# 11. GALVANIC CELLS

$$E = E_{\text{red,right}} - E_{\text{red,left}} + E_D = E_{\text{red,right}} + E_{\text{ox,left}} + E_D$$

$$\Delta G = -z \boldsymbol{F} E$$

$$\Delta S = +z\, F \left(\frac{\partial E}{\partial T}\right)_p \qquad\qquad \Delta H = z\, F \left[ T \left(\frac{\partial E}{\partial T}\right)_p - E \right] \qquad\qquad Q = T\, \Delta S \quad [p]$$

$$\Delta G^{\ominus} = -z\, \boldsymbol{F}\, E^{\ominus}$$

$$\Delta_r S^{\ominus} = -\left(\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right)_p = z\, \boldsymbol{F}\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p, \quad \Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\, \Delta_r S^{\ominus} = z\, \boldsymbol{F}\left[ T\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p - E^{\ominus} \right]$$

$$\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p \approx \left(\frac{\partial E}{\partial T}\right)_p$$

$$E = E^{\ominus} - \frac{\boldsymbol{R}T}{z\boldsymbol{F}} \ln\left( \prod_i a_i^{\nu_i} \right)_{\text{non-equil}} \quad, \qquad E^{\ominus} = \frac{\boldsymbol{R}T}{z\boldsymbol{F}}\, \ln K$$
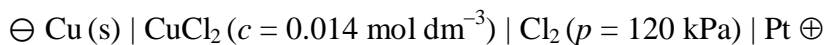
$$z_2\, E^{\ominus}(\text{Me}^{z_2}/\text{Me}) = (z_2 - z_1)\, E^{\ominus}(\text{Me}^{z_2}/\text{Me}^{z_1}) + z_1\, E^{\ominus}(\text{Me}^{z_2}/\text{Me})$$

$$I < 0{,}001\ \text{mol dm}^{-3}: \qquad \ln \gamma_{\pm} = -z_C \cdot z_A \cdot A \cdot \sqrt{I} \quad, \quad I = \tfrac{1}{2}\sum_i (c_i \cdot z_i^2)$$

$$I < 0{,}1\ \text{mol mol}^{-3} \qquad \ln \gamma_{\pm} = -\frac{z_C \cdot z_A \cdot A \cdot \sqrt{I}}{1 + a \cdot \sqrt{I}} \quad, \quad \text{constant a} \approx 1\ \text{mol}^{-1/2}\ \text{dm}^{3/2}$$

## Problem 11-01  Calculation of the cell potential, $\gamma_{\pm} \neq 1$

Calculate the potential of the electrochemical cell
$$\ominus \text{Cu (s)} \mid \text{CuCl}_2\ (c = 0.014\ \text{mol dm}^{-3}) \mid \text{Cl}_2\ (p = 120\ \text{kPa}) \mid \text{Pt} \oplus$$
at 25 °C. Standard reduction potentials of the half-cells are
$$E^{\ominus}(\text{Cu}^{2+}|\text{Cu}) = 0.337\ \text{V},\ E^{\ominus}(\text{Cl}_2|\text{Cl}^-) = 1.36\ \text{V}.$$

Standard states:  $\text{Cl}_2(\text{g})$ the state of ideal gas at the actual temperature and at pressure of $p^{\text{st}} = 101.325$ kPa; under actual conditions the chlorine can be taken as an ideal gas; electrolyte: infinite dilution, $c^{\text{st}} = 1$ mol dm$^{-3}$.

The mean activity coefficient calculate from the Debye-Hückel law ($A = 1.172$ dm$^{3/2}$ mol$^{-1/2}$). Decide if you use the limiting or enhanced form.

$$[E = 1.1872\ \text{V}\ (\gamma_{\pm} = 0.67121 - \text{from extended D-H, because } 0.001 < I < 0.1)]$$

