant cell voltage?

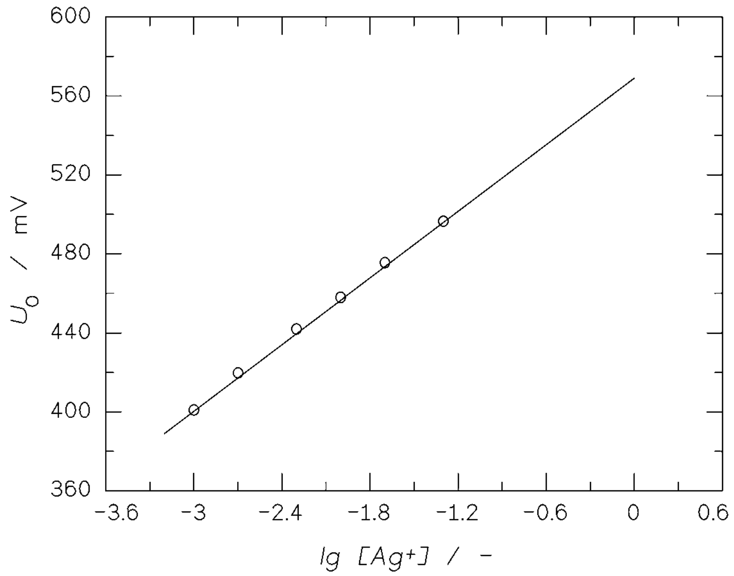

Fig. 2.4: Plot of the cell voltages obtained during the determination of the standard electrode potential of the silver electrode

Experiment 2.3: pH-Measurements and potentiometrically indicated titrations

Task

1: Registration of a calibration curve for a glass electrode and an antimony electrode

2: Calibration of a pH-meter for Measurements with a glass electrode

3: Potentiometrically indicated titration of formic acid, acetic acid, propionic acid, chloroacetic acid and dichloroacetic acid with KOH, determination of the respective pK_a-values[1] from the titration curves.

Fundamentals

Amid pH-measurement methods the potentiometric method is he most important one. Starting with the definition of the pH-value

$$\mathrm{pH} = -\lg a_{\mathrm{H}^+} \qquad (2.32)$$

it is obvious that a pH-measurement is strictly speaking the determination of a single ion activity. Even with cells without diffusion potentials (see exp. 2.2) only mean activity values can be obtained. They are equal only at very dilute concentrations (Debye-Hückel region). Thus as a standard for pH-measurements selected buffer solutions are used (IUPAC recommendation) with a hydrogen electrode as proton-selective electrode in a setup:

H_2-electrode/buffer solution/salt bridge 1 **M** KCl/reference electrode

The pH-value of the buffer solution is related to the measured cell voltage and the potential of the reference electrode E_{ref}:

$$\mathrm{pH} = (U_0 - E_{\mathrm{ref}})/(2.303 \cdot R \cdot T/F) \qquad (2.33)$$

This way the conventional pH-scale is established, he basis of practical pH-measurements. With these standard buffers as reference pH-values of solutions with unknown concentrations can be determined, the dependency of the voltage of a cell with a pH-sensitive electrode on the pH-value can be obtained (so-called “electrode function”).

Preferred pH-sensitive electrodes are the glass electrode, the quinhydrone electrode (EC:135) and some metal oxide electrodes (Sb- and Bi-electrode). The most popular electrode is the glass electrode. The most convenient constructions contain both electrodes (the pH-sensitive and the reference electrode) in a single cell body. These electrodes cannot be produced with exactly equal properties. In addition sensitivity and zero-point (the voltage measured with solutions of equal pH inside and outside the device) are subject to ageing. Calibration is done with at least two different buffer solutions.

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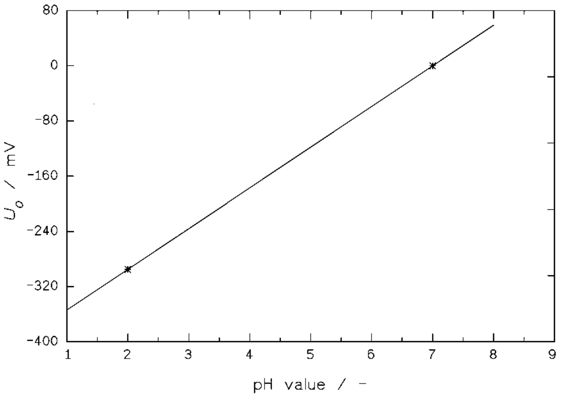
[1] The general concentration equilibrium constant K_c is modified and specified for acid dissociation K_a.

A typical result is displayed below:

Fig. 2.5: Calibration curve of a glass electrode



For exact measurements the pH-values of the used buffers should be similar to the unknown ones. With the calibration the slope in mV/pH-unit or (equivalent and more popular) the sensitivity in % (100 % equals the theoretical value from the Nernst-equation 59 mV/pH-unit) and the zero-point (pH-value with voltage 0 expected with equal pH-values inside and outside) are adjusted. In addition the temperature must be taken into account.

Quantitative concentration measurements for analytical purposes (e.g. determination of the concentration of a solution of HCl) are not very precise because of the logarithmic relationship between activity and electrode potential. Potentiometry can nevertheless be used conveniently for indication of the equivalent point in titrations. The electrode used to detect changes in the titrated solution is called indicator electrode; selection depends on the type of titration: In argentometry a silver electrode is used, in redox titrations a platinum or glassy carbon electrode may be appropriate, in acid-base titrations a glass electrode is suitable. The equivalent point is indicated by a large change in cell voltage (i.e. potential difference between indicator and reference electrode). A plot of cell voltage versus added volume of titration solution yields characteristic curves with a turning point (if necessary determined by drawing a tangent line) at the equivalent point. A typical case is shown below.

