Nernst equation with Cobra SMARTsense

Chemistry › Inorganic chemistry › Acids, bases, salts

Difficulty level	Group size	Preparation time	Execution time
medium	2	30 minutes	20 minutes

This content can also be found online at:

http://localhost:1337/c/5f0bf5a843b3a10003bf01e0

General information

Application

Experimental Setup

Any combination of two electrodes is called a galvanic cell (e.g. batteries, accumulators or also biological cells). Its open-circuit voltage U_0 (historically: electromotive force) is equal to the potential difference ΔE of the electrodes. This can be calculated by applying the Nernst equation to the half-cells as $U_0 = \Delta E = E_{Acceptor} - E_{Donator}$. Similarly, it allows the calculation of the equilibrium activities that occur when a voltage is applied to the half-cells.

The Nernst equation is of central importance in electrochemistry, electroplating and electroanalysis because it connects the electrical quantity voltage (or electrode potential) with the chemical quantity concentration. It is strictly only valid for cells without transfer and currentless processes. However, it offers a starting point for the derivation of equations in current-carrying electrochemical systems.

Other information (1/2)

Prior knowledge

The students should be familiar with the basics of electrochemistry. Furthermore, students should be familiar working autonomously with chemical agents and be familiar with good laboratory practice.

Scientific principle

The Nernst equation expresses how the electrical potential of an electrode in contact with a solution of ions depends upon the concentrations (more accurately, activities) of those ions. The equation may be experimentally verified using an electrochemical cell formed from an inert indicator electrode coupled with a convenient reference electrode. The potential of the indicator electrode, and hence the e.m.f. of the cell, is monitored as the ionic composition of the electrolyte solution is changed.

Other information (2/2)

Learning objective

The students learn to determine the standard electrode potential of the Fe^{III}, Fe^{II} redox couple and to calculate the standard redox potential of $E^{\Phi}[Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-}$.

Tasks

Using the ORP-electrode (combination electrode of an $Ag_{(s)}|AgCl_{(s)}|Cl$ -reference electrode with platinum as the working electrode), measure the potential in contact with solutions containing known concentrations of the iron(II) and iron(III) complex ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$.

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Safety instructions

For this experiment the general instructions for safe experimentation in science lessons apply.

For H- and P-phrases please consult the safety data sheet of the respective chemical.

Theory (1/6)

In the electrochemical cell used here, the $Ag_{(s)}|AgCl_{(s)}|Cl$- electrode, used as a reference electrode, supplies a constant potential against which we measure the potential of the redox electrode. The silver chloride electrode consists of a silver wire covered with silver chloride which is immersed into a potassium chloride solution of defined concentration. The redox system is an iron(III) / iron(II) couple

$$[Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-}$$

In general, a redox reaction in which X^{z+} ions are reduced by n electrons (supplied by an inert metal electrode) to Y ions of charge $(z-n)^{+}$ can be expressed as follows:

$$X^{z+}_{(aq)} + ne^{-} \rightarrow Y^{(z-n)^{+}}_{(aq)}$$

In this system, equilibrium is attained when the sums of the electrochemical potentials on each side of the reaction are equal:

Theory (1/6) PHYWE

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Theory (2/6)

In this system, equilibrium is attained when the sums of the electrochemical potentials on each side of the reaction are equal:

$$\mu_X(soln.) + n\mu_e(metal) = \mu_Y(soln.) \qquad \textbf{(1)}$$

From the definition of the electrochemical potential, it follows that

$$\mu_X(soln.) = \mu_X + zF\Phi_{soln.} \qquad \textbf{(2a)}$$

$$\mu_e(metal) = \mu_e + F\Phi_{soln.} \qquad \textbf{(2b)}$$

Theory (3/6)

$$\mu_Y(soln.) = \mu_Y + (z-n)F\Phi_{soln.} \qquad \textbf{(2c)}$$

With:

$\Phi_{soln.}$	Electric potential of the solution
Φ_{metal}	Electric potential of the inert metal electrode
μ_i	Chemical potential of species i

Combining equations (1) and (2) we obtain:

$$\mu_X^{z+} - \mu_Y^{(z-n)^+} + n\mu_{e^-} = nF\Phi_{soln.} - nF\Phi_{metal} \qquad \textbf{(3)}$$

Theory (4/6)

which allows the electric potential difference $\Delta\Phi$ between the solution and the metal to be expressed as:

$$\Delta\Phi = \Phi soln. - \Phi metal = \frac{1}{nF}(\mu_X^{z^+} - \mu_Y^{(z-n)^+} + n\mu_{e^-}) \quad \textbf{(4)}$$