## Problem 11-02  Determination of $\gamma_{\pm}$ from the cell potential

Find the value of the mean activity coefficient of the ferric chloride in the FeCl$_3$ solution at 25 °C. The potential of the cell
$$\ominus \text{Fe(s)} \mid \text{FeCl}_3\ (c = 0.01\ \text{mol dm}^{-3}) \mid \text{Cl}_2\ (p = 101.325\ \text{kPa}) \mid \text{Pt} \oplus$$
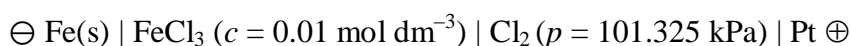
is $E = 1.5515$ V. You can assume the ideal behaviour of chlorine (standard state ideal gas at actual temperature and $p^{st} = 101.325$ kPa). As the standard state for electrolyte take infinite dilution, $c^{st} = 1$ mol dm$^{-3}$. Standard reduction potentials of the half-cells are
$$E^{\ominus}(Fe^{3+}|Fe) = -0.036 \text{ V} \quad \text{and} \quad E^{\ominus}(Cl_2|Cl^-) = 1.36 \text{ V}.$$

<div align="right">[ $\gamma_\pm = 0.4685$ ]</div>

## Problem 11-03 <small>Calculation of the cell potential, $\gamma_\pm \neq 1$</small>

Calculate the potential of the electrochemical cell
$$\ominus \text{ Pb(s) | PbSO}_4 \text{ (s) | H}_2\text{SO}_4 \text{ ($c = 0.002$ mol dm}^{-3})| \text{ H}_2 \text{ ($p = 112$ kPa) | Pt } \oplus$$
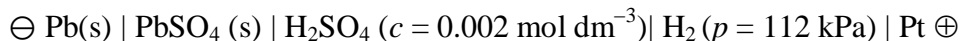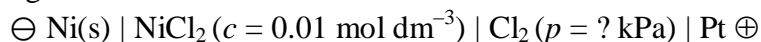
at the temperature of 25 °C. Assume that the sulphuric acid is completely dissociated to the second degree. To the determination of the mean activity coefficient use the Debye-Hückel law ($A = 1.172$ dm$^{3/2}$ mol$^{-1/2}$). Standard state for electrolyte: infinite dilution, $c^{st} = 1$ mol dm$^{-3}$. In these conditions, hydrogen exhibits ideal behaviour (standard state $p^{st} = 101.325$ kPa).

<div align="right">[$E = 0.1295$ V ($\gamma_\pm = 0.8449$ - extended D-H law) ]</div>

## Problem 11-04 <small>Gas pressure at the electrode from $E$; activity coefficients</small>

The potential of the galvanic cell
$$\ominus \text{ Ni(s) | NiCl}_2 \text{ ($c = 0.01$ mol dm}^{-3}) \text{ | Cl}_2 \text{ ($p = ?$ kPa) | Pt } \oplus$$
at the temperature of 25 °C is $E = 1.793$ V. Under assumption of ideal behaviour of chlorine, calculate its pressure on the right electrode (standard state $p^{st} = 101.325$ kPa). The mean activity coefficient of the cell electrolyte calculate using Debye-Hückel law ($A = 1.172$ dm$^{3/2}$ mol$^{-1/2}$) – according to the ionic strength choose an appropriate form of this law.
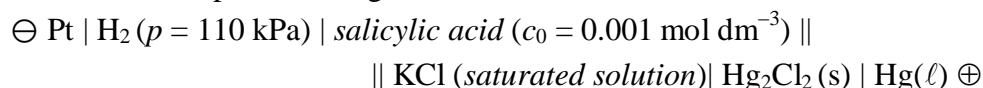$$E^{\ominus}(Ni^{2+}|Ni) = -0.250 \text{ V} \quad \text{and} \quad E^{\ominus}(Cl_2|Cl^-) = 1.36 \text{ V}.$$

<div align="right">[$p_{Cl_2} = 238.65$ kPa ($\gamma_\pm = 0.7075$ (extended Debye-Hückel law)]</div>

