# FORMAL ANALYSIS OF GALVANI AND VOLTA EXPERIMENTS RELATED TO THERMOELECTRICITY

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- *Formal analysis of Galvani and Volta (G&V) experiments related to thermoelectricity is made. The well-known Volta effect with inhomogeneously heated iron wire that is of complicated nature is classified in the paper as predominantly galvanothermal effect related to temperature dependence of electrode potentials of $Fe/H_2O/Fe$ cell.*

Experiments by Italian researchers – physician Galvani and physicist Volta (G&V) (Fig. 1), whose basic research results were published in 1791–1795 [1], to this date have attracted the particular attention of scientists working in different fields of science, including the theory of heuristics studying creative, productive thinking [2]. Of special interest for heuristics is a combination of relative simplicity of G&V experiments and huge importance of the results obtained by the authors for subsequent development of physics, chemistry, biology and other sciences.
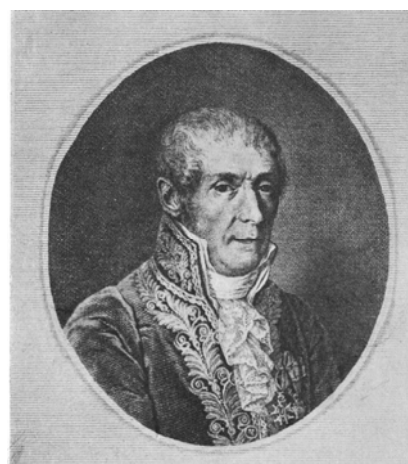


*Fig. 1. Luigi (Aloisio) Galvani (1737-1798) (on the left) and Alessandro Volta (1745-1827) [1].*

G&V in their experiments (Fig. 2, 3*a*) used "hybrid" cells consisting of conductors with electron (I class, according to Volta, metals) and ion conductivity (II class, water based liquid electrolytes), the constituent elements of the latter and at the same time sensors ("animal electrometers", according to Volta [1, page 207]), being parts of prepared frogs that had increased sensitivity of nerve-endings in their premortal period [1].

A series of G&V experiments are related to thermoelectricity (TE) [3 – 5]. In 1794 Volta carried out his well-known experiment with inhomogeneously heated iron wire, when he observed electric excitation of the frog's muscles with several consecutive immersions of the wire into water (up to 4 times). The above experiment, according to [3 – 5], indicates the priority of Volta in discovery of TE.

The purpose of this paper was formal analysis and classification of G&V effects on the basis of modern theory of heuristics [2]. To clear out separate details of Volta experiment with the iron wire, the latter was reproduced in the paper anew.
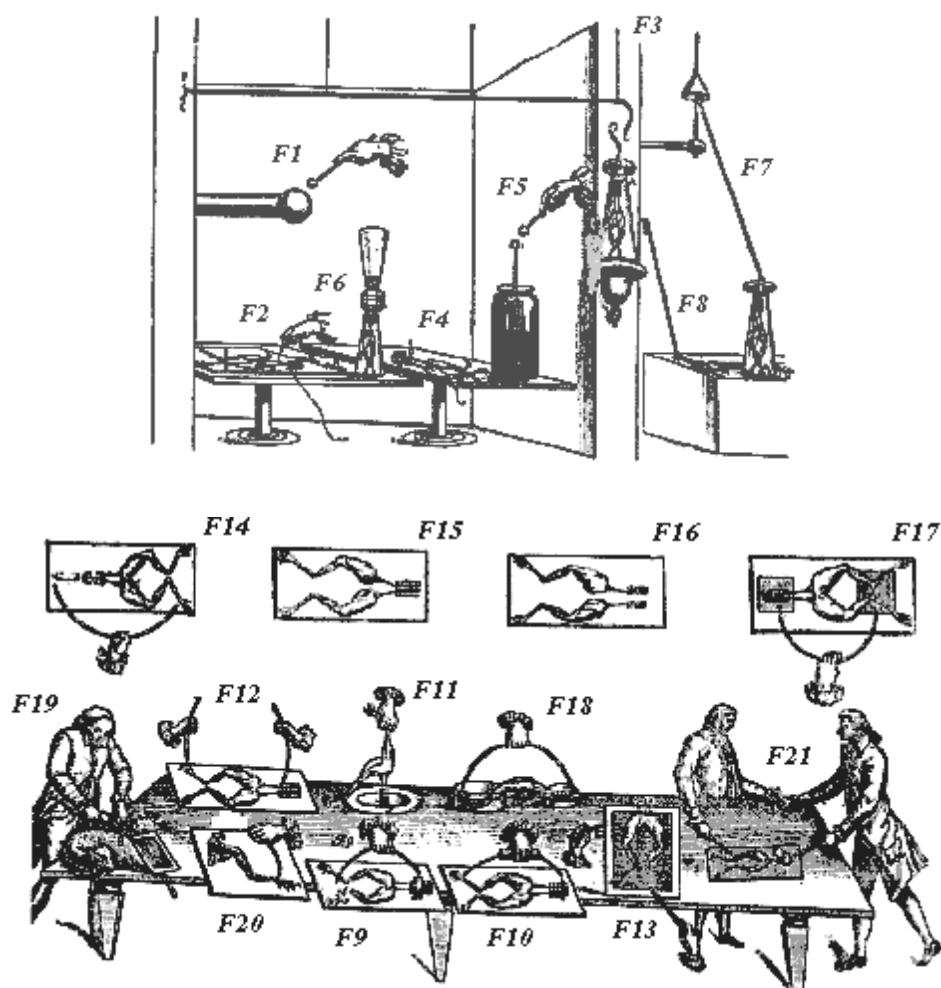
*Fig. 2. Galvani experiments (1791) on the observation of "animal" electricity [1].*