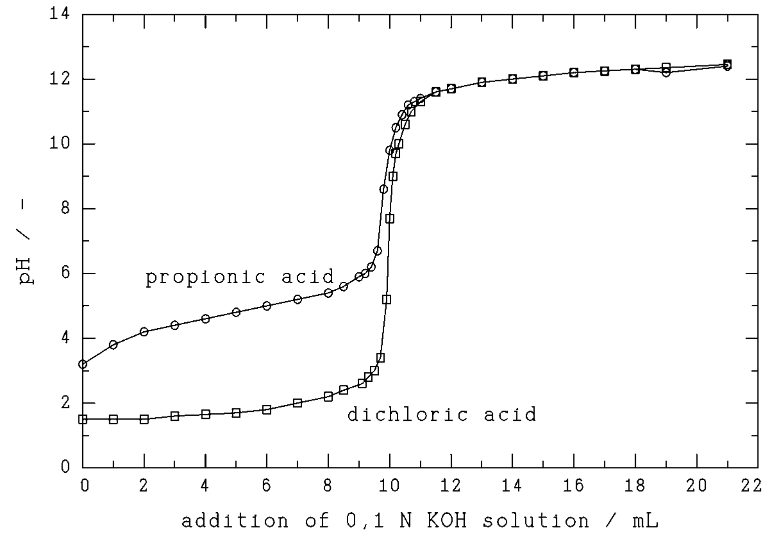


Fig. 2.6: Determination of equivalent points and pK_a-values

During titrations of weak or medium-strong acids the equivalent point is not located at pH = 0 because the salt formed as a product of neutralization is hydrolysed. When 50 % of the initially present acid is converted (i.e. neutralized) the titrated solution contains equimolar fractions of salt and acid, this equivalent to a buffer solution with well-defined pH-value. From the pH-value corresponding to this point of the titration curve the dissociation constant K_a can be determined according to

$$\mathrm{HA} \leftrightarrows \mathrm{H}^+ + \mathrm{A}^- \qquad (2.34)$$

$$K_a = (a_{\mathrm{H}^+} a_{\mathrm{A}^-}) / a_{\mathrm{HA}} \qquad (2.35)$$

$$-\lg K_a = -\lg a_{\mathrm{H}^+} - \lg a_{\mathrm{A}^-} / a_{\mathrm{HA}} \qquad (2.36)$$

With $a_{\mathrm{A}^-} \cong c_{\mathrm{salt}}$ and $a_{\mathrm{HA}} \cong c_{\mathrm{HA}} \cong c_{\mathrm{Acid}}$ an approximation is possible[1]:

$$-\lg K_a = \mathrm{pH} \qquad (2.37)$$

Eq. (2.37) is valid only for weak acids because only in case of very incomplete dissociation the activity of the formed salt will be approximately equivalent to the concentration $a_{\mathrm{A}^-} \cong c_{\mathrm{salt}}$ and the fraction of undissociated acid will be very close to the total acid concentration (and activity). The data plotted in Fig. 2.6 yield for dichloroacetic acid $K_a = 10^{-1.3}$, a literature value of $K_a = 10^{-1.28}$ has been reported (H.A. Staab, Einführung in die theoretische or-

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[1] The subscript HA indicates the undissociated fraction of acid; Acid refers to the total amount of acid added into he solution.

ganische Chemie, 4th ed., Verlag Chemie, Weinheim 1964, p. 610; ???). The value for propionic acid is $K_a = 10^{-4.8}$, a literature value is $K_a = 1.4\ 10^{-5}$ (P.W. Atkins, Physikalische Chemie, 2nd ed.,VCH, Weinheim 1996, p. 1045).

Execution

Standard buffer solutions pH = 9.18; 6.86; 4.01 and 1.68
aqueous solutions (0.1 M) of acetic acid, formic acid, propionic acid, chloroacetic acid and dichloroacetic acid
Aqueous titration solution of KOH (0.1 **M**)
pH-meter
Glass-electrode
Antimony electrode
Saturated calomel electrode
Glass beakers 10 0ml
Magnetic stirrer
Magnetic stirrer bar

Setup

During setup and execution mechanical sensitivity of the thin membrane of the glass electrode must be kept in mind.

Recording calibration curves

- Wiring of the measurement circuit (connect glass electrode to pH-meter, install antimony electrode and reference electrode, connect to pH-meter set to voltmeter mode).
- Put buffer solution into beaker, dip electrodes into solution, record cell voltage when value is stable. Discard buffer solution or return it into storage vessel; do not return into original bottles.

Hint: In strongly acidic solution the antimony electrode is unstable.

Calibration of pH-meter[1] with glass electrode

- Dip glass electrode into buffer solution pH = 6.86.
- Set range to 0 … 14

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[1] The actual labels on the front plate of the pH-meter may vary; instead of asymmetry zero-point may be found.

- Adjust “sensitivity” to 100 % (right limit)
- Adjust temperature setting to actual value in buffer solution
- Adjust displayed pH value exactly to pH = 6.86 with knob “sensitivity”[1]
- Rinse electrode carefully and exchange buffer solution:
- New solution pH = 4.01 for measurements at pH < 7
- New solution pH = 9.18 for measurements at pH > 7
- (Since following acids are investigated use pH = 4.01)
- adjust to exactly pH = 4.01 with knob “sensitivity”
- check with third buffer solution

Potentiometric titration of weak acids

- The acids are supplied a concentrations c = 0.1 **M**. Use the calibrated pH-meter with attached glass electrode.
- Put 10 ml of acid into beaker, add magnetic stirrer bar, place beaker on magnetic stirrer plate, adjust rate of rotation low enough to keep stirrer from hitting the glass membrane. Titrate by adding solution of KOH (0.1 **M**) in 1 ml steps.

Evaluation

- Plot the calibration curve and determine slope of curve in mV/pH-unit. Discuss electrode properties and estimate precision of measurement.
- Plot titration curve as shown in Fig 2.6. Determine equivalent point and pH-value at 50 % conversion of acid.
- Calculate K_a-value and compare with literature data. Set up table of results for all acids and discuss relationship between strength of acid, type of intramolecular bondings and deviation from literature data for chlorinated acids.

The following calibration curve was obtained with an antimony electrode as proton (and pH)-sensitive electrode and a saturated calomel electrode as reference electrode in buffer solutions of various compositions.

---

[1] In case no proper adjustment is possible the glass electrode may be degenerated by e.g. dryness, damage of membrane. When there is no visible damage or lack of solution in the glass electrode (some glass electrodes can be refilled) extended soaking in an aqueous solution of KCl (3 **M**) may regenerate the electrode The instruction manual of the electrode may provide further help.

