THERMODYNAMICS OF A GALVANIC CELL

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Task 3

THERMODYNAMICS OF A GALVANIC CELL

I. Aim of the task

The aim of the task is to study the electrochemistry of galvanic cells and in the process to determine the values of the thermodynamic functions $\Delta G, \Delta H$, and ΔS.

II. Introduction

1. Thermodynamics and its basis definitions.
    1.1. Forms of energy.
    1.2. How can the energy of a system be changed?
    1.3. State functions.
    1.4. The First Law of Thermodynamics.
    1.5. The Second Law of Thermodynamics.
2. The Gibbs free energy (G) and the Helmholtz free energy (F).
3. Characterization of a galvanic cell.
    3.1. How a spontaneous reaction can be used to generate an electric current?
    3.2. Cell potential.
4. Construction of the Clark cell.
5. The relation between the electromotive force and the reaction Gibbs energy.
6. The relationship between the electromotive force of cell and thermodynamic functions.

References:

1. B. Averill, P. Eldredge, „*Chemistry, Principles, Patterns, and Applications*", Pearson, San Francisco, 2007, 810 – 860, 880 – 885.
2. T. Engel, P. Reid, "*Physical Chemistry*", Pearson, San Francisco, 2006, 1– 139, 247 – 255.
3. P. Atkins, J. de Paula, "*Physical Chemistry*", W.H. Freeman Company, New York, 2007, 76 – 105, 216 – 240.
4. W. J. Hamer, (January 15, 1965). "*Standard Cells: Their Construction, Maintenance, and Characteristics.*" National Bureau of Standards Monograph #84, Washington D.C., 1965, 1-41.

III. Theory

III. 1.Thermodynamics and its basis definitions

Thermodynamics is a branch of science that provides description of matter and the transformation between different forms of energyon *a macroscopic scale*. *Thermodynamics description of matter does not refer to its structure and behaviour at the microscopic level* (i.e. does not refer to size of molecules, or their atomic structure, type of chemical bonds etc.). In this approach, the *universe* is divided into two parts, the systemand its surroundings. The interface between the system and its surroundings is called boundary.

- The thermodynamic *system* is the part of the world consisting all the materials involved in the process under study e.g.the contents of a reaction vessel, the contents of an engine, the electrolyte solution within an electrochemical cell.
- The region outside the systemwhere the measurements are made, the rest of universe is referred to as the *surroundings*.

$$System + Surroundings = Universe$$

If matter can be exchanged between the system and its surroundings, the system is called *an open system*. If matter cannot be exchanged, the system is classified as *a closed system*. Both open and closed systems can exchange energy with their surroundings. The system that can exchange neither matter nor energy with the surroundings is called *an isolated system*.

The system of interest is described in terms of its bulk properties i.e. pressure, density, volume and temperature, which can be classified as extensive or intensive properties.

- The value of *the extensive property* changes according to the amount of material which is present(e.g. mass, volume, internal energy). The increase of the material amount causes the increase of the value of the extensive property.
- The value of *the intensive property* is independent of the amount of material present (e.g. temperature, pressure, mass density –mass divided by volume).

Thermodynamic equilibrium refers to the condition in which the system and surroundings exist in the equilibrium with respect to the system properties such as temperature, *T*, pressure, *P,* and concentration, *c*. Equilibrium exists only if the property does not change with time, and if it has the same value in all parts in the system and surroundings. There are two main types of thermodynamic processes: reversible and irreversible.

- *A reversible process* refers to the process where the transfer of energy takes place in such a way that in any stage of the process, the transfer can be reversed by an infinite small modification of a state property as well it must be done infinitely slowly. Thus, such process is always at equilibrium even when undergoing a change.

– *An irreversible process* refers to the process where the transfer of energy takes place in such a way that some energy is dissipated. Thus, such process cannot be reversed because a proportion of this energy is dispersed irrecoverably, and the original conditions cannot therefore be generated without work being done on the system.

The reversible process is the ideal process which never occurs, while the irreversible process is the natural process that is commonly found in the nature.

III. 1.1. Forms of energy

1. *Energy, E*, is a property of matter that makes things happen, or, in the case of stored or potential energy, has the "potential" to make things happen. Energy can be transformed or changed from one type of energy to another, or, in the case of heat flow, can be transported from one place to another place, but energy cannot be created or destroyed. Therefore, *the total amount of energy in the universe remains constant*. There are different forms of energy:

a) *potential energy* – is the energy stored in a system because of relative positions (or orientations) of its components (body). It is associated with forces that act on a body in a way that depends only on the body's position in space. It is more like "energy-waiting-to-happen".