## Cell potential, dissociation constant, pH

### Problem 11-05 <small>Cell potential and dissociation constant</small>
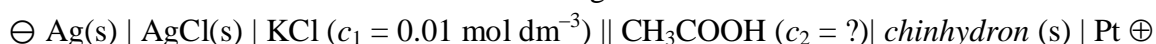
What is the value of the potential of galvanic cell
$$\ominus \text{ Pt | H}_2 \text{ ($p = 110$ kPa) | } \textit{salicylic acid} \text{ ($c_0 = 0.001$ mol dm}^{-3}) \text{ ||}$$
$$\text{|| KCl (}\textit{saturated solution})\text{| Hg}_2\text{Cl}_2 \text{ (s) | Hg($\ell$) } \oplus$$

at the temperature of 25 °C. The dissociation constant of salicylic acid for the standard state infinite dilution, $c^{st} = 1$ mol dm$^{-3}$, is $1.05 \cdot 10^{-3}$. Reduction potential of the saturated calomel electrode is $E_{red,calom} = 0.2438$ V. All activity coefficients can be taken as equal to one. Under given conditions hydrogen exhibits ideal behaviour. For standard state for hydrogen take the ideal gas at actual temperature and pressure $p^{st} = 101.325$ kPa.

<div align="right">[$E = 0.4343$ V]</div>

### Problem 11-06 <small>Concentration of the electrolyte from dissociation constant and cell potential</small>

Determine the concentration of the acetic acid in the galvanic cell
$$\ominus \text{ Ag(s) | AgCl(s) | KCl ($c_1 = 0.01$ mol dm}^{-3}) \text{ || CH}_3\text{COOH ($c_2 = ?$)| } \textit{chinhydron} \text{ (s) | Pt } \oplus$$
the potential of which is 0.1642 V at 25 °C. Dissociation constant of acetic acid at this temperature has the value of $1.75 \cdot 10^{-5}$ (standard state infinite dilution, $c^{st} = 1$ mol dm$^{-3}$). Standard reduction potentials are
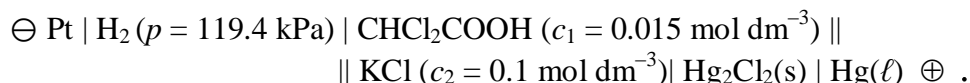$$E^{\ominus} \text{ (Chinon|Hydrochinon) = 0.699 V} \quad \text{and} \quad E^{\ominus} \text{ (AgCl|Ag|Cl}^-) = 0.222 \text{ V}$$
Assume that the activities can be replaced by relative concentrations.

<div align="right">[$c_2 = 0.0157$ mol dm$^{-3}$]</div>

## Problem 11-07  Concentration of dissociation constant from cell potential

The following galvanic cell was assembled to the determination of the dissociation constant of the dichloroacetic acid:
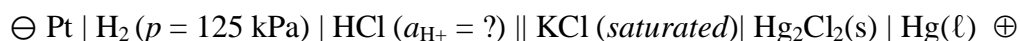
$$\ominus \; Pt \mid H_2 \, (p = 119.4 \text{ kPa}) \mid CHCl_2COOH \, (c_1 = 0.015 \text{ mol dm}^{-3}) \; \|$$
$$\| \; KCl \, (c_2 = 0.1 \text{ mol dm}^{-3}) \mid Hg_2Cl_2(s) \mid Hg(\ell) \; \oplus \; .$$

At the temperature of 25 °C the cell potential was $E = 0.449$ V. What is the value of the dissociation constant of the dichloroacetic acid for the standard state infinite dilution, $c^{st} = 1$ mol dm$^{-3}$ under assumption that activity coefficients are equal to one. The reduction potential of the right half-cell is $E_{red,calom} = 0.3338$ V. At given pressure hydrogen exhibits ideal behaviour. Standard state for hydrogen: ideal gas at 25 °C and $p^{st} = 101.325$ kPa.

$$[K_{dis} = 0.0547 \,]$$

## Problem 11-08  pH from cell potential

Hydrogen electrode, saturated under hydrogen pressure of 125 kPa (standard state $p^{st} = 101.325$ kPa), was immersed into an aqueous hydrogen chloride solution and this half-cell was connected via a salt bridge with saturated calomel electrode ($E_{red, calom} = 0.2503$ V), all at the temperature of 15 °C:

$$\ominus \; Pt \mid H_2 \, (p = 125 \text{ kPa}) \mid HCl \, (a_{H+} = ?) \; \| \; KCl \, (saturated) \mid Hg_2Cl_2(s) \mid Hg(\ell) \; \oplus$$

The potential of this cell was determined to be 0.39 V. Assuming ideal behaviour of hydrogen determine pH of the HCl solution.