## Formal analysis of G&V effects

In the present paper, G&V effects related to thermoelectricity [1] were written in a special form permitting their subsequent analysis and mathematical treatment (Table 1) [2].

*Table 1*

*Examples of designations of objects and parameters elaborated for solving heuristic tasks in [2]*

| Name | Designation | Name | Designation | Name | Designation |
|---|---|---|---|---|---|
| Dielectric | $D$ | Metal | $X6$ | Temperature | $T$ |
| Liquid | $Y$ | Semiconductor | $Z1$ | Current | $J$ |
| Solid | $X$ | Electrolyte | $Y3$ | Voltage | $K$ |

According to [2], galvanic effect (GE) consisting in the appearance of voltage ($K$) at the contact $\oplus$) between two different metal conductors ($X6$ and $X6'$) and electrolyte ($Y3$) (Galvani experiments - $F9$-$F12$, Fig.2), is expressed by the relationship

$$X6 \oplus Y3 \oplus X6' \to K \ (X6 \neq X6'),  \qquad (1)$$

in so doing, in case of using identical metals ($X6 = X6'$) GE is absent:

$$X6 \oplus Y3 \oplus X6 \rightarrow 0 \ (K, J = 0). \tag{2}$$

Volta repeated Galvani experiments (1–2) and discovered (1784) piezo- and thermoelectric effects in GE – appearance of voltage in cell (2) in the case when electrodes identical in chemical composition are physically inhomogeneous. "Cold-worked" or inhomogeneously heated ($1T$) on one end iron wire ($X6 \neq X6'$) was used, the last experiment (Fig. 3*a*) is described by the relationship

$$(X6 \oplus 1TX6) \oplus Y3 \oplus X6 \rightarrow K, \tag{3}$$

obtained from (2) via substitution $X6 \leftrightarrow (X6 \oplus 1TX6)$.

From relationship (3) it can be seen that Volta effect with iron wire is complicated and can be represented as a superposition of 2 effects:

1) galvanothermal effect (GTE) related to appearance of EMF of galvanic element ($K'$) due to temperature dependence of electrode potentials:

$$1TX6 \oplus Y3 \oplus X6 \rightarrow K'; \tag{4}$$

2) "bulk" Seebeck effect (SE) in the iron wire:

$$1TX6 \oplus X6 \rightarrow K'', \tag{5}$$

so that the resulting voltage in the cell $K = K' + K''$.