The forms of potential energy include e.g.:
   – *electrical energy* – one of an example can be lightning, which is due to the flow of electrically charged particles;
   – *nuclear energy* – is released when particles in nucleus of the atom are rearranged;
   – *chemical energy* – is released during the breaking and reforming of chemical bonds or the particular arrangement of atoms in a chemical compound;
   – *radiant energy* – is the energy in light, microwaves, and radio waves;
   – *thermal energy* – is the energy resulting from atomic and molecular motion.

b) *kinetic energy* – is the energy contained in a moving system. It is associated with the motion of components of the system.

The internal energy of the system is of special interest of thermodynamics. From the viewpoint of microscopic level, the internal energy results from a number of energy forms such as the kinetic energy of molecules, the potential energy of the component of the system, the internal energy stored in the form of molecular vibrations and rotations as well as in the form of chemical bonds. The total of all forms of energy mentioned previously for the investigated system is called the *internal energy (U)*.

III. 1.2. How can the energy of a system be changed?

The energy of the system can be changed only by the transfer of energy to or from the system in the form of *heat* (Q), *work* (W) performed on or by the system, or some combination of heat and work. Viewed at a microscopic level, it can be said that:

a) *Heat* is the way of transfer of energy where disordered motion (thermal motion) of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased.

1. *Work* is the way of transfer of energy that makes use of organized motion of the molecules in the system. When a system does work, it stimulates orderly motion in the surroundings.
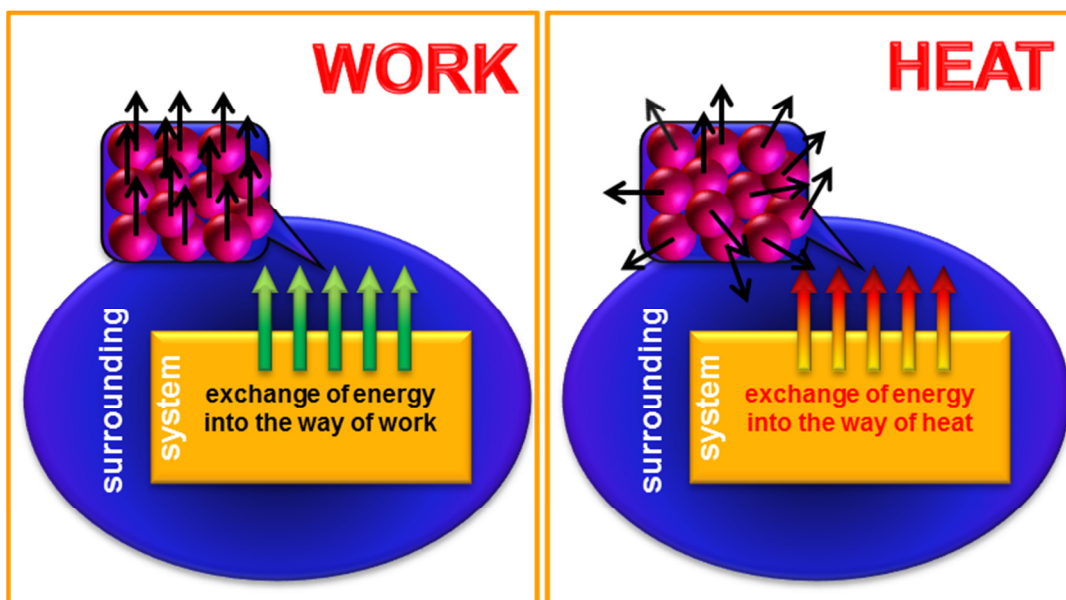

Fig.1. Schematic drawings of work and heat.

It should be emphasized that the main distinction between work and heat is made in the surroundings (see Fig.1). There is no difference between an energy change brought about by doing work on a system and an equal energy change brought about by heating.

There are many different types of work, including mechanical, electrical, work against a gravitational field, magnetic field or the surface tension, the work of expanding a surface etc. However, the work associated with the volume changes of the investigated system can be distinguished and is called *an expansion work* (W_{pV}). This type of work arises e.g. from a change in volume of a gas as it expands or compresses, also many chemical reactions result in the generation or consumption of gases, and thus the expansion work may accompany these reactions. The term 'expansion work' involves the work associated with negative (i.e. compression) and positive (i.e. expansion) changes of volume of the investigated system.

