Considerations Regarding the Mechanism of Electrical Energy Generation in *Karpen's Cells*

NICOLAE VASZILCSIN[1], DANUT-IONEL VAIREANU[2*]

[1] University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, 2 Victoriei Sq., 300006,Timişoara, Romani
[2] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, 313 Splaiul Independentei, 060042, Bucharest, Romania

The scope of this paper is to demonstrate the fact that Karpen's cells are not concentration cells, but rather types of double layer electrochemical capacitors, and their operation does not contravene to the second law of thermodynamics. The recharge of such capacitors is a spontaneous endothermic process, the necessary heat being extracted from the surrounding environment due to the existence of a temperature gradient between the solution near the electrode vicinity and the environment. In the absence of this temperature gradient the cell will shift towards an amortization phase, leading eventually to the stopping of the micro-motor. The paper also describe a mechanism of the electrical energy generation in Karpen cells.

Key words: Karpen's cells, compensated diffusion, capacitors, electrochemical cells

The electrochemical systems known as *Karpen's cells* were invented by Nicolae Vasilescu Karpen (NVK) and are described in his several papers [1-5]. The *K cells* were shrouded in mystery starting from the beginning, even by their author, who stated that their operation contravene to the second law of thermodynamics, generating electrical energy on the basis of heat absorbed from the outside: "these cells use exclusively the only one heat source of the constant temperature ambient environment" [5]. In other words, *K cells* are a 2nd kind *perpetuum mobile*. Moreover, this idea has been also supported until recent by other authors [6].

M. D. Cazacu *et al.* presented a modified version of a *K cell*, which ought to provide a continuous operation, highlighting a very important thing: the electrolyte solution cools during operation, absorbing some thermal energy from the surrounding environment. This means that this device runs on a heat transfer process from a hot source (the environment) and a cold source (the electrolyte solution), so that the *K cell* is not a 2nd kind *perpetuum mobile* [7,8].

K cells are basically manufactured by associating some inert metals (platinized/black platinum, bright platinum, gold, platinized gold) or graphite, immersed in the same electrolyte (a solution of sulphuric acid solution, pure sulphuric acid) or even distilled water, where there are minute amounts of dissolved oxygen or hydrogen (the corresponding air pressure or hydrogen pressure above the solution is about 1 cm H_2O (98.1 Pa) [5]. At these reduced oxygen or hydrogen concentrations, the electrodes surface is not saturated with O_2 (H_2) molecules or O (H) atoms, resulting from the respective molecules dissociation process.

Under these circumstances, one may estimate that the number of O_2 molecules or O atoms, respectively H_2 molecules or H atoms, adsorbed on the metal surface is proportional to the strength of the O – electrode material bonds, respectively to the strength of the H – electrode material bonds. This is the reason why NVK called these systems *concentration cells,* and based on its electronic theory deduced the relation for the electromotive force [9].

The 2nd kind perpetuum mobile false approach, the low current and the low amount of generated energy determined a restrained of the scientific community in addressing this issue, though Nicolae Vasilescu Karpen himself made an experimental demonstration at the French Academy in 1926 [6].

This paper aims to highlight the fact that *K cells* are not concentration cells, in the strict sense of the definition, but rather double layer electrochemical capacitors, and their operation does not contravene to the second law of thermodynamics and their recharge is a spontaneous endothermic process, the necessary heat being extracted from the environment due to the existence of a temperature gradient between the solution near the electrode vicinity and the environment.

The oxygen Karpen cells

The systematic studies of Nicolae Vasilescu Karpen in the field of electrochemistry were particularly oriented towards the oxygen cells, abbreviated as K_o. The most performant of them, (K'_o), is made of a platinized gold electrode (APt), having the physical dimensions of 200x6x0.04 mm, wrapped on a glass support, constituting the positive electrode, placed symmetrically between two bright gold electrodes (Au), similar in size with the platinized gold electrode, the gold electrodes (Au) being the negative terminal. The electrolyte used was pure sulphuric acid [9] (fig.e 1).

The deposition of the black platinum layer on gold has the effect of substantially increasing the contact surface between the platinum and the solution. The presence in the electrolyte of dissolved oxygen from the air is essential for the functioning of K'_o cell. Hermetically sealing the glass vessel carried out in K'_o cell ensured a stable operation by maintaining a constant concentration of dissolved oxygen inside the cell.

