

06.09 The Nernst equation



What you can learn about

- Electrode potentials and their concentration dependence
- Redox electrodes
- Electrochemical cells

Principle and tasks

The Nernst equation expresses how the electrical potential of an electrode in contact with a solution of ions depends upon the activities of these 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, are monitored as the ionic composition of the electrolyte solution is changed.

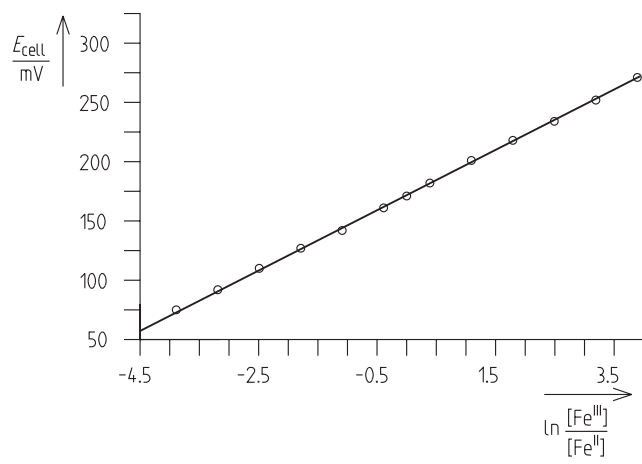
Here a silver - silver chloride electrode is used as reference electrode measuring the potential of a platinum electrode in contact with solutions containing different concentrations of iron(II) and iron(III) complex ions.

What you need:

Digital pH-meter	13702.93	1
Reference electrode, AgCl	18475.00	1
Platinum electrode in protective tube	45206.00	1
Connecting cord, $l = 500$ mm, black	07361.05	1
Temperature probe Pt1000	13702.01	1
Magnetic stirrer, Mini	47334.93	1
Magnetic stirrer bar, $l = 30$ mm	46299.02	1
Retort stand, $h = 750$ mm	37694.00	2
Right angle clamp	37697.00	2
Universal clamp	37715.00	1
Support for two electrodes	45284.01	1
Spring balance holder	03065.20	2
Burette clamp, roller mounting	37720.00	1
Burette, 50 ml, lateral stopcock	36513.01	2
Analytical balance CPA 224S (220 g/0.1 mg), set with software	49221.88	1
Weighing dishes, $80 \times 50 \times 14$ mm	45019.05	1
Glass beaker, 100 ml, tall	36002.00	2
Glass beaker, 150 ml, tall	36003.00	4
Volumetric flask, 1000 ml	36552.00	4
Volumetric pipette, 50 ml	36581.00	2
Pipettor	36592.00	1
Pipette dish	36589.00	1
Funnel, glass, $d_0 = 55$ mm	34457.00	2
Funnel, glass, $d_0 = 80$ mm	34459.00	2
Spoon	33398.00	1
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Wash bottle, 500 ml	33931.00	1
Potassium hexacyanoferrate(II), 250 g	30101.25	1
Potassium hexacyanoferrate(III), 100 g	30100.10	1
Water, distilled, 5 l	31246.81	1

The Nernst equation

P3060901



Verification of the Nernst equation for the $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-} | \text{Pt}$ redox electrode.

Related concepts

Electrode potentials and their concentration dependence, redox electrodes, electrochemical cells.

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.

Tasks

Using an $\text{Ag}_{(s)} | \text{AgCl}_{(s)} | \text{Cl}^-$ reference electrode, measure the potential of a platinum electrode in contact with solutions containing known concentrations of the iron(II) and iron(III) complex ions $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.

Equipment

Digital pH-meter	13702.93	1
Reference electrode, AgCl	18475.00	1
Storage flask for pH electrodes, filled with 250 ml 3.0 M KCl solution	18481.20	1
Platinum electrode in protective tube	45206.00	1
Connecting cord, $l = 500$ mm, black	07361.05	1
Temperature probe Pt1000	13702.01	1

Magnetic stirrer, mini	47334.93	1
Magnetic stirrer bar, $l = 30$ mm	46299.02	1
Retort stand, $h = 750$ mm	37694.00	2
Right angle clamp	37697.00	2
Universal clamp	37715.00	1
Support for two electrodes	45284.01	1
Spring balance holder	03065.20	2
Burette clamp, roller mounting	37720.00	1
Burette, 50 ml, lateral stopcock	36513.01	2
Set of analytical balance Sartorius CPA 224S and measure software	49221.88	1
Weighing dishes, 80 x 50 x 14 mm	45019.05	1
Glass beaker, 100 ml, tall	36002.00	2
Glass beaker, 150 ml, tall	36003.00	4
Volumetric flask, 1000 ml	36552.00	4
Volumetric pipette, 50 ml	36581.00	2
Pipettor	36592.00	1
Pipette dish	36589.00	1
Funnel, glass, $d_o = 55$ mm	34457.00	2
Funnel, glass, $d_o = 80$ mm	34459.00	2
Spoon	33398.00	1
Pasteur pipettes	36590.00	1
Rubber bulbs	39275.03	1
Wash bottle, 500 ml	33931.00	1
Potassium hexacyanoferrate(II), 250 g	30101.25	1
Potassium hexacyanoferrate(III), 100 g	30100.10	1
Water, distilled, 5 l	31246.81	1

Fig. 1. Experimental set-up.