The expansion work performed is thus:

$$W_{PV} = -P \cdot \Delta V \tag{1}$$

The total work done by the system on the surroundings is:

$$W_{tot} = W_{PV} + W_{el} \tag{2}$$

Internal energy, heat, and work are all measured in the joule (J). The joule is defined as: $[J] = [kg \cdot m^2 \cdot s^{-2}]$.

Calories (cal) and kilocalories ($kcal$) are other energy units still used. The current definition of the calorie in terms of joules is exactly: $1\ cal = 4.184\ J$

Note: The *temperature, T,* is the property that indicates the direction of the flow of energy through a thermally conducting, rigid boundary. Of course, if the systems A and B are in contact and energy flows from A to B, it is said that the system A has a higher temperature than B. Therefore, temperature is the property of the system that determines if the system is in thermal equilibrium with other systems or the surroundings.

III. 1.3. State functions

Complete description of the state of the investigated system at a given time involves its absolute temperature and pressure, the amount of matter the system contains, its chemical composition, and the physical state of the matter. The set of variables used for the description is based on the experience. A *state function* is a property of the system. A magnitude of the state function depends only on the present state of the observed system and is independent of its previous history i.e. of how that state has been attained (path independent). Thus, *temperature, pressure, volume and internal energy are all state functions*. On the other hand, *heat and work are not the state functions* because their magnitude strongly depends on the way of their change.

III. 1.4. The First Law of Thermodynamics

As it was mentioned above, *the total amount of energy in the universe remains constant*. The first law of thermodynamics is based on this experience and can be formulated in a number of equivalent forms.

This state can be stated as follows:

The internal energy, U, of an isolated system is constant.

Therefore, if changes of the internal energy occur in a system in contact with its surroundings, the first law becomes:

$$\Delta U_{total} = \Delta U_{system} + \Delta U_{surroundings} = 0 \tag{3}$$

Moreover, as it was discussed (see chapter III.1.2) the internal energy of the system can be changed by the flow of heat or work across the boundary between the system and surroundings. Thus, it leads to other formulation of the first law:

$$\Delta U = Q + W \tag{4}$$

To measure the internal energy changes that occur in the system which is allowed to change its volume (e.g. during chemical reactions) there is usually used a quantity called enthalpy. The *enthalpy, H*, of the system is defined as the sum of its internal energy **and the product of its pressure, P, and volume, V.**

$$H = U + PV \tag{5}$$

Because the **U, P,** and **V** are all state functions, enthalpy is also a state function. The definition of enthalpy has important implications for thermochemistry. From equation (5) it can be implied that the change in enthalpy (ΔH) is equal to the energy supplied as heat at constant pressure (provided the system does not do additional work):

$$dH = dQ \tag{6}$$

III. 1.5. The Second Law of Thermodynamics

The second law can be expressed in a variety of equivalent statements. The Kelvin formulation of the second law of thermodynamics is as follows:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

Chemical and physical changes in a system can be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy($\Delta S < 0$). *Entropy,S,* is a state function and a thermodynamic property of all substances that is proportional to their degree of disorder.

Some important statements are:
The process in which $\Delta S > 0$ increases is the direction of natural changes in the isolated system. The reverse process for which $\Delta S < 0$ is the unnatural direction of changes. Only for a reversible process in an isolated system $\Delta S = 0$.
If the system and the part of the surroundings, which it is close to, are viewed as an isolated composite system:

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} > 0 \tag{7}$$

Thus the decrease of the universe will never be observed, because $\Delta S \geq 0$.

III. 2. The Gibbs free energy and the Helmholtz free energy

The Helmholtz free energy F is defined as:

$$F = U - TS \tag{8}$$

where U is the internal energy of the system, S is the final entropy of the system, and T is the absolute temperature.

From the First Law of thermodynamics (with a constant number of particles and where it is assumed that changes in the system are quasi-static and reversible):

$$dU = \delta Q - \delta W \tag{9}$$

where δQ is defined as heat added to the system and δW is the work done by the system. Simultaneously, for a reversible process from the Second Law of Thermodynamics one may say:

$$\delta Q = TdS \tag{10}$$

It can be also expressed as:

$$dU - TdS = \delta W \tag{11}$$

It enables rewriting Equation (4) as follows:

$$d(U - TS) = \delta W \tag{12}$$

The definition of the Helmholtz free energy, F, makes it possible to rewrite it as:

$$dF = \delta W = -PdV + W_{el} \tag{13}$$

where W_{el} is the non-expansion work (e. g. electrical work). From Equation (13) it can be stated that for a reversible process at a constant temperature, the change of free energy F is equal to the maximum amount of work that the system can do in a thermodynamic process.