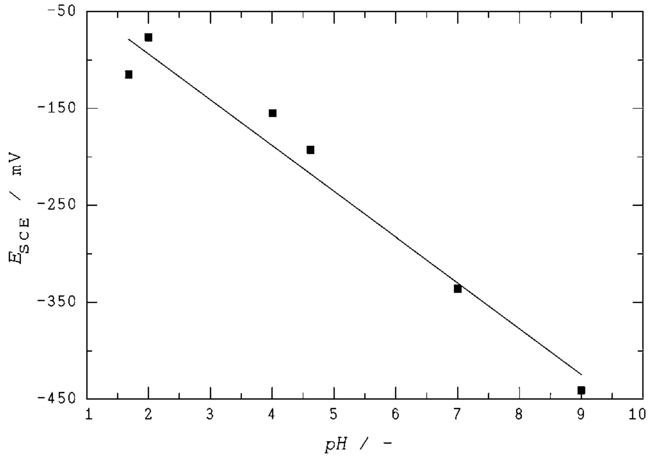

Fig. 2.7: Calibration curve of an antimony electrode as pH-sensitive electrode

The calculated sensitivity of 53 mV/pH-unit is somewhat below the theoretical value of 59 mV/pH-unit. The instability of he electrode at low pH-values is obvious.

Questions

- Describe the establishment of the cell voltage of a glass electrode
- What is a conventional pH-scale? Why was it established?
- Which electrode reactions are proceeding at a quinhydrone and at an antimony electrode?
- Describe he advantages of a potentiometric titration
- What is a buffer solution? Describe representative acidic, neutral and alkaline buffer systems

Experiment 2.4: Redox titrations (Cerimetry)

Task

The amount of Fe(II) ions in a sample solutions shall be determined by redox titration with a solution of Ce(IV) ions and a platinum indicator electrode.

Fundamentals

Ce(IV) ions are strong oxidants ($E_{00,\mathrm{Ce}^{3+}/\mathrm{Ce}^{4+}} = +\ 1.44$ V [1]) and can be used as titrands (“cerimetry”). Because of their weak coloration detection of the equivalent point based on color changes is not feasible. Potentiometric determination with an indicator electrode made of an inert electron conducting material like e.g. platinum are possible. The observed titration curve shows an almost horizontal part at additions of titration solution before the equivalent point, a large slope around the equivalent point and again an almost horizontal line beyond it.

The potential of the indicator electrode is always determined by he concentrations (or more precisely the activities) of the participating redox ions. At low degrees of titration (at the beginning) and at high degrees (considerable excess of titrand). In the first case the potential is solely controlled by the concentrations of the ions o be titrated because the titrand itself is present in one form only (the added form is consumed immediately and completely by the homogeneous redox reaction) and thus cannot determine a redox potential itself. At a degree of titration 0.5 (half way to the equivalent point) the ratio of concentrations of the reduced and the oxidized form of the titrand is 1, thus the concentration dependent term in the Nernst equation vanishes. The electrode potential of the indicator electrode is equal to the standard potential. A degree of titration 2 ions of the kind to be determined are present only in their converted form, they cannot establish a redox potential. The concentration of the oxidized and the reduced form of the titrand are equal, again the concentration-depending term in the Nernst equation vanishes. Now the potential of the indicator electrode is equal to the standard po-

---

[1] Values of E_{00} published in reference books vary considerably; the value given here is conformed by the subsequent. The value depends on the composition of the electrolyte solution (“real potential”)

tential of the titrand. Accordingly titration curves obtained during redox titrations can be used to determine further electrochemical data beyond the concentration.

Execution

Chemicals and instruments

Aqueous solution of Fe^{2+} (0.01 **M**)
Aqueous solution of Ce^{4+} (0.01 **M**)
Beaker
Burette
Saturated calomel reference electrode
Platinum electrode as indicator electrode
High input impedance voltmeter
Magnetic stirrer
Magnetic stirrer bar

Setup

The solution containing iron ions at unknown concentration is put in the beaker; pure water and the magnetic stirrer bar are added. The platinum and the calomel electrode are placed in safe distance from the stirrer bar. The reference electrode is connected to the "low" input of the voltmeter.

Execution

The cerium-on solution is added in small volumes (initially 0.5 ml close to the equivalent point even smaller) Additions are stopped at a total volume equivalent to double the amount added at the equivalent point (degree of titration 2)

Evaluation

A typical titration curve is shown in Fig. 2.8 (next page). At a degree of titration 0.5 the indicator electrode shows a potential E_{SCE} = 0.53 V, the literature value for the Fe(II)/Fe(III) redox system is E_{SCE} = 0.53 V. At a degree of titration 2 a potential of E_{SCE} = 1.12 V is found, the literature value for the Ce(III)/Ce(IV) redox system is E_{SCE} = 1.2 V(note the conversion from the value relative to the standard hydrogen electrode given above to the value on the saturated calomel scale). The observed deviations are mostly due to differences in composition of the electrolyte solution

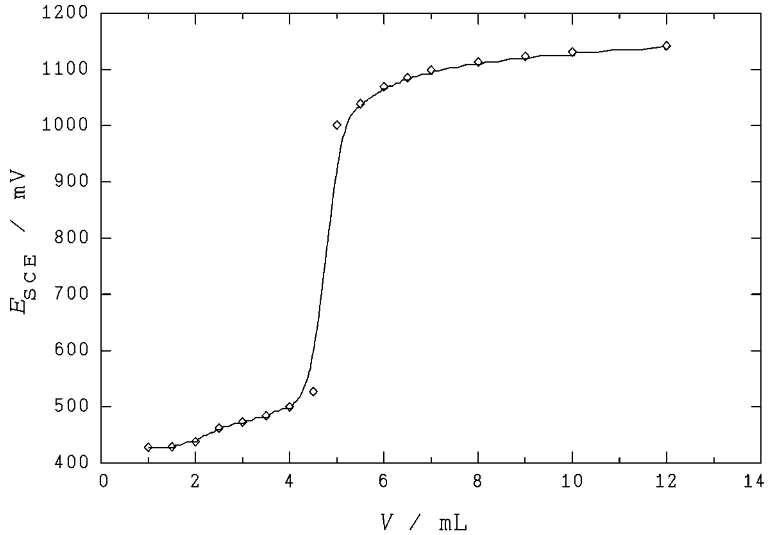

Fig. 2.8: Titration curve of the titration of Fe(II) ions (5 ml solution with c = 0.01 **M**) with Ce(IV) ions (c = 0.01 **M**)