Set-up and procedure

Set up the experiment as shown in Fig. 1.

Prepare the solutions required for the experiment as follows:

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

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. Prepare the sample solutions to be investigated as listed in Table 1.

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 and the temperature probe to the pH-meter, and dip them into the solution. 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.

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

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

Table 1: Preparation of the sample solutions

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
2	48
1	49

Theory and evaluation

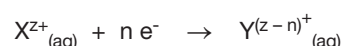
In the electrochemical cell used here, the $Ag_{(s)} | AgCl_{(s)} | Cl^-$ electrode used as a reference electrode supplies a constant potential against which we measure the potential of the redox electrode.

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



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



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

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

From the definition of the electrochemical potential, it follows that

$$\mu_X \text{ (soln.)} = \mu_X + z F \Phi_{\text{soln.}} \quad (2a)$$

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

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

with

$\Phi_{\text{soln.}}$ 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

$$\mu_{X^{z+}} - \mu_{Y^{(z-n)+}} + n \mu_{e^-} = n F \Phi_{\text{soln.}} - n F \Phi_{\text{metal}} \quad (3)$$

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

$$\Delta\Phi = \Phi_{\text{soln.}} - \Phi_{\text{metal}} = \frac{1}{n F} (\mu_{X^{z+}} - \mu_{Y^{(z-n)+}} + n \mu_{e^-}) \quad (4)$$

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

$$\mu_{X^{z+}} = \mu_{X^{z+}}^\ominus + RT \cdot \ln a_{X^{z+}} \quad (5a)$$

$$\mu_{Y^{(z-n)+}} = \mu_{Y^{(z-n)+}}^\ominus + RT \cdot \ln a_{Y^{(z-n)+}} \quad (5b)$$

with

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

Eq. (4) may thus be rewritten as

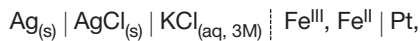
$$\Delta\Phi = \frac{1}{n F} (\mu_{X^{z+}}^\ominus - \mu_{Y^{(z-n)+}}^\ominus + n \mu_{e^-}) + \frac{R T}{n F} \left(\ln \frac{a_{X^{z+}}}{a_{Y^{(z-n)+}}} \right) \quad (6)$$

which is the form of the Nernst equation for the simple redox electrode (see equation 1).

For the redox system employed here, we obtain

$$E_{\text{Fe}^{\text{III}},\text{Fe}^{\text{II}}} = E_{\text{Fe}^{\text{III}},\text{Fe}^{\text{II}}}^{\ominus} + \frac{RT}{nF} \ln \left(\frac{a_{\text{X}^{z+}}}{a_{\text{Y}^{(z-n)+}}} \right) \quad (7)$$

The cell used in this experiment is



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

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

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

Data and Results

A plot of E_{cell} against $\ln ([\text{Fe}^{\text{III}}] / [\text{Fe}^{\text{II}}])$ should be a straight line of gradient RT/F and intercepts $E_{\text{Fe}^{\text{III}},\text{Fe}^{\text{II}}}^{\ominus} - E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}$ (see Fig. 2). If the potential of the reference electrode used is known, the standard electrode potential of the $\text{Fe}^{\text{III}}, \text{Fe}^{\text{II}}$ redox couple can be determined.

The measured gradient (determined by simple linear regression) is 25.2 mV (lit. value: $RT/F = 25.4$ mV at $\vartheta = 22^\circ\text{C}$).

From the value of E_{cell} at the y-axis intercept we have $E_{\text{Fe}^{\text{III}},\text{Fe}^{\text{II}}}^{\ominus} - E_{\text{Ag} | \text{AgCl} | \text{Cl}^-} = 172$ mV. At 20°C the $\text{Ag}_{(\text{s})} | \text{AgCl}_{(\text{s})} | \text{Cl}_{(\text{aq})}$ reference electrode is stated to have a potential of 210 mV. From this, the standard redox potential $E^{\ominus} \{[\text{Fe}(\text{CN})_6]^{3-}, [\text{Fe}(\text{CN})_6]^{4-}\}$ is therefore 38 mV (literature value: 36 mV from 'R. Parsons, Handbook of electrochemical constants, Butterworth, London, 1959').

Table 2: Experimental data

i	Volume of 0.001 M Fe^{II} -solution (V/ml)	Volume of 0.001 M Fe^{III} - solution (V/ml)	$\ln \frac{[\text{Fe}^{\text{III}}]}{[\text{Fe}^{\text{II}}]}$	E_{cell} (mV)
1	49.0	1.0	- 3.89	75
2	48.0	2.0	- 3.19	92
3	46.0	4.0	- 2.49	110
4	43.0	7.0	- 1.79	127
5	38.0	12.0	- 1.09	142
6	30.0	20.0	- 0.39	161
7	25.0	25.0	0.00	171
8	20.0	30.0	+ 0.39	182
9	12.0	38.0	+ 1.09	201
10	7.0	43.0	+ 1.79	218
11	4.0	46.0	+ 2.49	234
12	2.0	48.0	+ 3.19	252
13	1.0	49.0	+ 3.89	271

Electrolyte temperature: $22.0 \pm 0.2^\circ\text{C}$