As said by NVK, K'_o cell has been studied for a long time "*during its 15 years of operation the cell was often short-*

email:di_vaireanu@chim.upb.ro, Tel. 021-402-3939

cutted for a prolonged time or put on relatively small resistances, but one has noticed no alteration of the electrodes surface "[5].
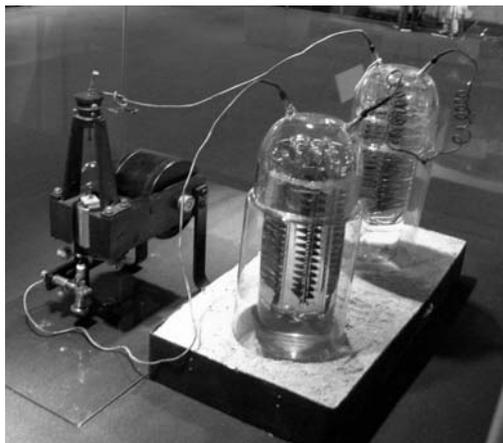

Fig.1. Oxygen K'_2 cell. (Courtoasy of "Dimitrie Leonida" National Technic Museum)

The deposition of the black platinum layer on gold has the effect of substantially increasing the contact surface between the platinum and the solution.

According to the interpretation given by NVK, the oxygen dissolved in sulphuric acid is adsorbed more onto the platinized gold electrode than on the bright gold electrode. As a result, the concentrations of oxygen adsorbed on the two electrodes are different, so that K'₂ cell has been considered by its creator "*an oxygen concentration cell*". The electromotive force of the cell, determined experimentally was of 350 mV [5]. The origin of the electromotive force is considered to be the exchange of electrons between the contacting environments (metal - electrolyte solution), the processes of generating the electrical energy in the external circuit being explained by a simplistic mechanism, become anachronistic. NVK showed that in the electrolyte solution, the water molecules dissociate in H+ and HO- ions. H+ ions move towards the cathode (APt) and are subjected to a reduction reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$
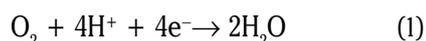
At the same time, the HO- ions move towards the anode (Au) and are subjected to an oxidation reaction:

$$4HO^- \rightarrow 2H_2O + O_2 + 4e^- \qquad (2)$$
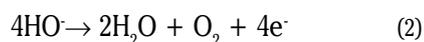
According to NVK "*theory of free electrons*" reactions (1) and (2) take place in a homogeneous phase, in the electrolyte solution, in the vicinity of electrodes. The occurrence of reactions (1) and (2) leads to a decrease in the concentration of molecular oxygen O_2 at the cathode and to an increase of its concentration at the anode, their concentrations tending to equalize as time goes by. When the cell is returned to its rest position, the oxygen diffuses from the anode towards the cathode, the electromotive force returning to its initial value. Based on the very "theory of free electrons" NVK found the relation for the electromotive force Ea of the concentration cells, deduced starting from Nernst's relations for gas electrodes:

$$E = \frac{RT}{4F} ln \frac{[O_2]_{APt}}{[O_2]_{Au}} \qquad (3)$$

where: R is the universal gas constant, T – thermodynamic temperature, $[O_2]_{APt}$ and $[O_2]_{Au}$ – concentration of adsorbed oxygen on platinized electrode, respectively on Au electrode.

NVK showed at the same time that the experiment proved the electromotive force is about 6.3 times higher than the theoretical one given by equation (3). Following this line of reasoning it is cited the work of Tamann and F. Runge [10]. The NVK's understanding is that the deviation from the theoretical formula (3) occurs as a consequence of the fact that this type of cell breaches the second law of thermodynamics [5].

Calculations carried out by NVK based on the relation (3) led him to the conclusion that the adsorbed molecular oxygen concentration on APt is 5.4' . 10^{23} times greater than that on Au, while, based on the corrected relationship, with a correction factor of 6.3, the adsorbed oxygen concentration is 0.58 . 10^4 times higher than that on Au, only the last value being credible.

K'₂ cell powered intermittently an electrical micro motor; the motor was placed in contact with the cell for 0.5 s, followed by a break of 18 s. Due to the inertia, the motor operated continuously. During the contact period, the current reached 17.5 µA, the cell terminal voltage dropping to 0.02 ÷ 0.03 V. During the rest period, K'₂ cell regenerated itself, the terminal voltage increasing to 0.25 V [9].

