14th PRACTICE:

CHEMICAL EQUILIBRIUM. THERMODYNAMICS OF BATTERIES.

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GOALS

- In an interval of temperature, calculate the voltage of a battery.
- Verify the effectiveness of the measurement when obtaining interesting thermodynamic magnitudes.

THEORETICAL BASIS

What is a galvanic cell? Electrical energy is created from chemical energy by this apparatus.

Composition: Two electrodes submerged in the corresponding electrolyte solutions, connected by a salt bridge.

Oxidation and reduction happen at the same time, each in one of the electrodes when the system is closed.

THEORETICAL BASIS

Thermodynamic view? When equilibrium is established the reaction will stop as the reaction mentioned are irreversible.

Metal conductors resistance high, the reaction slower.

Electrodes can be connected to a conductor with infinite large resistance, there will always be equilibrium between the electrodes and the solutions.

The reaction will be **almost-reversible**.

THEORETICAL BASIS

Reversible thermodynamic transformation

When this takes place in a battery:

Wrev (The maximum electric work) is obtained and the voltage difference between electrodes (**Erev**) is called electromotive force (**emf**) because it is able to maintain the potential difference as it is in constant equilibrium.

THEORETICAL BASIS

Reversible processes:

Total variation of free energy: dG = - SdT + VdP + dWrev

When P and T are constant in a system: dG = dWrev

The electric work: dWrev = Erev dq = dG

q is the charge movement: q = nxF

(n: number of e- and F: Faraday constant)

dWrev = - nFE = dG

The sign (-) indicates that the work is done by the cell.

THEORETICAL BASIS

Reversible processes:

At constant P and T, if an spontaneous electrochemical reaction generates a voltage difference between the electrodes. i.e. $\Delta G<0$ and $E>0$.

Combining this equations; $\Delta G = DH - T\Delta S$ with $\Delta G = - nFE$, we will end up with the following one:

$$nFE = -\Delta G = -\Delta H + T\Delta S$$

THEORETICAL BASIS

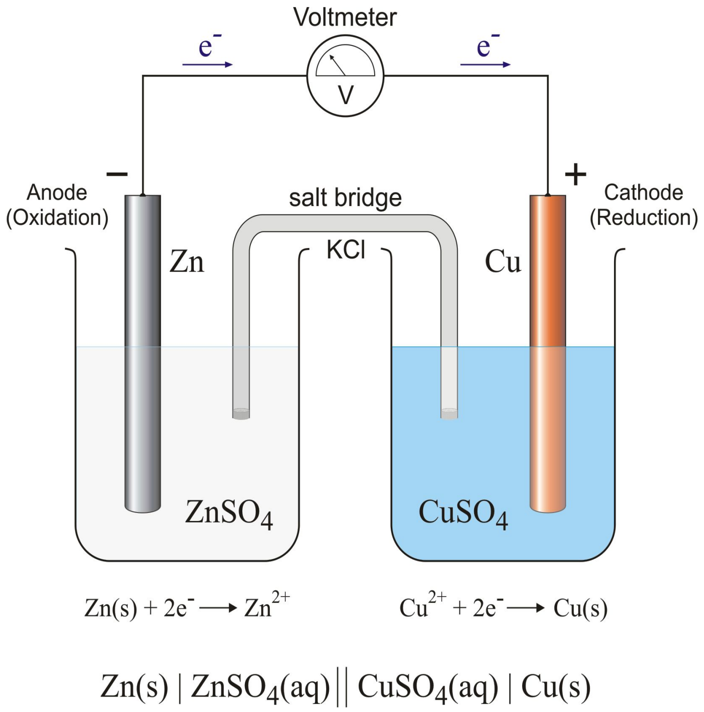
Deriving the last equation from T ($nFE = -\Delta G = -\Delta H + T\Delta S$), we will obtain the next equation:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = nF\left(\frac{\partial E}{\partial T}\right)_P$$

$\left(\frac{\partial E}{\partial T}\right)_P$: The emf temperature coefficient.

This is calculated experimentally measuring the voltage of a cell in equilibrium in an interval of temperatures.

EXPERIMENTAL PROCEDURE



This is more or less the system we are going to prepare so as to measure the voltage of the cell at different temperatures.

EXPERIMENTAL PROCEDURE

1. Prepare the electrolyte solutions:

   250 mL of $ZnSO_4$ 0.1 M

   250 mL of $CuSO_4$ 0.1 M

EXPERIMENTAL PROCEDURE

2. Prepare the salt bridge (might be prepared):

   100 mL of water + 2 g of agar-agar + 15 g of KCl.

   Dissolve the first in 50 mL of hot water and the second in other 50 mL and combine both.

   Homogenise the resulting dispersion properly, fill a U tube and leave it to cool until it has solidified.

EXPERIMENTAL PROCEDURE

3. Assembly the battery:

   Use both 150 mL beakers of the Zn^{2+} and Cu^{2+} solutions, Zn and Cu electrodes and the salt bridge.

   Close the electric circuit connecting them to a potentiometer and insert the battery in the thermostatic bath.

EXPERIMENTAL PROCEDURE

4. Measure the voltage in the system at 25, 30, 35, 40 and 45 ºC:

   Heat the bath and wait the appropriate thermostating time until the solutions reach the adequate temperature.

   Connect the electrodes to the voltmeter and note down the voltage in mV when it is stable and unplug the electrodes from the voltmeter.

   Heat it until the next temperature and do the same.

EXPERIMENTAL PROCEDURE

5. Determine the concentration of CuSO4 when starting and finishing:

   For this iodometry is going to be used.

   Prepare 100 mL of 0.1 M $Na_2S_2O_3$ and 50 mL of 0.1 M IK both in water. Take 10 mL of CuSO4, add 10 mL of 0.1 M IK and 3 mL of concentrated CH_3COOH. Mix it carefully and leave it to rest for 1 min. After that valorate it with 0.1M $Na_2S_2O_3$, using starch as an indicator (added close to EP).

DATA TO BE COLLECTED

Mainly the most important data to be collected:

- The equilibrium voltage (one at each temperature).
- The concentration of $CuSO_4$ (when the procedure starts and when it ends).

BIBLIOGRAPHY

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