Experiment 2.5: Differential potentiometric titration

Task

Determination of the content of Fe(I) ions by redox titration with Ce(IV) ions with differential potentiometric titration method and platinum indicator electrodes

Fundamentals

Aqueous solutions of Ce(IV) ions are strong oxidants ($E_{00,Ce^{3+}/Ce^{4+}}$ = + 1.44 V), because of higher stability when compared with permanganate solutions they are preferred reagents in redox titrations (“cerimetry”). Their color is weak only; color changes are insufficient for detection of the equivalent point. A plot of the change of cell voltage (of the cell composed of the platinum indicator electrode and the reference electrode) observed after addition of a fixed volume of titration solution as a function of total volume yields a plot as shown below:

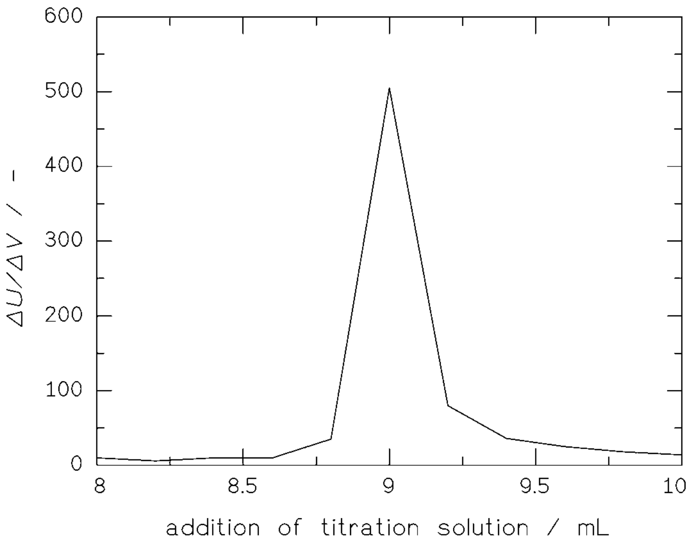

Fig. 2.9: $\Delta U/\Delta V = \mathrm{f}(V)$ during a potentiometric titration

The plot is equivalent to the first derivative of the corresponding titration curve showing the cell voltage as a function of the added volume of titrand (see fig. 2.8). The maximum in fig. 2.9 indicates the equivalent point. In a differential potentiometric titration this curve is obtained directly (i.e. without differentiation). Two indicator electrodes of the same material are dipped in the solution; one electrode is surrounded by a capillary. The capillary keeps changes in the titration solution caused by he addition of titrand away from this indicator electrode, this electrode maintains its potential. The cell voltage now corresponds to the concentration change effected by the addition, the cell is a “concentration cell” (EC:??). In this cell the cell voltage (electrode potential difference) is not generated by a chemical cell reaction, but by differences in concentration of the participating ions and the subsequent transfer f ions from places of higher activity to those of lower activity. With activities inside the capillary *a’* the cell voltage before reaching the equivalent point is given by:

$$U = E - E' = ((R\cdot T)/F)\cdot \ln((a_{\mathrm{Fe}^{3+}} \cdot a'_{\mathrm{Fe}^{2+}})/(a_{\mathrm{Fe}^{2+}} \cdot a'_{\mathrm{Fe}^{3+}})) \quad (2.38)$$

The cell voltage is solely caused by differences in activity; any terms related to the standard potentials of the electrode reactions is vanished. If he solution inside the capillary is not exchanged during the whole titration a normal titration curve (see fig. 2.8) is obtained. When the solution inside the capillary is mixed with the bulk solution after every addition of titrand the ratio $\Delta U/\Delta V$ is obtained directly. It shows a maximum at he equivalent point.

Execution

Chemicals and instruments

Aqueous solution of Fe^{2+} (0.01 **M**)
Aqueous solution of Ce^{4+} (0.01 **M**)
Cell for differential potentiometric titration with platinum electrodes
High input impedance voltmeter
Burette
Magnetic stirrer
Magnetic stirrer bar

Setup

The cell is shown schematically in fig. 2.10 Exchange of solution in he capillary is effected by pressing the rubber bulb.

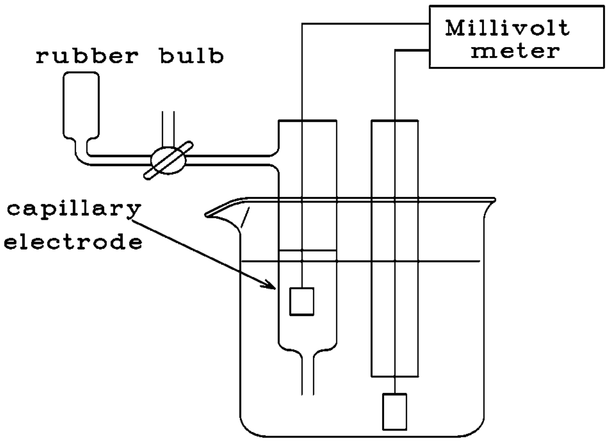

Fig. 2.10: Cell for differential potentiometric titration

Procedure

- To 10 ml of a sample solution with Fe(II) ($c = 0.01$ **M**) in the beaker water is added until capillary and indicator electrode are immersed. With he rubber bulb the capillary volume is purged and filled with sample solution.
- Connect electrodes to voltmeter, switch on voltmeter

- Record data for the normal titration curve by adding titration solution without exchange of solution in he capillary volume. Start with additions of 1 ml, close to the equivalent point smaller volumes are added, later larger ones may be added.
- Record data for the differential potentiometric titration curve by exchanging the solution inside the capillary with the bulk in he beaker by pressing and releasing he rubber bulb carefully after every addition of titrand until the cell voltages reaches a minimum Amounts off added volume are adjusted as before.
- Calculate the amount of Fe(II) in the initial sample.

Evaluation

Plot both titration curves and determine equivalent points. Typical results are shown below.

