Paper: ASAT-16-094-TH

16th International Conference on
AEROSPACE SCIENCES & AVIATION TECHNOLOGY,
ASAT - 16 – May 26 - 28, 2015, E-Mail: asat@mtc.edu.eg
Military Technical College, Kobry Elkobbah, Cairo, Egypt
Tel : +(202) 24025292 – 24036138, Fax: +(202) 22621908

An Entropy Approach to Modified Natures of Thermoelectric, Photoelectric and Photovoltaic Effects

Salama Abdelhady*

Abstract
The thermoelectric effect is defined in literature as conversion of flow of thermal energy into flow of electrical energy due to replacing the thermal potential of the flowing thermal energy by an electric potential or vice-versa. Following an entropy approach, it was possible to prove a common nature of the flow of thermal and electric energies as flow electromagnetic waves. According to this entropy approach it is possible to modify the previous definition of the nature of thermoelectric effects. Following the same entropy approach and reviewing experimental results, it is found also in this study modified definitions of the photoelectric and photovoltaic effects.

Keywords: Entropy, Heat Energy, Electric Energy, Thermoelectric, Photoelectric and Photovoltaic effects.

1. Introduction:

According to the similarity of laws that govern the flow of heat and electric current and reviewing their common nature as a flow of energy and entropy; it was possible in a previous studies to prove that the nature of electric current resembles a flow of electromagnetic waves that have an electric potential similar to the flow of thermal energy which is defined as electromagnetic waves that have a thermal potential [1]. As the heat flow is expressed in terms of thermal potential times and entropy flow, the flow of electric charge is expressed also in terms of electric potential time a flow of entropy. Such entropy approach was expressed into an introduced fundamental equation of thermodynamics stated as follows [1]:

$$dU + p\,dV = T\,dS_t + E\,dS_e + H\,dS_m + \sum \mu_i\,dn_i \qquad (1)$$

In Equation (1), dU represents the change of internal energy of a considered control mass and p dV represents the added mechanical energy in terms of the pressure p and the change of volume “dV”. The first term in the left side of Equation (1) expresses the heat in terms of temperature T times a corresponding change in thermal entropy dS_t of the considered control mass. The next term expresses, by analogy, the electric energy in terms of the electric potential E, times a change of electric entropy dS_e. Similarly, the magnetic flux is expressed in terms of the magnetic potential, H times the change of corresponding entropy dS_m [1]. The last term in the equation expresses the chemical energy in terms of are the chemical potential μ_i and the number of molecules n_i of the i^{th} chemical specie.

* Professor of Energy Systems, Head of Department of Power Engineering, Faculty of Energy Engineering, Aswan University, Salama_Abdelhady@hotmail.com

However, The flow of energy as electromagnetic waves is expressed in literature by the Maxwell's equations in terms of the electric field E and the magnetic field H of such waves and the time t as follows [2]:

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{t^2})\,E = 0 \tag{2}$$

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{t^2})\,H = 0 \tag{3}$$

Where c is the speed of light in the medium, in vacuum $c = c_0$ = 299,792,458 meters per second. According to Eddington, the arrow of time indicates the direction of progressive increase of random elements. Following a lengthy argument into the nature of entropy in thermodynamics, Eddington concluded that in so far as physics is concerned, time's arrow is a property of entropy alone as the entropy is an energy property that defines the measure of randomness in time [3]. Replacing the time in the previous Maxwell's equations by entropy, it was possible to express the Maxwell's equations into an energy frame of reference formed of the electric potential E and the magnetic field H as parameters that express the potentials of electric and magnetic energies and the flowing entropy S associated by the flow such energies as follows of [1]:

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{s^2})\,E = 0 \tag{4}$$

$$(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{s^2})\,H = 0 \tag{5}$$

Such modified Maxwell's equations, as formulated by equations (4) and (5), are represented graphically in the introduced coordinates system, E-H-S, as seen in FIG. 1:

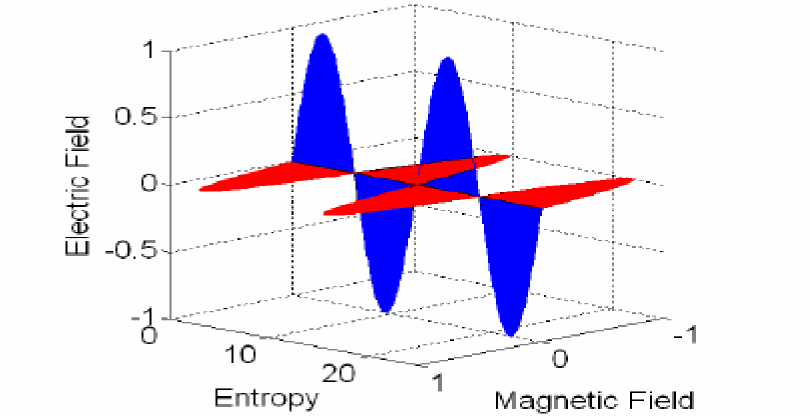

Fig. 1: Flow of electromagnetic waves in an energy frame of reference that shows the electric energy flow in an Electric field- Entropy plane and the magnetic energy flow into a Magnetic field – Entropy plane [1].

The time in the figure is replaced by entropy as replaced in Maxwell's equations. Such replacement transfers the space frame in Maxwell's wave equations and graphical representation into an energy frame of reference. According to Eq. (1), the electric and magnetic energies imparted during the electromagnetic wave propagation can be expressed in terms of the electric or magnetic potentials times the corresponding changes of entropy. According to thermodynamic literatures, the heat energy is expressed by the following integral in the T-s plane [4]:

$$Q_{th} = \int T \; dS_{th} \tag{6}$$

Accordingly, the following equations represents the imparted electric and magnetic energies in the flowing electromagnetic waves as the areas swept by the electric and magnetic waves in the E-s and H-s planes in Fig. 1:

$$Q_{el} = \int E \; dS_e \tag{7a}$$

$$Q_{mag} = \int H \; dS_m \tag{7b}$$

According to such mathematical and graphical representation of flowing energy, light or thermal, the defined electric energy as flow of electromagnetic waves that have electric potential can be represented graphically as seen in Fig. 2. The defined electric energy is seen as electromagnetic waves whose part in the electric plane oscillates around a negative, or positive, electric potential [1]. In this case, the net electric energy imparted per wave will be energy of net positive charge which can be estimated as follows:

$$Q_{el} = \int_0^{2\pi} E \; dS_e \tag{8}$$

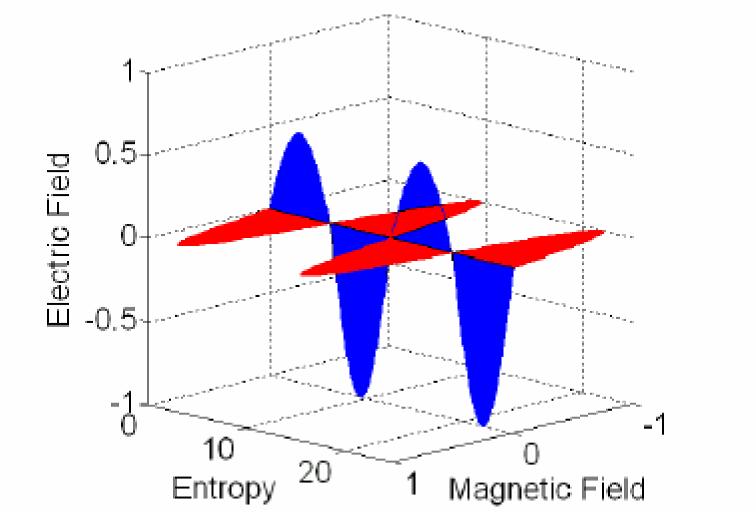

Fig. 2: Flow of electric charges as E.M. waves of non-zero electric potential [1].

Such definition of electric energy will be used into the following sections to introduce modified definitions of the natures of the thermoelectric, photoelectric, and photovoltaic effects by following the previously introduced entropy approach and reviewing found experimental results.