Hydrogen Karpen cell

Preliminary tests carried out by NVK in order to obtain a hydrogen Karpen cell using platinized platinum and bright gold electrodes showed that, at normal hydrogen pressures, the electromotive force is zero. Based on the relationship of the electromotive force of the hydrogen concentration cell:

$$E = \frac{RT}{2F} ln \frac{[H_2]_{Pt}}{[H_2]_{Au}} \qquad (4)$$

NVK concluded that, at normal hydrogen pressures, the concentrations of adsorbed hydrogen on platinum $[H_2]_{Pt}$ and on gold $[H_2]_{Au}$ become equal. These results led him to the conclusion that only a low hydrogen pressure above the electrolyte solution may determine a difference in the concentration of the adsorbed hydrogen on the two precious metals and thus the obtaining of a non-zero electromotive force [5].

A considerable electromotive force was obtained in cell equipped with platinized platinum and gold electrodes having identical dimensions (20x30 mm). One used as electrolyte a diluted solution of sulphuric acid (0.36%), the hydrogen pressure above the solution being of 1 cm H_2O (98,1 Pa). In these circumstances, the electromotive force of the cell, abbreviated as K_H, was 0.15 V at 20°C. NVK interpretation was that, at a sufficiently low hydrogen pressure, Pt adsorbs more hydrogen than Au, thus forming an element of concentration, the generation of current in the external circuit being the result of hydrogen oxidation reaction on platinum electrode and that of the hydrogen release reaction on gold electrode [5].

As in the case of K'₂, the electromotive force of K_H cell decreases sharply during the generation of current in the external circuit, having a specific behaviour of a capacitor.

The mechanism of electrical energy generation in oxygen Karpen cells

Modern theories of the electrical double layer at the interface of an electronic conductor - ionic conductor show that a potential difference occurs between the contact phases due to the redistribution of component particles in the contact zone, including that of electrical charge carriers, due to the net dipole orientation of the solvent on the

surface of the electronic conductor, that of a selective adsorption of chemical species located at the interface, as well as the establishment of redox equilibria [11-13].

The introduction of APt electrode, respectively Au electrode in sulphuric acid solution, induces an adsorption of the dissolved molecular oxygen molecules O_2 from solution adsorb at the two interfaces metal - electrolyte. Taking into account that the oxygen solubility in sulphuric acid solution is limited, and that the cell vessel was sealed, hence the gold and platinum electrodes surface is not saturated with oxygen, the interfaces being far from the equilibrium state of a corresponding gas electrode. Since the strength of Pt - O bond is higher than Au – O bond, the concentration of molecular oxygen adsorbed on platinum will be higher than that on gold [14].

On the other hand, the actual real size of platinized platinum is from 2 to 5 orders of magnitude greater than that of the geometrically calculated surface associated to the bright electrodes. Taking into account that the plating leads to the creation of sites favouring the adsorption of oxygen, it can be said that the amount of oxygen adsorbed on platinized platinum is much higher than that adsorbed on bright gold [15].

In order to simplify, we shall represent with the symbol O_2 the oxygen species adsorbed on metals surface, even though, in many cases, the preponderant adsorbed species is that of the atomic oxygen. Besides, the process of molecular oxygen dissociation does not modify the charge of metal - electrolyte interfaces. In contact with an electrolyte solution, platinum and gold, being noble metals, tend to release electrons and not metallic ions. Consequently, redox equilibrium is achieved at the interface, given by the reversible reaction:

$$O_2 + 4H_3O^+ + 4e^- \leftrightarrows 6H_2O \qquad (5)$$
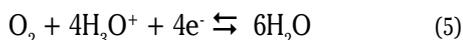
Given that the concentration of molecular oxygen adsorbed on platinum is greater than that on gold, the redox balance depicted in (5) on platinum will be moved, in accordance with the law of mass action, stronger towards the right comparing to that on gold. The platinum, under these conditions, will release more electrons per unit of area than the gold and hence platinum shall be the positive electrode in the K'_2 cell, while gold shall be the negative one, according to the electrochemical chain:(+) Au/Pt[O_2(ads)]/H_2SO_4(aq), O_2(aq)/Au[O_2(ads)] (-).

It should be noted that, in reality, both metals shall be positively charged comparing to the adjacent electrolyte solution, but the platinum charge will be more consistent. Pt[O_2(ads)]/H_2SO_4(aq) and Au[O_2(ads)]/H_2SO_4(aq) interfaces will be in equilibrium when the two potential differences at $\Delta\phi_{Pt/S(eq)}$ and $\Delta\phi_{Au/S(eq)}$ interfaces reach sufficiently high values.