Volta experiment (3) had been reproduced earlier in [6], where for imitation of frog's body use was made of a metal conductor (experiment schematic $1TX6 \oplus Y3 \oplus X6 \oplus Y3 \oplus X6 \rightarrow K$). To determine the relative contribution of components (4) and (5) to effect (3), we have reproduced Volta experiment anew.
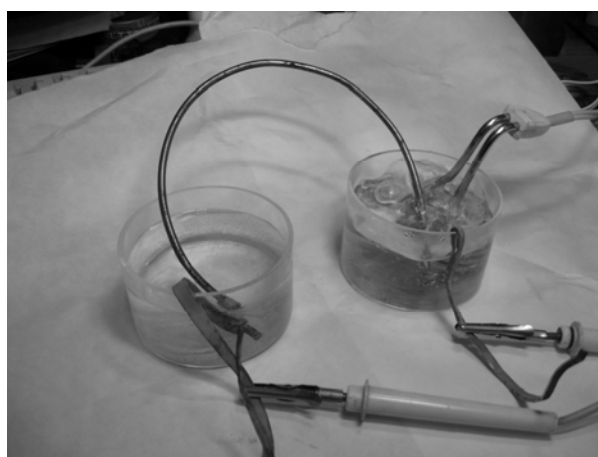
## Reproduction of Volta experiment

As long as the frog's tissues are an organic composite permeated with water-based electrolyte, and transfer of pulses along the nerve endings is related to transport of ions ($K^+$, $Na^+$, $Ca^{++}$) with a change in membrane potential of axons [7], for the imitation of the frog's body a purely ionic conductor was selected (foam sponge wetted with water) (Fig. 3*a*). Raw tap water was used, the necessary thickness of iron wire ($\varnothing = 4$ mm) was determined from the analysis of proportions of objects shown in the original pictures (Fig. 2). The EMF was measured versus "hot" electrodes by the digital voltmeter with voltage sensitivity $10^{-7}$ V and input resistance $R_{in} > 100$ MΩ.



*a*                                                                   *b*

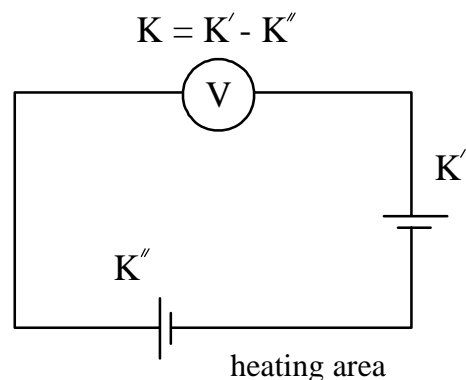c                                                                 d

*Fig. 3. Schematics of the present paper on the reproduction of Volta experiment with the iron wire:*
*a – original experiment according to schematic (3); b – EMF measurement of galvanic cell*
*Fe(T = 296 K)/H₂O/Fe (T = 373 K); c – thermoEMF measurement of inhomogeneously heated*
*iron wire versus lead at temperature difference 296 – 373 K according to schematic (5);*
*d – equivalent schematic of voltages involved in Volta effect.*

According to Volta schematic (3) in a dynamic mode the voltage K was determined (3), occurring with consecutive contacts between vessel water and iron wire, preheated from the end in boiling water (for 30 s) (Fig. 3*a*). The times of wire contact with water and the intervals between consecutive contacts were 5 s. According to schematic (Fig. 3*b*) the same voltage *K* was measured in static mode in the cell (*Fe* (*T* = 296 K) /water/*Fe* (*T* = 373 K)), according to schematic (Fig. 3*c*) – the Seebeck thermoEMF *K″* of inhomogeneously heated iron wire versus lead in temperature difference 296 – 373 K. The time of isothermal exposure of thermocouples in experiments *b* and *c* (Fig. 3) made 1 hour. The results obtained are given in Table 2.