If our system is kept at constant pressure and temperature ($dP = 0, dT = 0$):

$$d(F + PV) = W_{el} \tag{14}$$

Hence, there is obtained the Gibbs free energy which is a state function:

$$G = F + PV \tag{15}$$

Equation (14) also can be rewritten as:

$$dG = W_{el} \tag{16}$$

The Gibbs free energy is the maximum amount of non-expansion work that can be done for the surroundings (at a constant temperature and pressure). This maximum can be attained only in a completely reversible process. Summing up:

- the Helmholtz free energy has natural variables T and V. At a constant T and V, the Helmholtz free energy is the energy to do work.

- the Gibbs free energy has natural variables T and P. At a constant T and P the Gibbs free energy is the energy to do work.
- The change in the free energy tells us about the spontaneity of the reaction:

$\Delta G < 0$ **reaction is spontaneous;**

$\Delta G = 0$ **reaction at equilibrium;**

$\Delta G > 0$ **reaction is nonspontaneous (reverse reaction is spontaneous).**

III. 3. The Gibbs–Helmholtz equation and its application

The Gibbs-Helmholtz equation is a thermodynamic equation which provides information about the temperature dependence of the Gibbs free energy of a system. It is usually associated with the equation:

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \tag{17}$$

where G is the Gibbs free energy, H is enthalpy, and T temperature, all at the constant pressure. However, this is just one of a very large number of equations of similar form, which, at various times have been called Gibbs-Helmholtz equations.

Equation (18) provides one form of the Gibbs-Helmholtz equation:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2} \tag{18}$$

The Gibbs-Helmholtz equation can be also written in terms of the change in the Gibbs free energy:

$$\left(\frac{\partial(\Delta G/T)}{(1/T)}\right)_P = \Delta H \tag{19}$$

The Gibbs-Helmholtz equation:

1) enables the calculation of the Gibbs free energy change for a chemical reaction at any temperature "T" knowing just the values of the standard Gibbs free energy change of formation (ΔG_f^o) and the standard enthalpy change of formation (ΔH_f^o) at 298 K for the individual components,
2) relates the Gibbs free energy to a chemical equilibrium constant,
3) enables study of the temperature dependence of the Gibbs free energy change for endothermic and exothermic reactions.

The investigation of electrochemical reactions offers a simple and direct method for determining the values of changes of thermodynamic state functions accompanying the reaction, because the quantity of electrical energy produced or consumed during an electrochemical reaction can be measured very accurately using the electrochemical cell.

III.4. Characterization of an electrochemical cell

In general, *an electrochemical cell* is a simple device in which an electric current (a flow of electrons through a circuit) is either produced by a spontaneous chemical reaction or used to cause a non-spontaneous reaction to occur. Therefore, two types of electrochemical cells: galvanic cells (often called voltaic cells) and electrolytic cells can be distinguished.

A galvanic cell is an electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current. Therefore it can be used as a source of electrical power. By their nature, galvanic cells produce direct current which can be used to do work, such as turn a portable CD player or a laptop computer, or power a light. Therefore, they have achieved considerable practical importance. On the other hand, electrochemical cells are also valuable laboratory instrument, because they can be used to determine the equilibrium constant in the cell reaction, mean activity coefficients for ions in solution, and also thermodynamic quantities such as enthalpies and Gibbs energies.