The simplified equivalent electrical circuit of K'_2 an electrode, such as the two electrodes of K'_2 cell, is made of a capacitor, representing the capacitance of the electrical double layer, connected in parallel with the charge transfer resistance (fig. 2A) [16]. Given that in the absence of a faradic current the transfer resistance can be considered as being very high, the equivalent circuit of K'_2 cell is simplified (fig. 2B), where C_{d1} and C_{d2} represent the capacitance of the electrical double layer at Pt-electrolyte interface, respectively that of Au-electrolyte interface, and R_S is the electrolyte solution resistance. If one represents qualitatively the electric potential alongside of K'_2 cell (fig. 2C), one may notice that there is a potential difference between the terminal phases, representing the electromotive force (E) of K'_2 cell. It is known that the

electron work function has similar values for gold and platinum (4.46 eV vs 4.52 eV) [17], so that the voltage drop for Pt-Au junction can be considered as being negligible.

As seen from the above said considerations, the load difference occurs exclusively due to the formation of the electrical double layer at Pt and Au - electrolyte solution interfaces, which is why we may consider cell as a capacitor. Since the capacitors C_1 and C_2 are connected in series, the K'_2 electrochemical system capacity will be given by:

$$\frac{1}{c} = \frac{1}{c_1} + \frac{1}{c_2} \qquad (6)$$

Short-cutting the electrodes through a resistance (e.g. for K'_2 cell, a micro motor), the electrons shall move from the gold electrode to the platinum electrode, generating an electrical work. The potential of platinum decreases, while the potential of gold increases, meaning that that the potential $\Delta\phi_{Pt/S}$ becomes smaller than the equilibrium value $\Delta\phi_{Pt/S(eq)}$, and the value of $\Delta\phi_{Au/S}$ becomes larger than the equilibrium value of $\Delta\phi_{Au/S(eq)}$ (fig. 2C). The modality K'_2 cell discharges is another proof in favour of considering it as a capacitor (fig. 2D). The potentials $\Delta\phi_{Pt/S}$ and $\Delta\phi_{Au/S}$ tend to become equal over the time.

Balancing the Pt-electrolyte solution interface is carried out by the consumption of the platinum electron excess through the reduction reaction of the adsorbed oxygen (direct reaction 5) and that of the Au-electrolyte solution interface by the oxidation reaction of water molecules (reverse reaction 5). The fact that the electrode terminal voltage reaches in a very short time (0.5 s) a value close to zero, and that during the external circuit break period the electromotive force increases very slowly (18 seconds) to approximately 0.25 V shows that the electrochemical processes occurring at the two interfaces are far too slow than the discharge process through the external circuit, so that the K'_2 cell can function only intermittently.

At the interruption of the external circuit, the occurrence of the electrochemical reactions will lead to the restoration of the electrical double layer at the two interfaces. Pt-
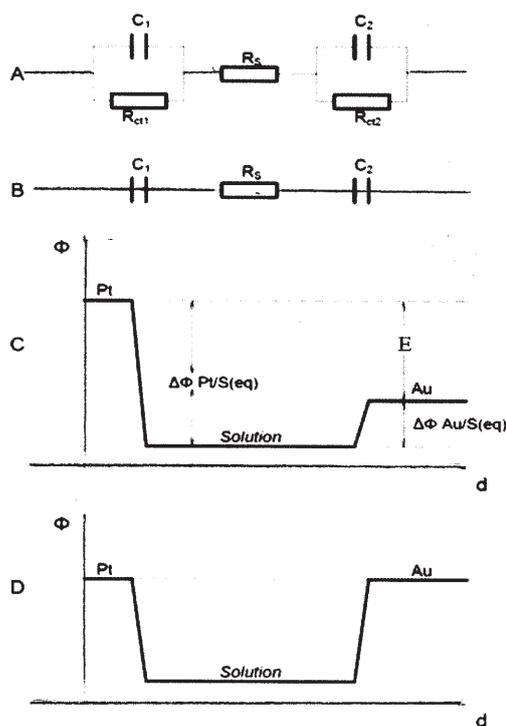

Fig. 2. A, B – The equivalent electrical circuits of cell; C, D – The electrical potential variation alongside cell.

electrolyte solution interface will deplete in oxygen and the Au-electrolyte solution interface will enrich with the same amount of oxygen. Therefore, the overall electrochemical process may be represented by the reaction:

$$O_{2(ads)Pt} \rightarrow O_{2(ads)Au} \qquad (7)$$

As the strength of Pt - O the bond is greater than that of Au – O bond, reaction (7) is an endothermic one. Therefore, the spontaneous recharging of the electrical double layer interfaces will lead to a cooling of the cell during the cell operation.

The existence of a temperature gradient between the cell and the external environment is the reason that will determine the occurrence of a thermal flow from the environment to the cell interior. Therefore, the cell uses thermal energy drawn from the environment, which is converted into electrical energy, so that it is not a second kind perpetuum mobile.