The chemical potentials of the ionic species depend upon their activities in solution:

$$\mu_X^{z+} = \mu_X^{\theta_{z^+}} + RT \cdot ln\, a_X^{z^+} \quad \textbf{(5a)}$$

$$\mu_Y^{(z-n)^+} = \mu_Y^{\theta_{(z-n)^+}} + RT \cdot ln\, a_Y^{(z-n)^+} \quad \textbf{(5b)}$$

With:

μ_i Standard chemical potential of species i at unit activity $a_i = 1$

Equipment

Position	Material	Item No.	Quantity
1	Cobra SMARTsense - Thermocouple, -200 ... +1200 °C (Bluetooth + USB)	12938-01	1
2	Cobra SMARTsense - ORP (Bluetooth)	12927-00	1
3	Sheath Thermocouple, NiCr-Ni, Type K, -40°C ... +1000°C	13615-06	1
4	Connecting cord, 32 A, 500 mm, black	07361-05	1
5	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
6	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
7	Retort stand, h = 750 mm	37694-00	2
8	Right angle boss-head clamp	37697-00	2
9	Universal clamp	37715-01	1
10	Burette clamp, roller mount., 2 pl.	37720-00	1
11	Burette, lateral stopcock, Schellbach, 50 ml	MAU-24022024	2
12	Weighing dishes, square shape, 84 x 84 x 24 mm, 500 pcs.	45019-50	1
13	Beaker, Borosilicate, tall form, 100 ml	46026-00	2
14	Beaker, Borosilicate, tall form, 150 ml	46032-00	4
15	Volumetric flask 1000ml, IGJ24/29	36552-00	4
16	Volumetric pipette, 50 ml	36581-00	2
17	Pipettor	36592-00	1
18	Pipette dish	36589-00	1
19	Funnel, glass, top dia. 80 mm	34459-00	2
20	Funnel, glass, top dia. 50 mm	34457-00	2
21	Pasteur pipettes, 250 pcs	36590-00	1
22	Rubber caps, 10 pcs	39275-03	1
23	Spoon, special steel	33398-00	1
24	Wash bottle, plastic, 500 ml	33931-00	1
25	Potass.hexacyanoferrate/II/250 g	30101-25	1
26	Potass.hexacyanoferrate/III/100g	30100-10	1
27	Water, distilled 5 l	31246-81	1
28	Holder for Cobra SMARTsense	12960-00	2

Theory (6/6)

The cell used in this experiment is:

$$Ag_{(s)} \mid AgCl_{(s)} \mid KCl_{(aq,3M)} \mid Fe^{III}, Fe^{II} \mid Pt$$

for which the cell e.m.f. (E_{cell}) is:

$$\begin{aligned} E_{cell} &= E_{Fe^{III},Fe^{II}} - E_{Ag\,|\,AgCl\,|\,Cl^-} \\ &= E^{\theta}_{Fe^{III},Fe^{II}} + \frac{RT}{F} ln \frac{[Fe^{III}]}{[Fe^{II}]} - E_{Ag\,|\,AgCl\,|\,Cl} \end{aligned} \quad \textbf{(8)}$$

For the dilute solutions used here, ion activities have been substituted by molar concentrations.

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8	Right angle boss-head clamp	37697-00	2
9	Universal clamp	37715-01	1
10	Burette clamp, roller mount., 2 pl.	37720-00	1
11	Burette, lateral stopcock, Schellbach, 50 ml	MAU-24022024	2

Setup and procedure

Setup (1/5)

Prepare the solutions required for the experiment as follows:

- 0.01 M $K_4[Fe(CN)_6]$ solution: Weigh 4.2239 g of potassium hexacyanoferrate(II) (yellow prussiate of potash: $K_4[Fe(CN)_6] \bullet 3H_2O)$ into a 1000 ml volumetric flask. Dissolve it in distilled water, and make up to the mark with distilled water.
- 0.001 M $K_4[Fe(CN)_6]$ solution: pipette 100 ml of 0.01 molar potassium hexacyanoferrate(II) solution into a 1000 ml volumetric flask and make up to the mark with distilled water.
- 0.01 M $K_3[Fe(CN)_6]$ solution: Weigh 3.2925 g of potassium hexacyanoferrate(III) (red prussiate of potash): $K_3[Fe(CN)_6]$ into a 1000 ml volumetric flask. Dissolve it in distilled water, and make up to the mark with distilled water.
- 0.001 M $K_3[Fe(CN)_6]$ solution: pipette 100 ml of 0.01 molar potassium hexacyanoferrate(III) solution into a 1000 ml volumetric flask and make up to the mark with distilled water.