III. 4.1. How can a spontaneous reaction be used to generate an electric current?

An apparatus which can be considered as a galvanic cell is schematically presented in Figure 2. It consists of two half-cells (metal electrode immersed in an aqueous solution containing metal cations) connected by an ionic conductor known as a salt bridge (which allows ions to flow between the solutions while preventing their mixing) and the wires which are fastened to each metal electrode (allowing the electron current to flow).
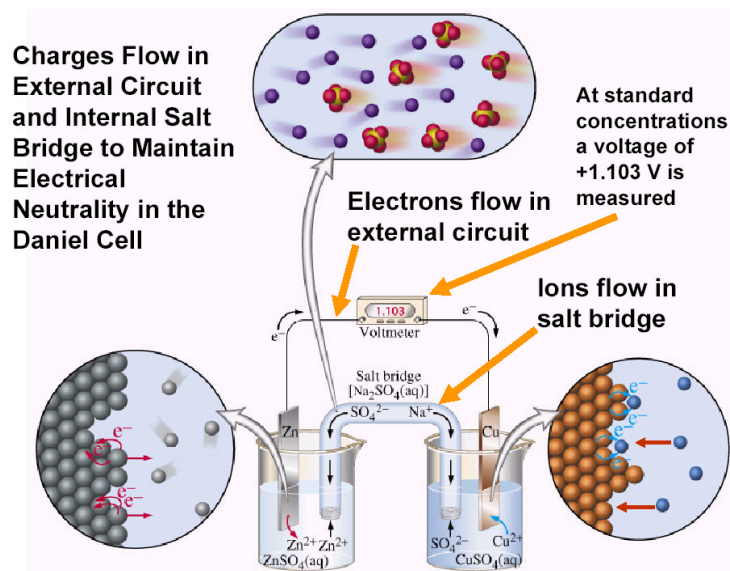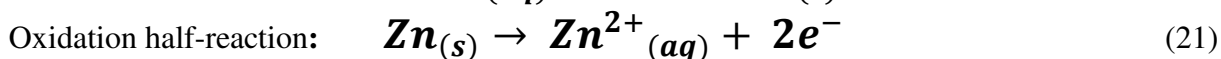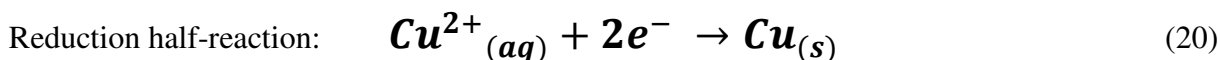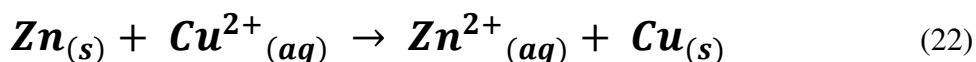

Fig.2. Schematic diagram of the Daniell cell [2].

If one could watch the reaction at the atomic level such as the one shown in Figure 2, one would see that if the zinc and copper electrodes (a piece of zinc and cooper metal,

respectively) are connected by external circuit, the reaction takes place and atoms leave zinc electrode to form Zn^{2+}ions in solution (oxidation process) whereas the "excess" of electrons that remain when Zn^{2+}ions go into solution, is delivered to Cu^{2+}ions which become "discharged" and deposited as Cu atoms on the Cu electrode (reduction process). It is impossible to have reduction without oxidation, and vice versa. A redox reaction can be described as two half-reactions, one representing the reduction process eq.(20) and one the oxidation process eq. (21). By the convention, in galvanic cells the electrode at which oxidation occurs is called the *anode,* and the electrode at which reduction occurs is called the *cathode.* Moreover, a commercial galvanic cell has its cathode marked with a + sign and its anode with a – sign.

Reduction half-reaction: $$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \tag{20}$$

Oxidation half-reaction**:** $$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \tag{21}$$

The overall reaction can be written as follows:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{22}$$

Note that electrons do not appear in the overall reaction (eq.22) because the electrons produced at the anode are consumed at the cathode. Therefore, the overall chemical reaction in a galvanic cell can be considered as pushing electrons onto one electrode (an anode) and pulling them off the other electrode (a cathode). This "push–and–pull" process causes a flow of electrons in the external circuit joining the two electrodes, and that current can be used to do electrical work.

III. 4.2. Cell potential

The cell potential, known as the potential difference, E, is a measure of the ability of a cell reaction to force electrons to flow through a circuit. If the "push–and–pull" process is endowed with a lot of power in a galvanic cell, it generates a high cell potential. On the other hand, a little power of the "push–and–pull" process generates a small cell potential. Thus, when the cell potential is large, a given number of electrons travelling between the electrodes can do a large amount of electrical work. Whereas if the cell potential is small, the same number of electrons can do only a small amount of work.

A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero. An exhausted battery is a cell in which the reaction is at equilibrium; it has lost its power to move electrons and has a potential of zero.

A cell in which the overall cell reaction has not reached chemical equilibrium can do electrical work. When the cell potential is measured under reversible conditions, its potential is then referred to as *the electromotive force (emf, E) of the cell.* The potential difference measurement under reversible conditions consist in the balancing of this potential by an external potential (e.g. a voltmeter which is a resistor) so that no current flows in a cell.