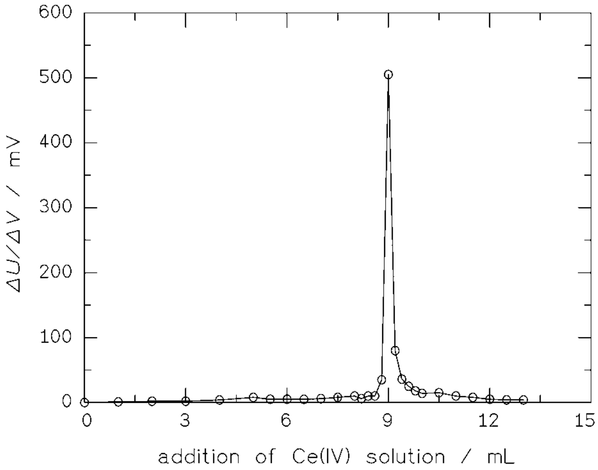

Fig. 2.11: Titration curve of a differential potentiometric titration with exchange of solution after every addition of titrand

The advantage of this approach becomes immediately visible when comparing this plot with the result obtained with the same setup without exchange of solution as displayed in fig. 2.12 (next page.)

Questions

- Describe a concentration cell
- Develop a setup for differential potentiometric titration with the argentometric method

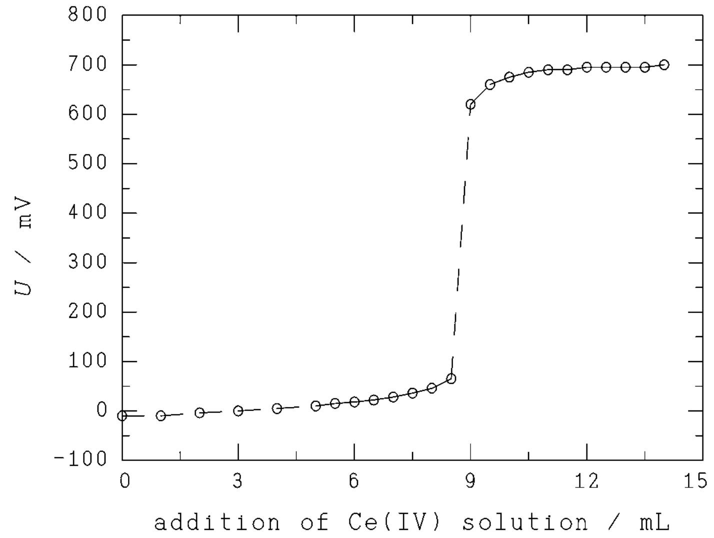

Fig. 2.12: Titration curve of a differential potentiometric titration without exchange of solution after every addition of titrand

Experiment 2.6: Potentiometric measurement of the kinetic of the oxidation of oxalic acid

Task

The homogeneous oxidation reaction of oxalate with permanganate is monitored potentiometrically at different temperatures in order to obtain reaction rate constant and energy of activation.

Fundamentals

The oxidation of oxalic acid proceeds according to

$$2\,\mathrm{MnO_4^-} + 5\,\mathrm{C_2O_4^{2-}} + 16\,\mathrm{H^+} \rightarrow 2\,\mathrm{Mn^{2+}} + 8\,\mathrm{H_2O} + 10\,\mathrm{CO_2} \qquad (2.39)$$

This reaction was studied for the first time by Harcourt in Oxford as the first chemical reaction with respect to the elucidation of he laws of chemical reaction kinetics. The choice was a rather unlucky one – the reaction is autocatalytical.

For a simple autocatalytic reaction

$$\mathrm{A} \xrightarrow[\mathrm{B}]{k} \mathrm{B} \qquad (2.40)$$

with initial concentration $c_{\mathrm{i},0}$ of substance I and – to simplify subsequent integration – the degree of conversion x (the fraction x of the total concentration of reactant converted at time t)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \cdot (c_{\mathrm{A},0} - x) \cdot x \tag{2.41}$$

At $x = c_{\mathrm{A},0}/2$ the rate is at a maximum. At $x = 0$ the rate is zero. Assuming a finite – albeit small – initial concentration of B with $c_{\mathrm{B},0}$ eq. (2.41) is modified into

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1 \cdot (c_{\mathrm{A},0} - x) \cdot (c_{\mathrm{B},0} + x) \tag{2.42}$$

Double integration from 0 to t and 0 to x yields

$$\frac{1}{c_{\mathrm{A},0} + c_{\mathrm{B},0}} \ln\left(\frac{c_{\mathrm{A},0} \cdot (c_{\mathrm{B},0} - x)}{c_{\mathrm{B},0} \cdot (c_{\mathrm{A},0} - x)}\right) = k \cdot t \tag{2.43}$$

With $c_0 - c_\mathrm{t} = x$ simplification is possible

$$k = \frac{1}{t \cdot (c_{\mathrm{A},0} + c_{\mathrm{B},0})} \ln \frac{c_{\mathrm{A},0} \cdot c_{\mathrm{B,t}}}{c_{\mathrm{B},0} \cdot c_{\mathrm{A,t}}} \tag{2.44}$$

Observation of color changes enables simple examination of the claimed autocatalysis. During the application of this reaction in quantitative analysis in measurements of oxalic acid after the initial addition of permanganate solution no decoloration is observed; actually one might be afraid of having added too much already. After several seconds decoloration proceeds nevertheless, and subsequently decoloration occurs rapidly after every addition of permanaganate solution until the equivalent point is reached. The Mn^{2+} ions formed in the titration reaction are acting as catalysts (autocatalysis).

Advance of the reaction can be monitored visually quite easily – disappearance of the pink color very strong even at low permanganate concentrations conversion with respect to the added permanganate can be assumed to be completed. More precisely it can be stated only, that conversion has proceeded to a state where the (low) concentration of permanganate cannot be observed visually any more. Instead the reaction can be monitored potentiometrically by measuring the redox potential of the electrode $\mathrm{MnO_4^-/Mn^{2+}}$. The redox electrode potential is given by

$$E_0 = E_{00} + \frac{R \cdot T}{z \cdot F} \ln \frac{a_{\mathrm{ox}} a_{\mathrm{H^+}}^8}{a_{\mathrm{red}}} \tag{2.45}$$

