A 23 Measuring the Electromotive Force (EMF)

Task:

I) Determine the electromotive force of the following galvanic cells:

A.) Cu / 1.0 M $CuSO_4$ / sat. KCl – sol. / 1.0 M $ZnSO_4$ / Zn
B.) Cu / 1.0 M $CuSO_4$ / sat. KCl – sol. / 0.1 M $CuSO_4$ / Cu
C.) Zn / 1.0 M $ZnSO_4$ / sat. KCl – sol. / 0.1 M $ZnSO_4$ / Zn
D.) Cu / 1,0 M $CuSO_4$ / sat. KCl – sol. / AgCl / Ag
E.) Zn / 1.0 M $ZnSO_4$ / sat. KCl – sol. / AgCl / Ag
F.) Cu / 0.1 M $CuSO_4$ / sat. KCl – sol. / 0.1 M $ZnSO_4$ / Zn

II) Determine the solubility product of AgCl.

III) Determine, from the temperature dependency of the EMF of the galvanic cell F, the reaction enthalpy and the reaction entropy.

Basics:

A galvanic cell, made up of two half-cells, allows us to observe the work done by a chemical reaction as electrical energy. If, during the measurement process, a negligible current is flowing, then a galvanic cell operates reversible (this can also be obtained with the use of a high-ohm voltmeter, where the typical input current is $< 10^{-9}$ A). The electrical work correlates to the maximum producible work or the free energy of a corresponding reaction. The potential-building process in a metal electrode, which is immersed in a salt solution of the same metal (half-cell), is based upon the attempt of the metal atoms to reach equilibrium with the ions in the solution.

There are differing ways to explain this process, which all lead to the Nernst-equation:

$$\Delta\varphi = \Delta\varphi^0 - \frac{R \cdot T}{z \cdot F} ln \prod_i a_i^{v_i} \qquad (1)$$

$\Delta\varphi$: Potential difference

$\Delta\varphi^0$: Standard potential difference

R: Gas constant

T: Temperature

z: Transferred charge per formula unit of the reaction

F: Faraday constant

a_i: Activity of the species i

v_i: Stoichiometric factor of the species i

Generally, the EMF is measured at constant pressure. The work performed corresponds to the free enthalpy ΔG:

$$\Delta G = -z \cdot F \cdot E = -z \cdot F \cdot \Delta\varphi \qquad (2)$$

E: EMF

The use of equation (2) should be illustrated using the Daniell-Element as an example: Metallic Copper immersed in an aqueous $CuSO_4$ solution, metallic Zink immersed in a $ZnSO_4$ solution. The solutions are separated by a porous separator (diaphragm). The overall reaction is as follows:

$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$$

whereby the following expression for ΔG arises from Thermodynamics:

$$\Delta G = \Delta G^0 + RTln\frac{a_{Cu} \cdot a_{Zn^{2+}}}{a_{Zn} \cdot a_{Cu^{2+}}} \tag{3}$$

However, ion diffusion can occur at the interface in half-cells, which can contribute to ΔG and considerably falsify the measured EMF. The scale of the diffusion potential depends on the difference of the ion mobility in the solution. For current transporting ions of equal mobility the diffusion potential vanishes. Therefore, the two half-cells are not directly linked, but are connected using a salt bridge, which is filled with a highly concentrated electrolyte solution whose anions and cations have approximately equal mobility (e.g. KCl). Instead of a single interface between the electrolytes, two interfaces develop at which the potentials are small and opposite to each other, so that their product approaches zero. This is referred to as a Galvanic Cell without transport.

From equation (1) follows:

$$E = E^0 - \frac{RT}{zF} \cdot ln\frac{a_{Cu} \cdot a_{Zn^{2+}}}{a_{Zn} \cdot a_{Cu^{2+}}} \tag{4}$$

whereby, analogous to equation (1), the EMF is divided into a standard value E^0 and an activity dependant term. E and E^0 can be further divided into single electrode potentials:

$$E = \varphi_{Cu/Cu^{2+}} - \varphi_{Zn/Zn^{2+}} \tag{5a}$$

$$E^0 = \varphi^0_{Cu/Cu^{2+}} - \varphi^0_{Zn/Zn^{2+}} \tag{5b}$$

$$\varphi_{Cu/Cu^{2+}} = \varphi^{0}_{Cu/Cu^{2+}} + \frac{RT}{zF} ln \frac{a_{Cu^{2+}}}{a_{Cu}} \qquad (6a)$$

$$\varphi_{Zn/Zn^{2+}} = \varphi^{0}_{Zn/Zn^{2+}} + \frac{RT}{zF} ln \frac{a_{Zn^{2+}}}{a_{Zn}} \qquad (6b)$$

Since the activity of a pure metal is not dependant on the solution, the corresponding/equivalent value can be added to the standard potential:

$$\varphi_{Cu/Cu^{2+}} = \varphi^{0}_{Cu/Cu^{2+}} + \frac{RT}{zF} ln a_{Cu^{2+}} \qquad (7a)$$

$$\varphi_{Zn/Zn^{2+}} = \varphi^{0}_{Zn/Zn^{2+}} + \frac{RT}{zF} ln a_{Zn^{2+}} \qquad (7b)$$

Since the activity of single ions cannot be measured, we define the mean ionic activity coefficient of a salt A_xB_y as:

$$\gamma_{\pm}^{(x+y)} = \gamma_{+}^{x}\gamma_{-}^{y} \qquad (8)$$

and the mean ionic activity as:

$$a_{\pm}^{(x+y)} = a_{+}^{x}a_{-}^{y} \qquad (9)$$

For 1:1 electrolytes this gives:

$$a_{\pm} = a_{+} = a_{-} = C\gamma_{\pm} \qquad (10)$$

where C is the molar concentration of the salt.