The SI unit of potential is the volt (V). A volt is defined so that a charge of one coulomb ($1\ C$) falling through a potential difference of one volt ($1\ V$) releases one joule ($1\ J$) of energy $[J] = [V \cdot C]$

Note: One coulomb is the magnitude of the charge delivered by a current of one ampere flowing for one second, $[C] = [A \cdot s]$.

III. 5. Construction of the Clark cell

The Clark cell was invented by the English engineer Josiah Latimer Clark in 1873. It is a wet-chemical cell that produces a suitably stable voltage which is particularly useful in laboratory work.

The original design of the cell was set up in a glass jar (Fig.3). The cathode was a pool of mercury (Hg) at the bottom of the jar. Hg was in a contact with the mercurous sulfate paste ($Hg_2SO_4 + Hg$) and, above that the saturated solution of zinc sulfate ($ZnSO_4$) containing crystals of ($ZnSO_4 \cdot 7H_2O$) was placed. A short zinc rod was dipped into the zinc sulfate solution. Into a glass tube, reaching to the bottom of the cell, a platinum wire was stuck which made contact with Hg. Therefore, the cell was closed by a cork (with two holes) and sealed with a layer of marine glue [4].
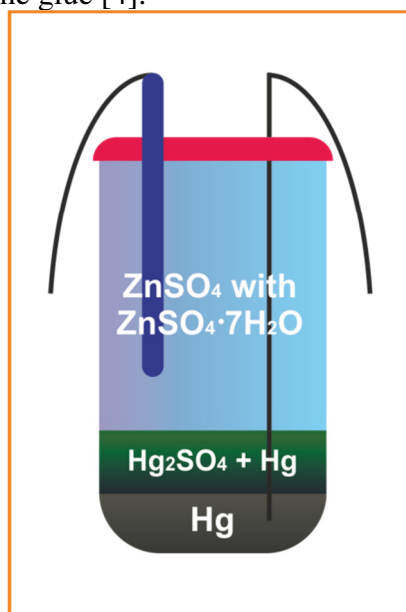

Fig.3. The original design of the Clark cell.

Almost ten years later, Lord Rayleigh introduced the H-form of the Clark cell presented in Fig. 4. The cell was set up in an H-shaped glass vessel with zinc amalgam (Zn/Hg) in one leg and pure mercury (Hg) in the other. Above Hg there was a layer of mercurous sulphate paste ($Hg_2SO_4 + Hg$). The vessel was filled, nearly to the full, with the saturated zinc sulfate solution ($ZnSO_4$) containing crystals of $ZnSO_4 \cdot 7H_2O$. Electrical connections to the zinc amalgam and mercury were made by platinum wires fused through the lower ends of the glass vessel legs.
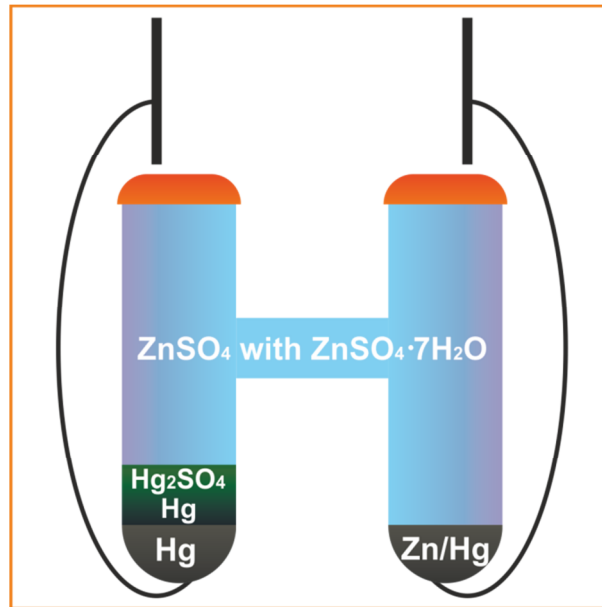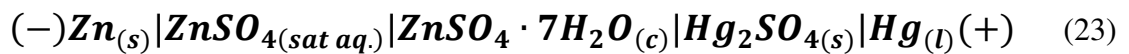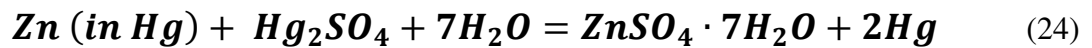
Fig.4. The H-form of the Clark cell.