2. The Thermoelectric Effect

Defining the nature of electric current as electromagnetic waves that have an electric potential explains Felming experiments that measured the flow of electric current through conductor by the velocity of light [5]. Similarly, Tesla's discovery of wireless power transmission of electric energy proves the introduced definition of flow of electric charge by velocity of light [6]. However, the classical definition of electric energy, according to traditional literatures, as flow of electrons limits the velocity of electric currents by the drift velocity of such electrons which does not exceed few millimeters per minute in good conductors. In addition, such classical definition leads to the impossibility of flow of electrons in air [7]. According to the postulated definition of electric current, an analysis of the thermoelectric effect will be performed to improve the definition of its nature. Seebeck effect, as a thermoelectric effect, is defined in literature as the production of an electromotive force, or potential difference, and consequently an electric current in a loop of materials consisting of at least two dissimilar conductors when its two junctions are maintained at different temperatures [8]. When the junctions of such loop have a temperature difference "ΔT", the generated electric potential difference "V_L" is found according to the following equation or law [8]:

$$V_L = \propto_{\text{junction}} \Delta T \quad (9)$$

In Equation (9); the term "$\propto_{\text{junction}}$" is defined as the Seebeck coefficient of the junction [8]. According to this relation, Seebeck coefficient represents the increase of the electrical potential in the loop per unit rise in the temperature difference between its two junctions; such coefficient is found in the range of 40 – 60 μV/K for metal thermocouples and in the range of 100 – 200 μV/K for semiconductor thermocouples [8]. Thermocouples and advanced thermoelectric generators depend on the Seebeck effect for temperature measurements or for generating electric power [9]. Introducing the modified definition of electric current, it is possible to modify also the classical definition of the nature of Seebeck effect as phenomena that convert the flow of electromagnetic waves of a thermal potential, or heat, into flow electromagnetic waves of an electric potential, i.e. electric current. The converted electrical potential of the output electric current is proportional to the thermal potential of incident's thermal potential.

3. The Photoelectric Effect:

The modified definitions of the electric current and of the Seebeck effect will be introduced in this section to review classical definitions of the photoelectric effect. Such approach depends firstly on investigating the measurement results of photocells that were elaborated to find the Planck's constant experimentally [10]. When light of a known frequency is shone upon a potassium cathode in the evacuated tube in Fig. 3, it was emitted or reflected from the metal plate as flow of electric charges [11]. According to the elaborated experiments; flow of the reflected waves was stopped by imposing a stopping potential on the anode. The measured stopping potential was found to increase by the increase of the temperature of the source of the incident radiation and to be independent on the metal of the reflecting plate [12]. Such results mean that the reflected waves should have an equal electric potential that is balanced by the anode's potential and it is not just a flow of electrons of no potential from the metal plate. Hence, definition of the electric current as flow of electromagnetic that has resistible electric potential helps in finding a plausible explanation of the results of this experiment. The results of these measurements were found as a linear relation between the wavelength of the incident radiation, or the temperature of the source of incident radiation according to Wien's law of radiation, and the negative potential of a cathode plate that is able to stop the emitted electric current in the photocell's circuit shown in Fig. 4 [13]. The slope of the correlated linear relation between the measured stopping potential and the temperature of the source of the incident radiation is found according to Fig. 4 as 160 μV/K. Comparing such measured slope and the Seebeck coefficient of metals and semiconductors, both are found in the same order of magnitudes and relate the potential of the electric potential of the output current to the thermal potential of the incident radiation [14, 15]. According to such results, it is possible to conclude a similarity option between the photoelectric effect and the Seebeck effect. Accordingly, it is possible to modify the definition of the nature of the photoelectric effect as conversion of the incident thermal radiation on the photocells into reflected electric current by Seebeck effect where the electric potential of the emitted current or electromagnetic waves is proportional to the thermal potential of the incident radiation.

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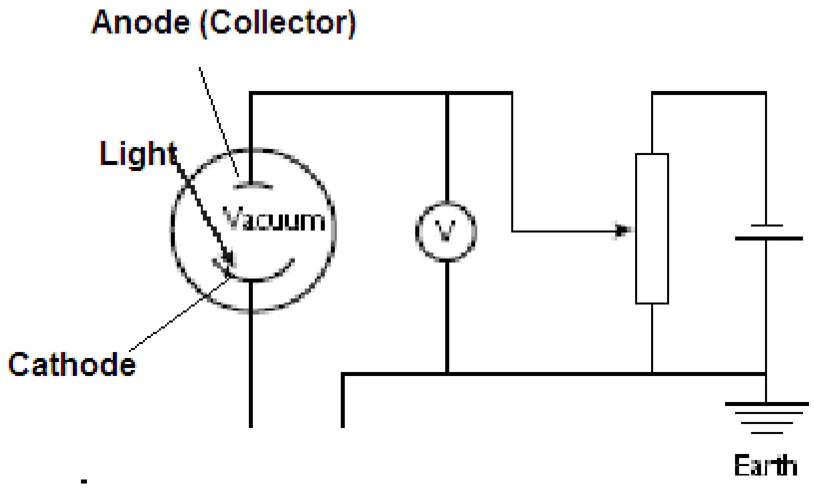

Fig. 3: The photocell experiment is designed to measure the stopping potential on the anode (collector) that stops the flow of electric current from the cathode by applying a negative potential on the anode. The incident light is reflected on a Silicon cathode plate with an electric potential that is proportional to the difference between temperature of the source of radiation and the cathode plate..