In the evaluation of the electrode potential vs. time curves we study the turning point (at which visually observed permanganate is apparently completely converted). We identify the educt A in eq. (2.40) with the permanganate; the manganese ion refers to B. A change of the electrode potential from the initial value E_i to a value E_t at he turning point can be correlated with the concentration of permanganate and manganese ions and the respective concentration ratios:

$$\Delta E = E_\mathrm{i} - E_\mathrm{t} = E_{00} - \frac{R\cdot T}{z\cdot F}\ln\frac{a_\mathrm{ox,i}a^8_{\mathrm{H^+,t}}}{a_\mathrm{red,i}} - E_{00} - \frac{R\cdot T}{z\cdot F}\ln\frac{a_\mathrm{ox,t}a^8_{\mathrm{H^+,i}}}{a_\mathrm{red,t}} \qquad (2.46)$$

Assuming a constant pH-value fixed by the added sulfuric acid and activities being approximately equal to concentrations at the small values employed here simplification yields

$$\Delta E = \frac{R\cdot T}{z\cdot F}(\ln(c_\mathrm{ox,i}/c_\mathrm{red,i}) - \ln(\mathrm{c}_\mathrm{ox,t}/c_\mathrm{red,t})) \qquad (2.47)$$

or

$$\Delta E = \frac{R\cdot T}{z\cdot F}\ln\frac{c_\mathrm{ox,i}\cdot c_\mathrm{red,t}}{\mathrm{c}_\mathrm{ox,t}\cdot c_\mathrm{red,i}}$$

Rearrangement results in

$$\ln\frac{c_\mathrm{ox,i}\cdot c_\mathrm{red,t}}{\mathrm{c}_\mathrm{ox,t}\cdot c_\mathrm{red,i}} = \frac{\Delta E\cdot z\cdot F}{R\cdot T} \qquad (2.49)$$

This equation can be inserted in eq. (2.44), k is obtained as

$$k = \frac{\Delta E\cdot z\cdot F}{R\cdot T\cdot t_\mathrm{tp}(c_\mathrm{ox,i} + c_\mathrm{red,i})} \qquad (2.50)$$

with time t_tp at the turning point of the potential versus time plot. The term ($c_\mathrm{ox,i} + c_\mathrm{red,i}$) is equal to the initially added concentration of permanganate.

Execution

Chemicals and instruments

Aqueous solution of sulfuric acid 0.01 **M**
Aqueous solution of $KMnO_4$ 0.01 **M**
Aqueous solution of oxalic acid 0.05 **M**
Platinum electrode
Saturated calomel electrode

High input impedance voltmeter
Thermostat
Double-walled measurement cell (thermostat jacket)
Stop watch
Pipet 5 ml
Graded cylinder 100 ml

Setup

Electrodes are connected to the voltmeter (calomel electrode to “low”, platinum electrode to “high” input, the thermostat jacket is connected to the thermostat.

Procedure

Into the cell thermostatted at 35 °C 100 ml water, 5 ml sulfuric acid and 5 ml permanganate solution are added. If everything works well a cell voltage of about 0.9 V shall be observed. The oxalic acid is added with the pipet, when half the complete volume has been added the stopwatch is started. The initially small potential changes are recorded at longer time intervals, around the turning points he time intervals should be smaller, and after the potential drop only a few more values should be recorded. The experiment is repeated at higher temperatures, now recordings shall be made at very short time intervals.

Evaluation

Fig. 2.13 (next page) shows typical potential versus time plots at various reaction temperatures. From the time t_{tp} passed up to the turning point the value of k can be calculated according to

$$(\Delta E\cdot z\cdot F)/(R\cdot T)=\ln(c_{ox,i}/c_{ox,t})=k\cdot t \qquad (2.51)$$

From the plotted data the following rate constants were obtained:

T/°C	k/l·mol^{-1}·s^{-1}	T/°C	k/l·mol^{-1}·s^{-1}
35	41.7	55	270.7
40	76.6	60	389.6
45	125.3	65	534.7
50	163.2	70	867.8

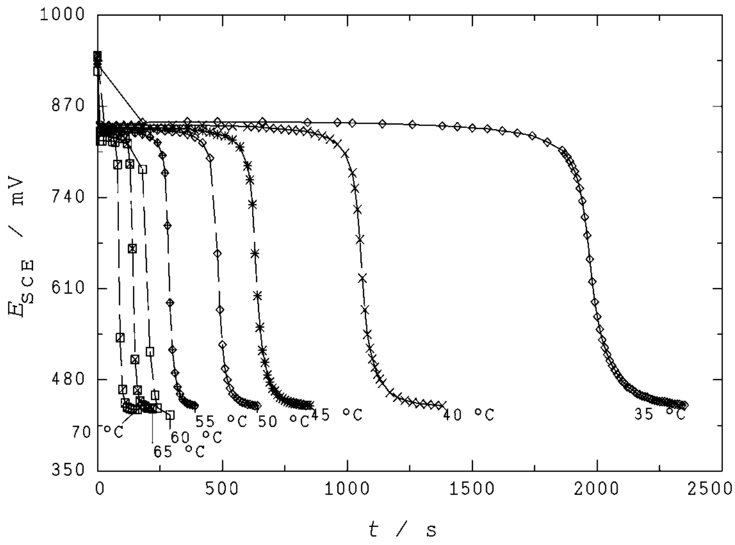

Fig. 2.13: Potential versus time curves recorded during oxidation of oxalic acid with $KMnO_4$ in aqueous acid solution

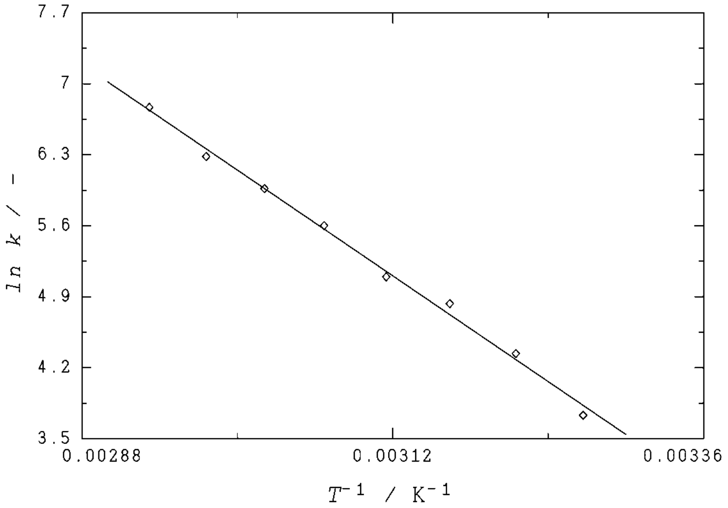

Fig. 2.14: Arrhenius plot of ln k vs. T^{-1}

From the Arrhenius plot the activation energy of E_a = 72 kJ·mol^{-1} is calculated.