Moreover, NVK himself determined the value of the temperature coefficient for the electromotive force of K'_2. Its positive value ($+1.9$ mV K^{-1} [5]) shows that electricity supplied to the external circuit is higher than the overall process enthalpy that occurs when generating the actual electricity and, therefore, the cell will cool down during the operation process.

Reaction (7) will be offset by the process NVK called it "compensated diffusion", namely the reverse transport of O_2 molecules under the influence of the concentration gradient.

As the recovery reaction of the electrical double layer at the metal - electrolyte solution interfaces takes place spontaneously by non-faradic electrochemical processes, we may consider K'_2 cell as a *self-recharging electrochemical capacitor*.

The mechanism of electrical energy generation in hydrogen Karpen cell

According to the literature data, the strength of Pt - H bond is greater than that of the Au - H bond [18-21]. If the hydrogen partial pressure above the solution is sufficiently low at the introduction of the two metals in diluted sulphuric acid solution, the metal surface will be saturated with hydrogen. The amount of hydrogen adsorbed per unit of area is proportional to the strength of the metal - H bond, due to the thermal agitation, meaning that the amount of hydrogen adsorbed on platinum surface will be higher than that on the gold surface.

The hydrogen adsorbed on platinum is found in considerable proportion as its atomic form [22], the proportion of atomic hydrogen versus molecular hydrogen in equilibrium conditions being over 0.9 [23]. The proportion of adsorbed hydrogen on gold versus its molecular form is much smaller than 1 [22], but given that the hydrogen partial pressure above the electrolyte solution is very low, the concentration of the adsorbed hydrogen in its atomic state becomes appreciable.

An electrical double layer is formed at the two interfaces, Pt - solution or Au - solution. Considering the chemical species present, the established redox balance shall be the one given by the following reversible reaction:

$$H + H_2O \rightleftarrows H_3O^+ + e^- \qquad (8)$$
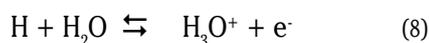
As the concentration of the hydrogen adsorbed on platinum $[H_{(ads)Pt}]$ is greater than the concentration of hydrogen adsorbed on gold $[H_{(ads)Au}]$, the reversible reaction on platinum (8) is moved further to the right comparing to

that on gold, namely the excess of electrons on platinum is greater than that on Au, therefore, in K_H cell Pt is the negative electrode and Au – the positive one. The electric potential of platinum will be more negative than that of gold (fig. 3A).

A potential difference $\Delta\phi_{M/S(eq)}$, shall be establish at the two interfaces Pt (Au) - electrolyte solution, at equilibrium, which will resist further to the net transfer of the electric charges (electrons) between the contact phases. As shown in figure 3A, it is found that: $|\Delta\phi_{Pt/S(eq)}| > |\Delta\phi_{Au/S(eq)}|$.

When the electrodes are shortcut, the excess electrons of platinum pass through the external circuit to the gold electrode, producing an electric work. The electrodes terminal voltage will decrease rapidly over the time, similarly like in the case of cells, allowing us to consider that K_H cell is also a capacitor cell.

The rapid discharge of the capacitor will lead to a reduction of the potential drop $|\Delta\phi_{Pt/S}|$ and to the increase of the potential drop $|\Delta\phi_{Au/S}|$ with respect to the equilibrium value, so that electric potentials will become virtually equal (fig. 3B). In order to restore the equilibrium at the two interfaces, respectively of the values of $|\Delta\phi_{Pt/S(eq)}|$ and $|\Delta\phi_{Au/S(eq)}|$, a spontaneous oxidation reaction of the molecular hydrogen will take place on platinum (direct reaction 8) and a reduction reaction of hydronium ions (reverse reaction 8) will take place on gold electrode. As the discharge speed of K_H cell is much faster than the direct or reverse reaction rate (8) the electrodes terminal voltage reaches quickly a value close to zero, so that the current in the external circuit is insignificant.

At the external circuit interruption, the reactions occurring at the two electrodes, lead in time to a spontaneous recharge of K_H cell, and, at the same time, to the restoration of the electrical double layer at the two interfaces, the overall process being represented by reaction (9):

$$H_{(ads)Pt} \rightarrow H_{(ads)Au} \qquad (9)$$

According to Hess's law, reaction (9) is an endothermic one, meaning that the spontaneous K_H cell recharge leads to its cooling, allowing a thermal flow from the environment to the cell. In other words, K_H cell does not contradict the second law of thermodynamics, so it is not a perpetuum mobile of the second kind.