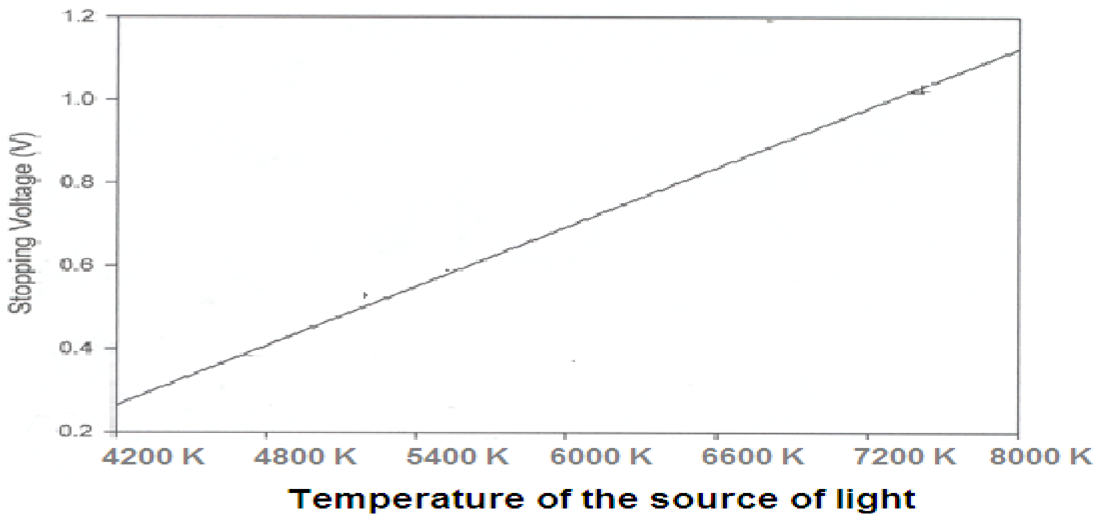

Fig. 4: Dependence of the stopping voltage in a photoelectric cell on the temperature of the source of light. The found slope for Sodium plate, as found in the current measurement, is identical to the measured slope for potassium plate as measured by other authors. However, the wavelength in the abscissa is replaced by the temperature of the source of radiation according to Wien's law of radiation [15].

4. The Photovoltaic Effect

According to literature, the photoelectric effect and the photovoltaic effect are related to the emission of electrons by bouncing photons [16]. Hence, in this section we are going to follow a similar procedure to review the photovoltaic effect as that followed in reviewing the photoelectric effect in the previous section. Reviewing the measured performance of a single crystal silicon solar photovoltaic cell, as seen in Figure 5, the potential of the output current is found to depend mainly on the frequency or the thermal potential of the incident radiation while it is independent on the intensity of solar radiation [17]. The measured open circuit voltage "V_{oc}" of the cell is found in the range 0.6 – 0.7 Volts while the temperature difference between the source of radiation, or the temperature of the sun, and the junction's temperature "$T_{SOURCE} - T_{JUNCTION}$" is about 5800 K. According to such measurement data, the potential rise per unit thermal potential of the incident radiation is in the range 120 – 150 μV/ K. Comparing such values that relate the temperature of the source of radiation to the electrical potential of the output current in photovoltaic cells to the values that relate the same parameters in thermocouples, or Seebeck coefficients of semiconductors as Silicon, both are found in the same order of magnitude. So, there is a similarity option between the thermocouples that is driven by the Seebeck effect and the photovoltaic effect that is influenced mainly by the temperature of the source of radiation or the wavelength of such incident radiation. Accordingly, it is possible to modify also the definition of the nature of the photovoltaic effect as conversion of the incident thermal radiation on the photovoltaic cell into electric current by Seebeck effect that replaces the thermal potential of the incident radiation by a proportional electrical potential. Such conclusion gives a plausible explanation also of the thermal photoelectric phenomena in semiconductors as influenced by flow of heat [17]