Literature

S.R. Logan: Chem. Kinet.

Experiment 2.7: Polarization and decomposition voltage[1]

Task

The temperature dependency of the decomposition voltage of an aqueous solution of HCl (1.2 **M**) and the concentration dependency of the decomposition voltages of HBr and HI shall be determined.

Fundamentals

The equilibrium voltage U_0 of a galvanic or an electrolysis cell calculated fro thermodynamic data can be examined experimentally in a static method (see experiment 2.2) or in a dynamic one. In the second approach the voltage applied to an electrolysis cell is raised slowly; a plot of the measured current versus the applied voltage yields from extrapolation to $I \rightarrow 0$ the decomposition voltage U_d equivalent to U_0. Differences between experiment and calculation are caused by slow electrode reaction (polarization or overvoltage[2]); in the halogen evolution reaction studied here these deviations are not significant.

The relation between the Gibbs energy of a spontaneously proceeding reaction and the cell voltage is given by

$$\Delta G = -\, z \cdot F \cdot U_0 \qquad (2.52)$$

Because electrolysis proceeds only when an external voltage is applied, i.e. at $\Delta G > 0$, the relationship between ΔG and U_0 is

$$\Delta G = z \cdot F \cdot U_0 \qquad (2.53)$$

With the Gibbs equation the enthalpy of reaction ΔG and after determination of the temperature dependency of U_0 he entropy of reaction can be obtained.

---

[1] Because a current – although a small one only - is flowing in this experiment strictly speaking it belongs into the following chapter. Because the aim is the determination of thermodynamic data at equilibrium by extrapolation to current zero the experiment seems to be better placed here. The term decomposition voltage is a linguistic compromise. It refers to the minimum cell voltage needed for decomposition of the electrolyte, i.e. deposition of electrolysis products. Unfortunately the term deposition voltage does not seem to be any better.

[2] Overvoltage ΔU is the difference between the cell voltage at current zero and at a finite current $\Delta U = U - U_0$. With respect to a single electrode the term overpotential with its own symbol η is defined in the same manner: $\Delta E = E - E_0$.

Execution

Chemicals and instruments

Aqueous solution of HC 1.2 **M**
Potassium bromide
Potassium iodide
Hydrogen
Platinum tip electrode
Platinized platinum wire net electrode (used as hydrogen electrode)
Adjustable voltage source
Miroammeter
Thermostat
Double-walled measurement cell (thermostat jacket)

Setup

- In the electrochemical cell connected to the thermostat and equipped with electrodes as depicted schematically below (Fig. 2.15) U_d for HCl is measured at standard conditions ($a_{\mathrm{Cl}^-} = 1$ **M**, $p = 1$ atm (= 101325 Pa), $a_{\mathrm{H}^+} = 1$ **M**).

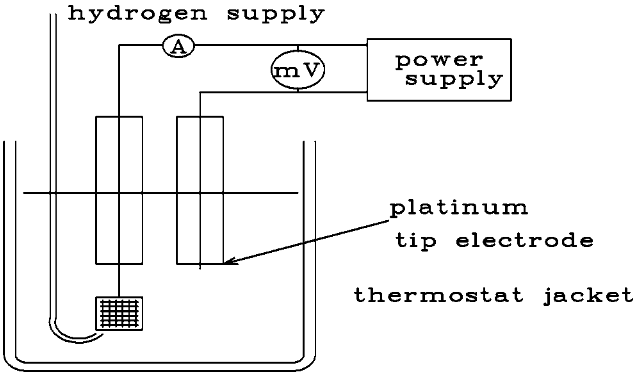

Fig. 2.15: Experimental setup for decomposition voltage measurement

- 75 ml of hydrochloric acid solution (1.2 **M**) are placed in the cell, he hydrogen stream is adjusted to a constant slow flow of bubbles around the platinum net electrode, the cell temperature is adjusted to 15 °C.
- The experiment is started with $U = 0$ V. The voltage is slowly increased (Please explain the current oscillations observed on the microammeter). When a voltage of $U = 1.2$ V is reached the

increase is stopped. After the current has dropped to zero the actual measurement starts. The voltage is raised in steps of 0.02 V, current is recorded after one minute. When the current approaches 100 µA the experiment is finished.

- The measurement is repeated at T = 25 °C, 35 °C and 45 °C.
- U_d for 0.1 **M** and 1 **M** solutions of HBr and HI are determined. To 75 ml of HCl solution 0.9 g KBr are added (this results in a solution 0.1 **M** in HBr). After completing the measurement further 8.1 g KBr are added (final concentration 1 **M** HBr). Again the current potential relationship is measured. To a fresh solution of HCl (1.2 **M**) first 1.26 KI (resulting in 0.1 **M** HI) and after the measurement further 11.34 g KI (final concentration 1 M HI) are added. As before the actual measurement starts at 0.4 V with HBr and at 0.8 V with KI. If currents at these voltages are to large recordings should be started at lower initial values. Above these voltages again currents are recorded after voltage increases in small steps (0.02 V).

Evaluation

The obtained current potential relationships are plotted as shown in a typical example below.

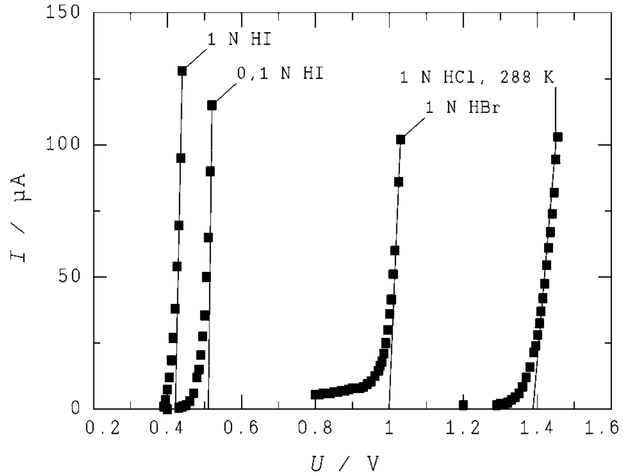

Fig. 2.16: Current potential curves with various halide solutions at T = 288 K.