$$[pH = 2.4 \,]$$

## Cells with redox reaction

### Problem 11-09  Potential of redox electrodel

5.4 g of ferric chloride and 2 g of ferrous chloride were dissolved in 2 dm$^3$ of the distilled water. Thin platinum wire was then immersed into this solution. Assuming that all activity coefficients are equal to one calculate the reduction potential of this half-cell at the temperature of 25 °C. For the standard state of the electrolyte choose the state of infinite dilution, $c^{st} = 1$ mol dm$^{-3}$. Additional data:

$$M_{Fe} = 55.847 \text{ g mol}^{-1}, \quad M_{Cl} = 35.453 \text{ g mol}^{-1}, \quad E^{\ominus}(Fe^{3+} \mid Fe^{2+}) = 0.771 \text{ V}.$$

$$[\, E_{Fe^{3+} \mid Fe^{2+}} = 0.7391 \text{ V} \,]$$

## Termodynamics of cells

### Problem 11-10  Equilibrium constant from standard cell potential

We can observe that on the iron nails immersed into a solution of bluestone metallic copper is deposited.

(a) Write the reaction taking place in this system.

(b) From the following set of standard cell potentials use appropriate data to calculate the equilibrium constant of this reaction at 25 °C.

$$E^{\ominus}(Cu^{2+}|Cu) = 0.337 \text{ V}, \qquad\qquad E^{\ominus}(Fe^{2+}|Fe) = -0.441 \text{ V}$$
$$E^{\ominus}(Cu^{2+}|Cu^{+}) = 0.167 \text{ V} \qquad\qquad E^{\ominus}(Fe^{3+}|Fe^{2+}) = +0.771 \text{ V}$$
$$E^{\ominus}(Cu_2S|Cu|S^{2-}) = -0.890 \text{ V} \qquad\qquad E^{\ominus}(FeS|Fe|S^{2-}) = -0.950 \text{ V}$$

$$[K = 2.01 \cdot 10^{26} \,]$$

## Problem 11-11  Equilibrium constant from standard potentials

Calculate the equilibrium constant of the reaction

$$CuCl_2 + SnCl_2 = Cu + SnCl_4$$
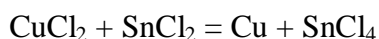
at the temperature of 25 °C. Choose the data suitable for this calculation:

$E^{\ominus}(Cu^{2+}|Cu) = 0.337$ V          $E^{\ominus}(Sn^{2+}|Sn) = -0.140$ V          $E^{\ominus}(CuCl|Cu|Cl^-) = +0.137$ V

$E^{\ominus}(Cu^+|Cu) = 0.521$ V          $E^{\ominus}(Sn^{4+}|Sn^{2+}) = +0.150$ V          $E^{\ominus}(Cl_2|Cl^-) = +1.360$ V

[$K = 2.1 \cdot 10^6$]

## Problem 11-12  Thermodynamics of the cell

Standard potential of the galvanic cell

$$\ominus \; Ag(s) \,|\, AgI(s) \,|\, AgI \; (saturated \; solution) \,|\, Hg_2I_2(s) \,|\, Hg(\ell) \; \oplus$$

is a linear function of temperature. At the temperature of 25 °C the potential cell is 0.1928 V and at 40 °C it is 0.1956 V. If you know that the enthalpy of AgI formation is −62.38 kJ mol$^{-1}$, calculate the enthalpy of Hg$_2$I$_2$ formation at 25 °C.

[$\Delta_f H^{\ominus}$ (Hg$_2$I$_2$) = –98.3 kJ mol$^{-1}$]

## Problem 11-13  Thermodynamics of the cell

Temperature dependence of the potential of cell consisting of two metal wires, nickel and copper, immersed in a solution of cupric and nickel chloride, is expressed by the equation

$$E^{\ominus}(T) = 0.5999 - 4.034 \cdot 10^{-8} \cdot T - \frac{85.25}{T^2} \quad [\text{V,K}] \; .$$

Write the equation occurring in this cell and calculate the reaction enthalpy at the temperature of 310 K. Further data needed for the calculation choose from the following values:

$E^{\ominus}(CuCl \,|\, Cu/Cl^-) = +0.137$ V          $E^{\ominus}(Ni(OH)_2 \,|\, Ni/OH^-) = -0.720$ V