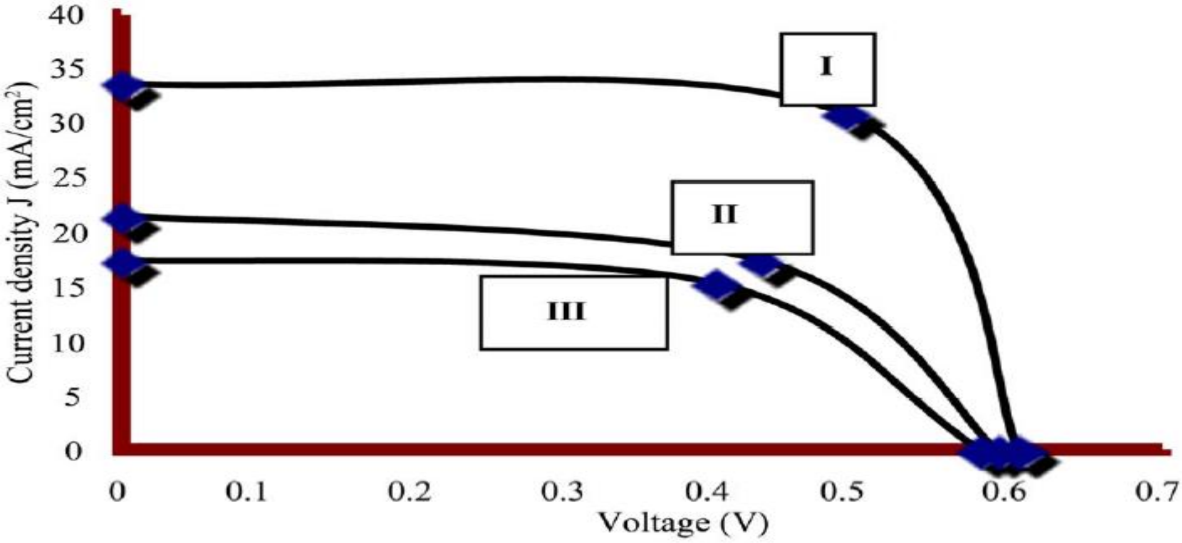

Fig. 5: Typical I-V Characteritics of an illuminated single crystal silicon solar cell at different values of solar radiation 100 mW/cm^2, 60 mW/cm^2 and 40 mW/cm^2 respectively. The open voltage potential is affected only by the temperature of the source of radiation, the sun, while the intensity of solar adiation influences the current density.

The similarity between natures of the photovoltaic effect and the Seebeck effect is already applied in using the same multijunction technique for magnifying the electrical potential difference in multijunction solar cells and in thermopiles or multijunction thermocouples [18]. Such multi-junction solar cells are considered as homo-junctions cells connected in series, so, their open circuit voltage is found as the sum of the voltages of the sub-cells or thermocouples, while their short circuit current is that of the sub-cell with the smallest current [19]. However, the state-of-the-art device of a multijunction solar cell is a lattice-matched triple-junction solar cell consisting from GaInP, GaInAs and Ge stacked on top of each other as seen in Fig. 6 [20]. The measured open circuit potential "V_{oc}" for the inserted subcells, when each is operated separately, is found in literature as seen in Fig. 6: 1.22 V for the GaInP subcell, 1.04 V for the GaInAs subcell and 0.25 V for the Ge subcell and the measured total open circuit potential of the whole cell is found 2.5 Volt [21]. Such multijunction solar cell has reached a measured conversion efficiencies of 41.6% at concentrations of 364 suns [22]. The detailed balance model calculations that depended on the classical definitions of electric current and photovoltaic effect which was derived by Shockley and Queisser, failed to predict such high efficiency [23]. In their analysis, Shockley and Queisser assumed the collisions of corpuscles or quanta of energy of quantity “$h\nu$ ” with electrons. However, the momentum of such quanta is proved to be too small to collide with electrons or cause the electrons to leave their orbits in the atom [24]. Similarly, the quantity “$h\nu$ ” represent a rate of flow of energy and it not a corpuscle of energy that behaves as a particle as previously discussed.