Now it is possible to calculate the activity coefficient from EMF measurements with known standard potentials. The standard potentials can be determined at very low concentrations as the Debye-Hückel Limiting Law sufficiently describes the activity coefficient in this range. Thus, one obtains the following equation for the Daniell-element:

$$E = (\varphi^0_{Cu} - \varphi^0_{Zn}) - \frac{RT}{zF} \cdot ln \frac{c_{ZnSO_4} \cdot \gamma_{\pm ZnSO_4}}{c_{CuSO_4} \cdot \gamma_{\pm CuSO_4}} \qquad (11)$$

Standard potentials are referred to T = 298.16 K and p = 1 bar at a hypothetical concentration of 1 mol/l. The standard hydrogen electrode is used as a reference, where its potential is fixed at 0 V. In practice, other reference electrodes would be used instead of the difficult to use hydrogen electrode.

Whereas, up until now, only half-cells with differing electrodes have been dealt with, it is also possible to have electrodes of the same material but differing concentration. For these “concentration cells”, analogous consideration gives us:

$$E = \frac{RT}{zF} \cdot ln \frac{c^1{}_{CuSO_4} \cdot \gamma^1{}_{\pm CuSO_4}}{c^2{}_{CuSO_4} \cdot \gamma^2{}_{\pm CuSO_4}} \qquad (12)$$

If there is only a slight difference in concentration, the activity coefficients will be almost equal, giving:

$$E = \frac{RT}{zF} \cdot ln \frac{c^1{}_{CuSO_4}}{c^2{}_{CuSO_4}} \qquad (13)$$

Experimental Procedure:

Important:

CONDUCT THE TEMPERATURE DEPENDANT MEASUREMENTS AT THE END OF THE EXPERIMENT (COOLING-TIME)

All equipment should be thoroughly cleaned with distilled water after the solution has been changed, and at the end of the experiment!

For the experimental series in Tasks I and II, a filter paper with the corresponding salt solution will be used as the salt bridge. For this, before beginning the experiment, a piece of filter paper should be cut to the appropriate size and placed in the salt solution until it has become thoroughly soaked.

The individual half-cells will be prepared in small beakers which will be fixed onto the stand (Caution: Ensure the magnetic stirrers are still operating). The previously cleaned (using sand paper) electrodes are positioned – using clamps - in the beakers so that they do not touch either the walls of the beaker, or the magnetic stirrers. Finally, the salt bridge is placed between the two beakers (**Ensure there is no contact with the electrodes!**). The insertion of the salt bridge is the starting point for the measurements. The salt bridge **must** be replaced after **each** measurement.

To determine the solubility product of silver chloride, and identical experimental setup is used with two silver electrodes which are immersed in silver nitrate solutions of equal concentration (each 2 ml 0.1 M $AgNO_3$ + 20 ml water). As a salt bridge, a 1 M KNO_3 solution is used. The connection is closed (insertion of the salt bridge). At this time, the multimeter should give a reading of 0 mV. A stoichiometric excess of 3 ml 0.1 M KCl solution is added to one half-cell. Record the EMF.

For the experimental series in Task III, glass apparatus which are closed at their lower end with a frit are used. The salt bridge is a temperature controlled, double walled beaker filled with saturated potassium chloride solution in which the two half-cells are inserted. The insertion of the electrodes – which are connected to the multimeter – is the starting point of the measurement. For the temperature dependant experiments, data will be collected for ca. 15 minutes at 25°C then, without pausing the experiment, the thermostat will be set to 50°C. The experiment will be continued until the temperature has reached the preset final value. The EMF is recorded at regular temperature intervals.

Data Analysis:

All results will be discussed and compared to the literature!

1) From the measured EMF values of the cells A.) and D.) and A.) and E.) respectively, calculate the EMF of the cells E.) and D.) respectively. Compare the results with the measured values.
2) Reference the electrode potential of Zn / Zn^{2+} and Cu / Cu^{2+} to the standard hydrogen electrode and order them in an electrochemical series.
3) Calculate the EMF of the cells B.) and C.) using equation (13). Compare the results with the measured values.
4) Repeat the calculation with equation (12) using the activity coefficient ($\gamma_{\pm CuSO_4}^{1M} = 0.041, \gamma_{\pm CuSO_4}^{0.1M} = 0.149$. The values for $ZnSO_4$ can be obtained from the literature). Discuss any potential discrepancies.
5) Calculate the silver ion concentration from the stoichiometry of the chloride ion concentration and the measured EMF.
6) Using the Gibbs-Helmholtz equation, calculate the enthalpy and entropy of the reaction at room temperature. How large is the effective work ΔG for this reversible reaction process? What is the efficiency of the Daniell-element?

What you should know:

- Error sources in EMF measurements
- Second order electrodes, Hydrogen electrodes
- Diffusion potential
- Overpotential
- Redox potential
- Electrochemical series
- Nernst Equation
- Solubility product
- Chemical and electrochemical equilibrium conditions
- Temperature dependency of EMF

Extra Question:

Derive the Nernst equation using the electrochemical equilibrium conditions.