$E^{\ominus}(Cu^{2+}|Cu) = +0.337$ V          $E^{\ominus}(Ni^{2+}|Ni) = -0.250$ V

$E^{\ominus}(Cl_2 \,|\, Cl^-) = 1.36$ V          $E^{\ominus}(O_2 \,|\, OH^-) = +0.401$ V

[CuCl$_2$ + Ni = Cu + NiCl$_2$ ($E^{\ominus} = E^{\ominus}(Cu^{2+}|Cu) - E^{\ominus}(Ni^{2+}|Ni) > 0$) , $\Delta_r H^{\ominus} = -115.45$ kJ mol$^{-1}$]

## Problem 11-14  Thermodynamics of the cell – solubility product

Calculate the solubility product of AgSCN at the temperature of 25 °C. For your calculation select appropriate data:

$E^{\ominus}(Ag^+|Ag) = 0.799$ V          $E^{\ominus}(AgCN|Ag, CN^-) = -0.017$ V

$E^{\ominus}(AgSCN|Ag, SCN^-) = 0.095$ V          $E^{\ominus}(AgCl|Ag, Cl^-) = +0.222$ V

[$K_{AgSCN} = 1.257 \cdot 10^{-12}$]

## Problem 11-15  Standard potential from solubility

The solubility of lead bromide in water at 25 °C is 3.82 g in 1 dm$^3$ of solution ($M = 367$ g mol$^{-1}$). The standard reduction potential of the lead electrode is $E^{\ominus}(Pb^{2+}|Pb) = -0.126$ V. If you can take all the activity coefficients as equal to one, calculate from these data the standard reduction potential of the second-kind electrode PbBr$_2$|Pb|Br$^-$.

[$E^{\ominus}(PbBr_2|Pb|Br^-) = -0.284$ V]

## Problem 11-16  Solubility product from the cell potential

The measurement of solubility of slightly soluble chloride MeCl$_2$ can be realized in this cell:

$$\ominus \; Me(s) \,|\, MeCl_2(s) \,|\, MeCl_2 \; (saturated \; solution) \,|\, Cl_2 \; (p = 130 \; kPa) \,|\, Pt \; \oplus \; .$$

At the temperature of 22 °C the cell potential was found to be 1.174 V. Determine the solubility product of $MeCl_2$ if you know the values of the standard potentials:

$$E^{\ominus}(Me^{2+}|Me) = +0.562 \text{ V} \quad , \quad E^{\ominus}(Cl_2|Cl^-) = 1.358 \text{ V}$$

You can assume the ideal behaviour of chlorine (standard state ideal gas at actual temperature and $p^{st} = 101.325$ kPa).

$$[K_{MeCl_2} = 1.58 \cdot 10^{-13}]$$

## Problem 11-17  Cell potential from thermodynamic quantities

The mean value of entropy change in the temperature interval $25 - 40$ °C associated with the formation of one mole of the solid silver chloride from the elements in their standard states is $\Delta_f S^{\ominus}(AgCl, s) = 57.9$ J $mol^{-1}$ $K^{-1}$. Calculate the standard cell potential and the cell potential at 25 and 40 °C of the cell

$$\ominus \text{ Ag(s) | AgCl (s)| KCl } (c = 0.1 \text{ mol dm}^{-3}) \text{ | } Cl_2 \text{ } (p = 250 \text{ kPa}) \text{ | Pt } \oplus$$

Chlorine exhibits ideal behaviour (standard state an ideal gas at actual temperature and pressure $p^{st} = 101.325$ kPa). From the following data pick up those which you need to your calculation:

$E^{\ominus}(AgCl|Ag|Cl^-) = 0.222$ V,    $E^{\ominus}(Ag^+|Ag) = +0.799$ V
$E^{\ominus}(K^+|K) = -2.925$ V    $E^{\ominus}(Cl_2|Cl^-) = +1.36$ V

$$[E^{\ominus}(25) = 1.138 \text{ V} , E(25) = 1.1496 \text{ V} ; E^{\ominus}(40) = 1.147 \text{ V} , E(40) = 1.1586 \text{ V}]$$