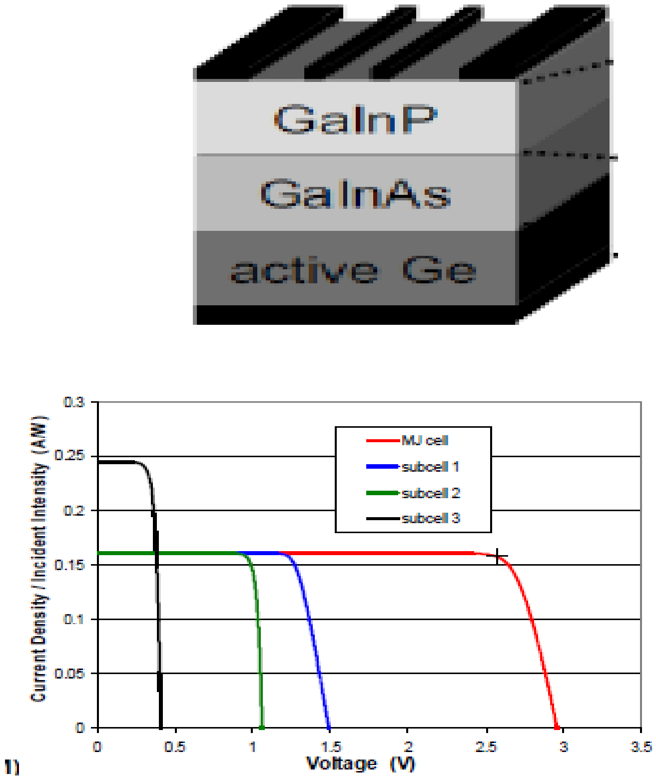

Fig. 6: Simple cross-sectional diagram and modeled IV characteristics of a typical triple junction solar cell GaInP/GaInAs/ Ge stacked on top of each other. The IV characteristics of each subcell and the whole multijunction solar cell, in red color, are seen under 1x concentration [25]

According to recognizing the nature of multijunction photovoltaic cell as a thermopile, it is possible to find the electromotive force or potential “ ” in such combined cell as the sum of the Seebeck coefficients of the corresponding junction times the thermal potential of the incident radiation relative to the temperature of the cell’s junctions; i.e. “$T_{SOURCE} - T_{JUNCTION}$,” according to the following equation [25]:

$$E = [\propto_{\mathrm{GaInP}} + \propto_{\mathrm{GaInAs}} + \propto_{\mathrm{Ge}}]\,(T_{SOURCE} - T_{JUNCTION}). \qquad (10)$$

In Equation (10), $\propto_{\mathrm{GaInP}}$, $\propto_{\mathrm{GaInAs}}$, and $\propto_{\mathrm{Ge}}$ are the Seebeck coefficients of the three junctions of the triple-junction solar cell seen in Fig. 6 [25]. The incident radiation on the three junctions of the considered cell belongs to the same source temperature “T_{SOURCE}” and it is assumed the three junctions to have the same temperature “$T_{JUNCTION}$”.
According to the mentioned measured data of the open circuit voltage, “V_{OC}”, for the subcells forming the considered triple junction solar cell, the Seebeck coefficient of these subcells can be calculated according to Equation (2) as follows: $\propto_{\mathrm{GaInP}}$ = 210 μV/ K, $\propto_{\mathrm{GaInAs}}$ = 179 μV/ K, and $\propto_{\mathrm{Ge}}$ = 43 μV/ K. Substituting the values of these Seebeck coefficients and thermal

potentials into Equation (10), we find the total open circuit voltage of the whole cell can be estimated as follows:

$$V_{oc} = (210 + 179 + 43\,)(6100 - 300) = 2{,}5\,Volts \tag{11}$$

Such value is identical to the measured "V_{oc}" of the cell [26]. Such result assures the truth of the postulated natures of the photovoltaic effect as a thermoelectric effect. According to the reversibility of the thermoelectric effect which allows the conversion of the electric energy to thermal energy and vice versa, it is possible to prove the efficiency of photovoltaic cells, working as thermoelectric generators, may approach the efficiency of Carnot cycle efficiency working reversibly between the temperature of the source of radiation and the temperature of the junction [27]. Such result adjusts the broken limit which was previously derived by Shockley and Queisser [23].

Author's contributions: S. A. started the entropy approach to analyze the energy interactions as a Professor of Thermodynamics since 2010. This paper summarizes the results of such approach to modify traditional definitions in the field of the thermodynamics of thermoelectric and photovoltaic systems.

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