*Table 2*

*EMF K and K″ measured according to schematics (Fig. 3, a–c), in reproduction of Volta effect (3)*

| Experiment | Effect under study | Measured EMF, mV |
|---|---|---|
| *a* | Volta with the iron wire [1] – consecutive contacts of heated wire with water (Dynamic variant) | $K =$ 74/53/46/37/ 34/27/22 |
| *b* | Volta with the iron wire [1] – in the cell: $Fe(T = 296$ K$)/H_2O/Fe$ ($T = 373$ K) (Static variant) | $K' =$ 114 ($\alpha_{GTE} = 1.5$ mV/K) |
| *c* | Distributed Seebeck effect in the thermocouple $Fe(T = 296$ K$)/H_2O/Fe$ ($T = 373$ K) (versus *Pb*) | $K'' =$ 0.944 ($\alpha_{Fe} = 12.9$ μV/ K) |

From Table 2 it follows that voltages *K′* and *K″* are included into equivalent electric circuit of the effect oppositely: K= *K′* – *K″* (Fig. 3*d*), and in the absolute value $|K'| \gg |K''|$. Accordingly, $K \cong K'$, that is, Volta in his experiment predominantly observed galvanothermoelectric effect in the cell metal *Fe/H₂O/Fe*, whose nature is different from that of "contact" Seebeck effect (1821) [6], observed on heating of *Bi/Sb* junctions:

$$1T(X6 \oplus. X6') \rightarrow K. \tag{6}$$

The signs of resulting voltages $K'$ and $K''$ (Table 2) correspond to movement from the hot to cold cell zone of electron "holes" in $Fe$ and $Fe^{2+}$ ions through phase boundary $Fe/H_2O$ (electrode reaction $Fe \rightarrow Fe^{2+} + 2e$) (Fig. 3). From the resulting value of $K''$ the value of absolute differential thermoEMF of iron $\alpha_{Fe}$ (Table 2) was estimated that coincided with the tabulated one [9]. GTE was also experimentally investigated by I. Ritter (1798) and I. Shweiger (1810) [4, 5, 8], theoretical explanation of the effect based on chemical thermodynamics was offered by V. Nernst who obtained expression for electrode potentials of GE in the form

$$E = E_0 + RT \ln C/zF, \tag{7}$$

where $E_0 = E(C = 1)$ – normal electrode potential, $R$ – universal gas constant, $T$ – absolute temperature, $C$ – concentration of metal ions in electrolyte being in equilibrium with electrode, $z$ – valence of metal ions in electrolyte, $F$ – Faraday's constant [10]. According to (7), the values of $K$, obtained for GTE (Table 2), are attributable to temperature difference of electrodes and the associated increase in the equilibrium concentration of $Fe^{2+}$ ions in the heated electrode (by a factor of ~20).

From Table 2 (*a*) we have also estimated the threshold level of electric excitation of the frog muscles contraction – $E_0 \sim 35$ mV, and from the description of experiments (1) with $Fe$ and $Cu$ [1] – the threshold of sensitivity of electrometers used by Volta – $E_0 \sim 0.16$ V/indicator's angular degree. Hence it follows that Volta in his experiments basically could not discover the Seebeck thermoEMF in metals ($E \sim 1$ mV) because of low sensitivity of measuring instruments at that time. On the other hand, relatively large values of $\alpha_{GTE} = 1.5$ mV/K (Table 2) show that relative "casual" contractions of frogs muscles observed by G&V in their experiments could be caused by thermal stimulation (heated hand (experiment F11, Fig. 2), inhomogeneous water evaporation) and for sure – with the use of boiling water [1].

## Heuristic analysis

By substituting the media and impacts and compiling combinations of expressions (1–5) according to procedure [2], one can obtain formulae for a large number of new effects related to G&V effects, part of which had been discovered and studied earlier. As an example, we cite Galvani experiment on the observation of GE without participation of metal electrodes, the role of which in the electrochemical cell was performed by different parts ($Y3$, $Y3'$, $Y3''$) of prepared frog:

$$Y3' \oplus Y3 \oplus Y3'' \rightarrow K' \ (Y3 \neq Y3' \neq Y3'') \tag{8}$$
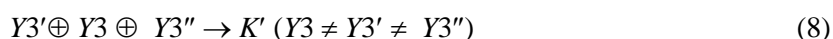
(substitution of $X6 \leftrightarrow Y3'$ and $X6' \leftrightarrow Y3''$ in expression (1)).

It is interesting that discovery of effect (1) predetermined the prospects for development of many lines in electrophysics and electrochemistry, whereas discovery of effect (8) has been of no less importance for the development of biophysics [1].