When the concentration of $[H_{(ads)Pt}]$ becomes less than that at equilibrium, the hydrogen molecules dissolved in the electrolyte solution are adsorbed and dissociated on the platinum surface. At the same time, the hydrogen
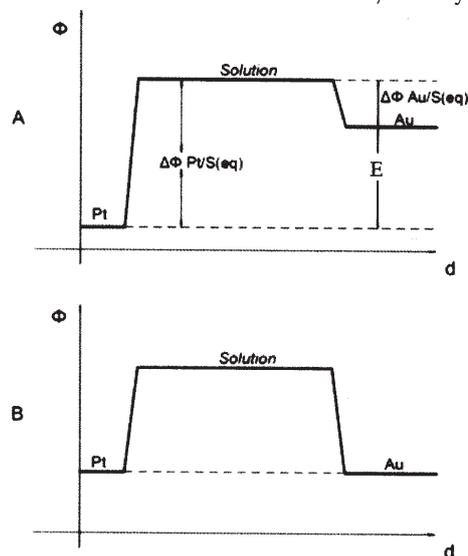

Fig. 3. A, B. The electrical potential variation alongside K_H cell.

atoms in excess on the surface of gold dimerize and pass into the electrolyte solution. The appearance of a concentration gradient of the dissolved hydrogen in the electrolyte solution will determine its diffusion from the gold electrode to the platinum one (compensated diffusion [5]).

One may consider that the generation of the electrical energy in the external circuit is the result of discharging and recharging processes of the electrical double layer at the Pt – electrolyte solution and Au – electrolyte solution interfaces. They are not accompanied by a faradic current, which is another argument in favour of considering that K_H cell plays the role of a capacitor.

The voltage across the capacitor terminals is a function of Gibbs energy of metal-hydrogen formation bond, as shown in Appendix I.

Conclusions

-The discharge characteristics of Karpen's cells suggest that these electrochemical systems are not galvanic cells, but capacitors;

- The charging mechanism of Karpen cells is an endothermic process that leads to the cooling of the considered electrochemical system;

- The appearance of a temperature gradient between the Karpen cell and the environment is responsible for the transfer of thermal energy from the environment to Karpen cell and implicitly for the long-term operation of cells;

- In the absence of this temperature gradient the cell will shift towards an amortization phase, leading eventually to the stopping of the micro-motor;

- It is necessary to have in the electrolyte solution very small quantities of dissolved oxygen and hydrogen respectively to provide for the *compensated diffusion*;

- The Karpen cell does not contradicts the second law of thermodynamics, hence is not a perpetuum mobile of the second kind;

- The Karpen cells are self-charging capacitors, as the charging process takes place spontaneously.

Appendix I
Deduction of the electromotive force relation for K_H cell

We can admit that, at normal hydrogen pressures (close to 1 bar), the noble metal surface (M) coverage degree of the adsorbed atomic hydrogen is at maximum. The overall balance established at the metal M - electrolyte solution (S) interface under these circumstances is obtained by the summation of the reversible processes (1) - (4):

$$H_3O^+(aq) + e^-(M) \leftrightarrows H(M) + H_2O(aq) \qquad (1a)$$
$$2H^+(aq) + 2e^-(M) \leftrightarrows 2H(ads) \qquad (2a)$$
$$2H(ads) \leftrightarrows H_2(ads) \qquad (3a)$$
$$H_2(ads) \leftrightarrows H_2(g) \qquad (4a)$$
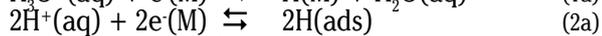
As a result, the overall process is given by the relation:

$$2H_3O^+(aq) + 2e^-(M) \leftrightarrows 2H_2(g) \qquad (5a)$$
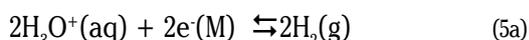
When the surface is saturated with adsorbed hydrogen the absolute M -S electrode potential does not depend practically on the nature of noble metal, its relation being given by the Nernst equation:

$$\Delta\phi_{M/S} = \Delta\phi^o_{M/S} + \frac{RT}{F} ln \frac{a_{H_3O^+}}{p_{H_2}^{1/2}} \qquad (6a)$$