From U_d obtained by extrapolation to zero current the Gibbs energy of HCl electrolysis is calculated assuming U_d = U_0 at zero current and compared with literature data. According to

$$\Delta G = z \cdot F \cdot U_0 \quad (2.53)$$

The Gibbs energy at T = 288 K is ΔG = 133.92 kJ·mol^{-1}. The respective value at T = 298 K is ΔG = 132.1 kJ·mol^{-1}. The corresponding literature value is ΔG = 131.23 kJ·mol^{-1} (Lit??).

From the values of U_d obtained at elevated temperatures the reaction entropy is calculated from $\partial U_d/\partial T$. For comparison reaction entropies shall be calculated from literature data, they shall be compared with the experimentally obtained ones. The reaction enthalpy ΔH is assumed to be constant in the studied range of temperatures. Fig. 2.17 shows typical data for electrolysis of HCl.

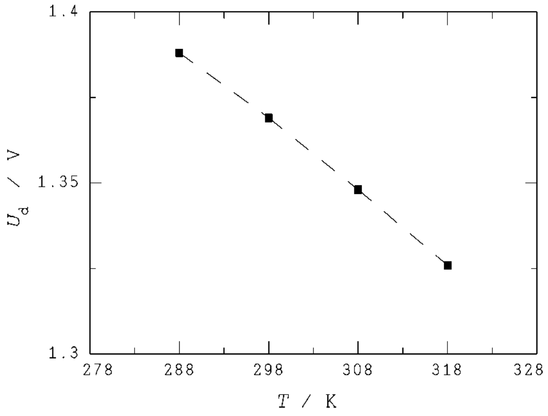

Fig. 2.17: Plot of U_d for an aqueous solution of HCl 1.2 **M**

From the temperature coefficient $\partial U_d/\partial T$ = – 2 mV·K^{-1} of U_d (which is assumed to be equal to U_0) the entropy of the electrolysis reaction is calculated according to

$$\Delta S = -\,\partial U_d/\partial T \cdot z \cdot F = 0.002 \cdot z \cdot F = 192.97\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \quad (2.54)$$

This result differs from the value ΔS = 120.4 J·K^{-1}· mol^{-1} calculated from literature data (EC:78, Atkins).

Appendix

In many cases the experimentally determined values of U_d differ substantially from those calculated from thermodynamic data As an example the calculated value for water electrolysis is U_d = 1.229 V. In a real cell even with platinum electrodes and water acidified with sulphuric acid voltages of 1.6 .. 1.8 V are needed. The electrode reactions are

$$2\,H^+ + 2\,e^- \rightarrow H_2 \quad (2.55)$$

$$H_2O \rightarrow ½\,O_2 + 2\,e^- \qquad (2.56)$$

The observed differences are associated (besides other, minor causes) with the electron transfer reactions at the phase boundary metal/solution. In case of unimpeded charge transfer i.e. of a very fast electron transfer reaction) a current-potential relationship as displayed in Fig. 2.16 with a measurable flow of current already at the decomposition voltage U_d = 1.229 V calculated from thermodynamic data would have been expected. If there is any hindrance of charge transfer at one or at both electrodes more or less considerable additional voltage (overvoltage) $\eta = U - U_d$ will be needed. I this case evaluation of the current-potential relationship will not result in useful thermodynamic data.

Investigations of the behavior of electrodes with flowing current are subject of electrode kinetic studies. It has been observed, that the chlorine evolution reaction

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad (2.57)$$

proceeds almost unimpeded. The reaction

$$H_2O \rightarrow 2\,H^+ + ½\,O_2 + 2\,e^- \qquad (2.58)$$

is strongly hindered whereas the hydrogen evolution reaction HER proceeds almost unimpeded

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (2.55)$$

The slow oxygen evolution reaction enables the experiment described above is possible only because of the sow oxygen evlution otherwise and from a thermodynamical point of view oxygen evolution will start before chlorine evolution.

The rate of an electrode reaction (whether it is impeded or accelerated) depends on the electrode material. Electrolysis of hydrochloric acid at a hydrogen generating mercury electrode and a platinum sheet for chlorine evolution results in an experimental value of U_d = 2 V. Hydrogen evolution is strongly impeded at the mercury electrode.

I order to avoid unwanted contributions to the observed cell voltage from the already small hindrance of hydrogen evolution kinetics he experiment is not done with smooth platinum sheets of approximately equal size with one electrode exposed to a strea of hydrogen bubbles. Instead a platinized platinum wire net electrode with relatively large effective surface area is used as hydrogen electrode whereas a smooth platinum tip with only a few mm^2 surface area is used as chlorine electrode. Because of this small surface area only very small currents will flow (up to approx. 50 µA). These currents do not affect the electrode potential of the large-area hydrogen electrode. More important than current is the current density j ($j = I / A$). Overpotentials increase with growing j.In this experiment the obtained current-potential curve is predominantly determined by the reaction at the chlorine electrode because of its relatively small surface area and thus larger j.

A chlorine electrode

$$2\ Cl^{-} \leftrightarrows Cl_2 + 2\ e^{-} \qquad (2.57)$$

is composed of a platinum electrode in contact with an aqueous solution of HCl exposed to a stream of chlorine gas. At standard conditions (a = 1 **M** (approx. c_{HCl} = 1 **M**), $p = p_0$ = 1 atm (= 101325 Pa)) the potential difference with respect to a standard hydrogen electrode according to

$$2\ H^{+} + 2\ e^{-} \rightarrow H_2 \qquad (2.55)$$

can be calculated from the thermodynamic data of the reaction

$$2\ Cl^{-} + 2\ H^{+} \leftrightarrows Cl_2 + H_2 \qquad (2.57)$$

as U_d = 1.37 V.

Literature

A.J. Bard and L.R. Faulkner: Electrochemical Methods, Wiley, New York 2001.

Questions

- Define the terms “overpotential” and “overvoltage”
- Describe the process from cell voltage measurements to Gibbs energies and reaction entropies
- Name the differences between static and dynamic measurements of equilibrium cell voltages.
- Explain the current potential curve for water and hydrochloric acid electrolysis