As examples of clones of G&V effects related to thermoelectricity we also cite a number of effects that we discovered earlier in the investigation of thermoelectric materials – solid electrolytes possessing mixed electron-ion conductivity ($Cu_{2-x}Se$, $Ge_{1-x}Te<Cu>$, $Bi_2Te_3<Cu>$ etc.) the formulae of which result from substituting $X6' \leftrightarrow (SY3)'$ and/or $X6' \leftrightarrow (SY3)'$ in expressions (1–5) and compiling the respective combinations of effects [11–15].

## Summary

By the end of XVIII century there had been known five different sources of electricity: 1) tribophysical – amber rubbing (Egyptian and Babylon priests, Thales of Miletus, about 525 B.C., electrofore machine of O. Gerike (1680); 2) electrical fish (cramp-fishes, eels, cat-fishes) (Redi et al, 1666); 3) atmosphere (B. Franklin, 1753); 4) pyroelectrics (tourmaline) (F. Aepinus, 1756, effect schematic: $1TD \rightarrow K$); 5) electrets in solidification of molten substances with polar molecules

(elektricitas spontanea) (K.I. Wilke, 1758). G&V (1790) supplemented the existing sources of electricity by chemical sources of current (GE), T. Seebeck (1821) – discovered thermoelectric current sources [8, 10].

The term "thermoelectricity" (from Greek thermos – hot and electron – amber) means generation of electricity due to heat [10] and in this most general determination is applicable to all sources of electricity exposed to thermal action. The processes of triboelectrification, as well as polarization of electrets and pyroelectrics (from Greek pyr – fire) are directly related to thermal actions. The term TE was first applied by Ch. Oersted (1823) to the Seebeck effect and was rooted in physics as a single-purpose physical term related to solids – I class conductors (metals and semimetals) (effects of T. Seebeck (1821), J. Peltier (1834), W. Thomson (1856), Benedicks (1916) [8, 10]. In the course of time, physical concept of thermoelectricity has extended and today includes "a group of physical effects caused by the existence of relation between thermal and electrical processes in electric current conductors" (including semiconductors, gases (plasma), solid electrolytes, etc.) [16]. The above "physical" definition traditionally does not refer to thermoelectricity chemical processes occurring with a change in composition (including those in galvanic cells), as well as purely physical processes ("bias" currents) occurring in polar dielectrics (electret, pyroelectric and electrocaloric effects) which in general corresponds to the frame of interests of present-day thermoelectric field.

On the other hand, in electrochemistry the term "thermoelectricity" according to the same historical tradition has broader interpretation and includes processes occurring in I and II class conductors at their interface boundaries [10, p. 213]. To this group of effects, according to data of this paper, also belongs GTE effect observed by Volta during his experiment with the iron wire. Note that in going to solid electrolytes, in particular "superionic" conductors with mixed electron and ionic conductivity, as well as to plasma, "physical" and "chemical" interpretations of TE exhibit a tendency to drawing together [17].

Due to the above ambiguity of terms, present-day specialists in history of physics in their attempts to determine the researcher – pioneer of thermoelectricity encounter difficulties. As the trail-blazers of thermoelectricity "prior to T. Seebeck", apart from the above-mentioned Volta, Ritter, Shweiger, Aepinus, the names of Ch. Oersted (1822), J. Fourier (1822) et al. [8] are referred to. Having analyzed the effects observed by the above authors, we have concluded that the process of discovery of thermoelectricity as phenomenon in its modern "physical" understanding can be represented by the schematic

$$Aepinus,\ G\&V \rightarrow Seebeck \rightarrow Peltier,\ Thomson, \tag{9}$$

where Aepinus, Galvani and Volta are the "forerunners" of discovery, and Peltier and Thomson - scientific "successors" of Seebeck who obtained decisive results for the formation of the respective division of physical science.

## Conclusions

1. Thermoelectric effect observed by Volta in his experiments with the iron wire is of a complicated nature and is classified in the paper as predominantly galvanothermal effect (GTE) related to temperature dependence of electrode potentials of the cell $Fe/H_2O/Fe$.

2. Heuristic analysis of formulae of G&V effects that included substitution of media and actions, as well as compiling of effects combinations according to procedure [2], indicates the possibility of existence of new phenomena related to G&V effects that are partially represented in this paper.

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