Setup (2/5)

Fig. 1: Experimental setup

- Make yourself familiar with the PHYWE measureLAB software using the extensive manual which can be found in the started program under 📖.
- Set up the experiment as shown in Fig. 1.
- Attach the two burettes, one for the Fe(II) solution and the other for the Fe(III) solution, to the retort stand, rinse twice with the respective 0.001 molar solution and fill them.

Setup (3/5)

- Prepare the sample solutions to be investigated as listed in the following table:

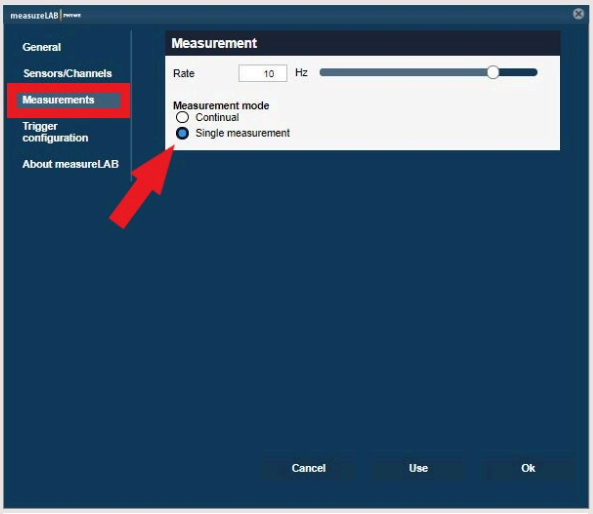
Fe(II) solution / ml	Fe(III) solution / ml
49	1
48	2
46	4
43	7
38	12
30	20
25	25
20	30
12	38
7	43
4	46

Setup (4/5)

- Place the beaker containing the first sample solution on the magnetic stirrer and put in a magnetic stirrer bar.
- Connect the platinum electrode, the reference electrode to the Cobra SMARTsense ORP sensor and dip them into the solution.
- Connect the temperature probe to the Cobra SMARTsense Thermocouple and dip them into the solution as well.
- Start the PHYWE measureLAB software (if nor running already).
- Switch on both sensors (see manual for the sensors).
- Load the presets for this experiment: P3060967 ("The Nernst equation with Cobra SMARTsense").
- If working without the presets, connect both sensors to the software (see measureLAB manual).

Setup (2/2)

- Make sure that the mode is set to "Single measurements". To do so, call up the the settings , go to "Measurements" and switch the mode (see also Fig. 2).
- Select in the drop-down menu "Index" for the x-axis.



Rate 10 Hz

Measurement mode
○ Continual
● Single measurement

Fig. 2: Mode for the measurement

Procedure (1/2)

- Start the measurement by pressing ▶.
- Record the temperature and the e.m.f. of the cell.
- Rinse the electrodes thoroughly in distilled water, dry them and place them in the next sample solution

Solutions must be changed quickly. Do not allow the reference electrode to remain out of solution for too long.

- Continue until all sample solutions have been measured.
- Stop the measurement by pressing ■.
- Repeat the procedure with the 0.01 molar solutions.
- The data is saved inside the data pool ☰ and can be exported from there.

Procedure (2/2)

- Start the measurement by pressing ▶.
- Record the temperature and the e.m.f. of the cell.
- Rinse the electrodes thoroughly in distilled water, dry them and place them in the next sample solution

Solutions must be changed quickly. Do not allow the reference electrode to remain out of solution for too long.

- Continue until all sample solutions have been measured.
- Repeat the procedure with the 0.01 molar solutions.

Evaluation (1/2)

PHYWE

- Plot the cell e.m.f. (E) as a function of:

$$ln\frac{[[Fe(CN)_6]^{3^-}]}{[[Fe(CN)_6]^{4^-}]}$$

A plot of E_{cell} against \(ln \frac{[Fe^{III}]}{[Fe^{II}] should be a straight line of gradient $\frac{RT}{F}$ and intercepts $E^{\theta}_{Fe^{III},Fe^{II}} - E_{Ag\,|\,AgCl\,|\,Cl^-}$.

If the potential of the reference electrode used is known, the standard electrode potential of the Fe_{III}, Fe_{II} redox couple can be determined.