If the hydrogen pressure is low enough, then only a fraction of the electrode surface is covered by adsorbed hydrogen atoms, and at the interface, the following equilibrium shall be established:

$$H_3O^+(aq) + e^-(M) \leftrightarrows H(M) + H_2O(aq) \qquad (7a)$$

Considering these conditions, the absolute electrode potential, according to Nernst relationships, for the interface M - S, will be given by:

$$\Delta\phi_{M/S} = \Delta\phi^o_{M/S} + \frac{RT}{F} ln \frac{a_{H_3O^+(aq)}}{a_{H(M)}} \qquad (8a)$$

Where $\Delta\phi^o_{M/S}$ from relation (8), is the absolute potential of M/S electrode, considering also that the activity of H_3O^+ ions, as well as the activity of H atoms adsorbed is equal to 1. We shall take as a reference state for the adsorbed atoms (activity equal to 1) the metal surface covered with atomic hydrogen, so that one may consider that $\Delta\phi^o_{M/S}$ does not depend on the nature of the noble metal.

Returning to K_H cell, the open circuit voltage (the electromotive force) is given by the difference between the Galvani potential of gold and platinum:

$$E = f_{Au} - f_{Pt} \qquad (9a)$$

As it results from figure 2A, the electromotive force is given by:

$$E = \Delta\phi_{Au/S} - \Delta\phi_{Pt/S} = \frac{RT}{F} ln \frac{a_{H(Pt)}}{a_{H(Au)}} \qquad (10a)$$

The activity of the adsorbed hydrogen atoms is directly proportional to the coverage degree θ and inversely proportional to the fraction of the free surface $1 - \theta$, namely, is directly proportional to the ratio $\theta / 1 - \theta$. According to the literature [24, 25], the hydrogen adsorption is governed by the Langmuir isotherm:

$$\frac{\theta}{1-\theta} = K_{ads} \cdot c_{H_2(aq)} \qquad (11a)$$

K_{ads} is the adsorption constant, – the concentration of molecular hydrogen dissolved in the electrolyte solution.

By customizing equation (11a) for Pt and Au, it results:

$$\frac{a_{H(Pt)}}{a_{H(Au)}} = \frac{K_{ads(Pt)}}{K_{ads(Au)}} \qquad (12a)$$

where $K_{ads(Pt)}$ and $K_{ads(Au)}$ are the adsorption constants of hydrogen on Pt and Au.

Between the adsorption constant and Gibbs energy there is a relationship [26]:

$$\Delta G_{ads} = -RTln(55.5 K_{ads}) \qquad (13a)$$

And hence:

$$K_{ads} = \frac{1}{55.5} e^{-\frac{\Delta G_{ads}}{RT}} \qquad (14a)$$

On the basis of relations (13a) and (14a), the ratio of the activities of hydrogen atoms adsorbed on platinum and gold becomes:

$$\frac{a_{H(Pt)}}{a_{H(Au)}} = e^{-\frac{\Delta G_{ads(Pt)} - \Delta G_{ads(Au)}}{RT}} \qquad (15a)$$

As the hydrogen adsorption on the two metals occurs with similar structural transformations, we can admit that the adsorption entropies are similar:

$$\Delta S_{ads(Pt)} \approx \Delta S_{ads(Au)}(\qquad 16a)$$

Under these circumstances it results:

$$\Delta G_{ads(Pt)} - \Delta G_{ads(Au)} = \Delta H_{ads(Pt)} - \Delta H_{ads(Au)} \qquad (17a)$$

On the basis of relations (10a), (15a) and (17a) one obtains the approximate E relation:

$$E = -\frac{\Delta H_{ads(Pt)} - \Delta H_{ads(Au)}}{F} \qquad (18a)$$

The adsorption enthalpy for hydrogen may be evaluated on the basis of relation (19a) [23]:

$$\Delta H_{ads} \approx -D_{MM} - 97.000(\chi_M - \chi_H)^2 \qquad (19a)$$

where: D_{MM} is the energy of metal-metal bond, χ_M and χ_H – metal and hydrogen Pauling electronegativities. The metal-metal bond energy is evaluated from the metal sublimation energy, ΔH_{vap}.

For metals which crystallize in face centered cubic system, $D_{MM} = \Delta H_{vap}/6$. For Pt and Au, the metal-metal bond energies are 94 and respectively 61 kJ mol^{-1} [27]. The values for Pauling electronegativity are:

$$\chi_{Pt} = 2.28, \chi_{Au} = 2.54, \chi_H = 2.20 \text{ [28]}.$$

One obtains the values for the adsorption enthalpies:

$$\Delta H_{ads(Pt)} = -94.6 \text{ kJ mol}^{-1} \text{ and } \Delta H_{ads(Au)} = -72.2 \text{ kJ mol}^{-1}$$

and hence the capacitor electromotive force: K_H: $E = 0.232$ V.