The abbreviated notation for the Clark cell can be presented as:

$$(-)Zn_{(s)}|ZnSO_{4(sat\ aq.)}|ZnSO_4 \cdot 7H_2O_{(c)}|Hg_2SO_{4(s)}|Hg_{(l)}(+) \quad (23)$$

The overall reaction in this cell is:

$$Zn\ (in\ Hg) +\ Hg_2SO_4 + 7H_2O = ZnSO_4 \cdot 7H_2O + 2Hg \quad (24)$$

The Clark cell has an electromotive force of 1.4328 volts at a temperature of 15°C (288 K). At a given temperature an emf (E) of the cell can be calculated according to the equation:

$$E = [1.434 - 0.0012\ (T - 15)] \quad (25)$$

The design of the Clark cell has two drawbacks:

a) quite large temperature coefficient of -1.15 mV/°C,
b) corrosion problems caused by the platinum wires alloying with the zinc amalgam connections where they enter the glass vessel.

III. 6. The relation between the electromotive force and the Gibbs energy of reaction

Electrical work W_{el} which is done in a galvanic cell is the work done when an amount n of electrons (in moles) travels through a potential difference E. Simultaneously, it is known that the electrical work is a type of non-expansion work which means that it is work other than that resulting from a change in volume. The value of the work is equal to the total charge

of electrons multiplied by the potential difference. The charge of one electron is – e; the charge per mole of electrons is – $e \cdot N_A$, where is N_A Avogadro's constant. Therefore, the total charge is– $n \cdot e \cdot N_A$ and the work done is:

$$W_{el} = -n \cdot e \cdot N_A \cdot E \qquad (26)$$

The Faraday's constant, F, is the magnitude of the charge per mole of electrons and it is abbreviated to . Thus, the preceding expression for work can be written as:

$$W_{el} = -n \cdot F \cdot E \qquad (27)$$

On the other hand, it is known that the maximum non-expansion work that a system can do at constant pressure and temperature is given by eq.(16), with identified with the change in the Gibbs energy of the reaction in the system. When equation (27) is combined with the thermodynamic equation (16), it is obtained:

$$\Delta G = -n \cdot F \cdot E \qquad (28)$$

In the current context the non-expansion work is electrical work, which the galvanic cell can do. However, to draw thermodynamic conclusions from measurements of the work a cell can do, the galvanic cell must be operated reversibly, only then it produces maximum work. Moreover, the reaction Gibbs energy is related to a specified composition of the reaction mixture. Therefore, to achieve these two conditions the measurement of the cell potential must be conducted in the cell when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows. Consequently, the cell reaction is poised for change, but not actually changing. The resulting potential difference is called the electromotive force (emf), E, of the cell.

It is very important to emphasize that eq.(28) provides "an experimental criterion of spontaneity". Since if the cell potential E is positive, then the change in the reaction Gibbs free energy is negative. Thus, the reaction in the investigated cell has a spontaneous tendency to form products. On the other hand, if the cell potential is negative, then the reverse of the cell reaction is spontaneous, and the cell reaction has a spontaneous tendency to form reactants.

It is worth noting that a working cell, such as the battery in a mobile phone, will produce a potential that is smaller than that predicted by eq. (28) since it is not operated reversibly.

III. 7. The relationship between electromotive force of cell and thermodynamic functions

The measurements of the electromotive force of a galvanic cell under reversible conditions and the variation of cell E with temperature, make it possible to determine the numerical value of thermodynamic parameters i.e. the ΔS (the entropy change) and ΔH (the enthalpy change) for chemical reactions.

The reaction entropy is related to the reaction Gibbs energy by:

$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_P \tag{29}$$

Introducing eq.(28) gives:

$$\Delta S = n \cdot F \cdot \left(\frac{\partial E}{\partial T} \right)_P \tag{30}$$

Thus, the enthalpy change is:

$$\Delta H = \Delta G + T \Delta S \tag{31}$$

If the electromotive force is known, ΔH can be determined as follows:

$$\Delta H = -n \cdot F \cdot \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right. \tag{32}$$

For obtaining the values of above mentioned thermodynamic state functions for chemical reactions, the reliable temperature coefficients $\left(\frac{\partial E}{\partial T} \right)_P$ should be known to three significant points. Therefore, this requires careful measurements of the temperature dependence of the electromotive force, E, in a galvanic cell. The limited precision of the temperature dependence of E limits the precision in determination of the reaction entropy ΔS.

IV. Experimental

A. Devices

1. Devices:
   – the Clark cell,
   – thermostat,
   – a contact thermometer,
   – a digital voltmeter.

B. Program

1. Preparation of the thermostat for measurements.
2. Measurement of the Clark cell potential (electromotive force in *V*) at a given temperature starting from 20°C (293K) to 40°C (313 K).
3. Development of the results.

C. Procedure

1. Thermostat with the Clark cell

   The H-shaped Clark cell is placed in the thermostat, equipped with a contact thermometer. It allows for measurement of the cell potential at a given temperature. The value of the electromotive force in Volts is measured with the digital voltmeter.

   To conduct measurements there are needed:

   – turn on the power to the thermostat and digital voltmeter,
   – set a small flow of water through the thermostat,
   – set the contact thermometer for 20°C (293K) and wait at least half an hour to reach thermal equilibrium.

2. The measurements of the temperature dependence of the electromotive force in the Clark cell

   The value of the electromotive force, (*E*) should be recorded every five degrees starting from 20°C (293K) to 40°C (313 K). The exact temperature, *T* at which the measurement of the electromotive force is taken should be recorded.

   Connect the wires to the voltmeter and measure the voltage of the cell on the voltmeter. Take at least three readings at each temperature every three minutes. Disconnect wire so that no reaction occurs during change of settings and thermal equilibration at higher temperature. For higher temperature adjust the temperature of the thermostat bath by changing the set of the contact thermometer. Allow at least fifteen minutes to the assembly to reach thermal equilibrium at a given temperature.

It is important to realize that the voltage measurements at each temperature should not be taken until the system is at thermal equilibrium!

3. Put the obtained values of the electromotive force and temperature in Table 1:

Number of series	t [^{o}C]	T [K]	E [V]
1.1			
1.2			
1.3			
2.1			
2.2			
2.3			
3.1			
3.2			
3.3			
4.1			
4.2			
4.3			
5.1			
5.2			
5.3			

D. Results and conclusions

1. The obtained values of the electromotive force and temperature from Table 1 present as a graph of the dependence $E = f(T)$.

The electromotive force E varies linearly with the temperature.

$$E = aT + b \qquad (33)$$

The slope of the plot of E(eq. 33) is inversely proportional to the temperature of the measurement in the Clark cell. For calculating the values of thermodynamic functions ($\Delta G, \Delta H$ and ΔS) for chemical reactions, eq. (24) in the Clark cell, it is needed to determine the coefficients a and b in equation (33) given above.

2. Determine a and b coefficients.

The experimental data is often accompanied by some level of uncertainty. Even though all control parameters (independent variables) remain constant, the resultant outcomes (dependent variables) may vary. Therefore, a process of quantitative estimation of the trend of the outcomes, also known as regression or curve fitting, is necessary. The curve fitting process fits equations of approximating curves to the raw experimental data. A curve with a minimal deviation from all experimental data points is desired. This best-fitting curve can be

obtained by the method of least squares (see Appendix). The method of least squares is a standard approach, and it assumes that the best-fit curve of a given type is the curve that has the minimal sum of the deviations squared (least square error) from a given set of data.

The method of least squares should be used to determine a and b coefficients.

3. Calculate the values of thermodynamic functions.

4. Calculate the change in Gibbs energy (ΔG) of the reaction in the system at each temperature from eq. (34).

$$\Delta G = -n \cdot F \cdot E = -n \cdot F \cdot (aT + b) \tag{34}$$

$$[\Delta G] = \left[\frac{J}{mol}\right]$$

5. Calculate the change in enthalpy (ΔH) of the reaction in the system at each temperature from eq. (36).

$$\Delta H = -n \cdot F \cdot \left[E - T \cdot \left(\frac{\partial E}{\partial T}\right)_P\right] = -n \cdot F \cdot \left[E - T \cdot \left(\frac{\partial (aT+b)}{\partial T}\right)_P\right] \tag{35}$$

$$\Delta H = -n \cdot F \cdot (E - aT) \tag{36}$$

$$[\Delta H] = \left[\frac{J}{mol}\right]$$

6. Calculate the change in entropy (ΔS) of the reaction in the system from eq. (38):

$$\Delta S = n \cdot F \cdot \left(\frac{\partial E}{\partial T}\right)_P = n \cdot F \cdot \left(\frac{\partial (at+b)}{\partial T}\right)_P \tag{37}$$

$$\Delta S = n \cdot F \cdot a \tag{38}$$

$$[\Delta S] = \left[\frac{J}{mol \cdot K}\right]$$

7. Taking into account the value of the change in the reaction Gibbs free energy assess if the spontaneous chemical reaction occurred in the Clark cell.