One may also calculate similarly the electromotive force for K_2 cell.

References

1. VASILESCU KARPEN, N., Acad. Sci., Paris, **T218**, 1944, p. 228
2. VASILESCU KARPEN, N., Acad. Sci., Paris, **T226**, 1948, p. 1273
3. VASILESCU KARPEN, N., C.R. Acad. Sci., Paris, **T228**, 1949, , p. 231
4. VASILESCU KARPEN, N., Bul. St. Acad. RPR, Sectia Mat – Fiz, **TVII,** nr. 1, 1955, p. 161
5. VASILESCU KARPEN, N., Fenomene şi teorii noi în electrochimie şi chimie fizica, Editura Academiei RPR, Bucuresti, 1957, p.126
6. ALEXANDRESCU, C., Journal of New Energy, **1,** nr. 2,1996, p.144
7. CAZACU, M.D., DOGARU, M., STAVARACHE, A., Vasilescu Karpen Pile as a Proceeding to Diminish the Earth Warming, Conferinta Nationala pentru o Dezvoltare Durabila, Bucuresti, 13 iunie 2003, p. 273 – 280.

8. DOGARU, M., CAZACU, M.D., For a Continuous Working of the Vasilescu Karpen's Concentration Pile, National Symposium of Theoretical Electrotechnics SNET '04, 22 – 23 October 2004, Univ.POLITEHNICA, Bucharest.
9. NICOLAIDE, A., Significance of the scientific research of Nicolae Vasilescu Karpen, AGIR Publishing House, Bucharest, 2006, p. 37 – 62
10. TAMANN, G., RUNGE, F., Z. Anorg. Chem., **156**, 1926, p.85
11. BOCKRIS, J.O'M., REDDY, A.K.N., GAMBOA-ALDECO, M., Modern Electrochemistry, 2A, Second edition, Kluwer Academic Publishers, New York, 2002, p.775
12. SCHMICKLER, W., HENDERSON, D., Surface Science, **22**, nr. 4, 1986, p.323
13. SCHMICKLER, W., Phys. Chem., **92,** 1988, p.1203.
14. KATSOUNAROS, I., CHEREVKO, S., ZERADJANIN, A.R., MAYRHOFER, K.J.J., Angewandte Chemie Int. Ed., **53,** 2014, p.102
15. FELTHAM, A.M., SPIRO, M., Chemical Reviews, **71** nr. 2**,** 1971, p.177
16. BAGOTSKY, V.S., Fundamentals of Electrochemistry, Second edition, John Wiley&So, Hoboken, New Jersey, 2006, p.208.
17. BOLZ, R.E., CRC Handbook of Tables for Applied Engineering Science, CRC Press, 2nd Edition, 1973, p.317
18. TRASATTI, S., J.Electroanal.Chem., **39**, 163, 1972.
19. DANILOCIC, N., SUBBARAMAN, R., STRMCNIK, D., STAMENKOVIC, V.R., MARKOVIC, N.M., Journal of the Serbian Chemical Society, **78**, nr. 12, 2013, p.2007
20. PARSONS, R.P., Volcano Curves în Electrochemistry, în (E. Santos and W. Schmickler) Catalysis în Electrochemistry, John Wiley & Sons, Hoboken, New Jersey, 2011, p.1
21. QUAINO, P., JUAREZ, F., SANTOS, E., SCHMICKLER, W., Beilstein Journal of Nanotechnology, 5, 2014, p.846
22. FRUMKIN, A.N., Hydrogen Overvoltage and Adsoption Phenomena, în (P. Delahay, editor), Advances în Electrochemistry and Electrochemical Engineering, Volume 3, Interscience Publishers, 1963, p.307
23. HAMANN, C.H., HAMNETT, A., VIELSTICH, W., Electrochemistry, 2nd Ed., Wiley-VCH Verlag, Weinheim, 2007, p.8
24. CHUN, J.H., RA, K.H., KIM, N.Y., International Journal of Hydrogen Energy, **26**, nr. 9, September 2001, p. 941
25 CHUN, J.H., RA, K.H., KIM, N.Y., Journal of the Electrochemical Society, **150, nr.** 4, 2003, p. E207
26. ZHANG, Q.B., HUA, Y.X., Materials Chemistry and Physics **119**, 2010, p. 57
27. PEARSON, R.G., Chem.Rev., **85**, 1985, p.41
28. ENGHANG, P., Encyclopedia of the Elements, Wiley – VCH Verlag, 2004, Weinheim, p.100, p.216, p.728.