

SUBTRACTION OF A NEW THERMO-ELECTROCHEMICAL EFFECT FROM THE EXCESS HEAT, AND THE EMERGING AVENUES TO COLD FUSION

Peter H. Handel

Dept. of Physics and Astronomy, Univ. of Missouri, St. Louis, MO 63121

Abstract

A new thermo-electrochemical effect similar to the thermoelectric effects known from solid state physics is introduced into the analysis of the enthalpy balance in electrochemistry. On this basis a new source of excess heat is defined, estimated and compared with the experiment. Most of the observed excess heat has the same current dependence as this new effect. The earlier irreproducibility of cold fusion excess heat in different laboratories is also interpreted on this basis. An optimistic outlook is presented for cold fusion nevertheless.

I. Introduction

Accelerated by the experimental observation of excess heat in heavy-water electrolytic cells by Pons and Fleischmann¹, cold fusion research has polarized the scientific community more than any other subject. Although the scientists involved in electrolytic cold fusion studies were bona fide investigators of a mind boggling puzzle which defied all attempts of scientific explanation, they were often ridiculed by members of the scientific community, who had no explanation for the excess heat phenomenon either². In spite of the lack of public support, these scientists continued the research of the excess heat phenomena with great personal sacrifices, trying to improve the reproducibility and the magnitude of the observed excess heat, while searching also for nuclear byproducts such as neutrons, tritium, He³, and γ rays. This search remained relatively unsuccessful, with nuclear byproducts observed at rates close to the background, a factor of 10^8 below the level consistent with the observed excess heat. This prompted many well-known scientists to explore the possibility of non-radiative transitions of a pair of deuterons into tritium or He⁴ with no nuclear byproducts, except for protons from the tritium channel³. These theoretical studies did not reveal any processes leading to large enough reaction rates, although a source of possible irreproducibility of the excess heat was found⁴.

The present paper examines the known energy balance of electrolysis, showing that a major heat (more precisely enthalpy) source term has been ignored in all known studies of this subject. In Sec. II we introduce and define the thermo-electrochemical effect which generates the new heat source term. This way, electrolytic cold fusion research is put on a more rigorous scientific basis, allowing for the first time a consistent definition of the excess heat, and eliminating a major source of uncontrollable irreproducibility in the calorimetry of electrolytic cells or molten salt cells. The results are compared with the experimental evidence in Sec. III. The paper also examines the main paths of achieving cold fusion and the prospects of cold fusion research in Sec. IV.

II. Thermo-Electrochemical Effect

The main elements of a calorimetric system including an electrolytic cell are shown on Fig. 1. We consider the system of two electrodes as a thermodynamic engine, operating with a cold source at the external temperature T_0 (the external medium, i.e., the laboratory or the atmosphere) and a hot source at the temperature T (the electrolytic solution). The efficiency of the engine is

$$\eta = \frac{W}{Q} = 1 - \frac{Q_0}{Q}, \quad (1)$$

where Q is the heat taken from the hot source, W the work done by the engine, and Q_0 the heat released to the cold source. The last form of Eq. (1) was obtained by applying the first principle of Thermodynamics in the form $W=Q-Q_0$. Eq. (1) remains valid if the engine is reversed, working as a heat pump with negative values of Q , W and Q_0 , differing in absolute value from the corresponding values when the engine was not reversed, unless all processes are reversible. We shall ignore the negative signs of Q , W and Q_0 in the heat pump case, considering a positive heat Q given by the engine to the electrolyte, a positive heat Q_0 given by the external medium to the electrodes which form our heat engine, and a positive work W done by an external electrical current source on the engine, which yields the same expression of η in Eq. (1). The work W is the total work UJt done by the applied electric current J in the time t , minus the chemically stored energy U_0Jt present in the electrolytic products in the final state

$$W = (U-U_0)Jt, \quad (2)$$

where $U_0 = 1.54V$ is the equilibrium emf.

The heat given to the hot source is

$$Q = (\Pi J + J^2R + J\Delta U)t = (TSJ + J^2R + J\Delta U)t, \quad (3)$$

where $\Pi = \Pi_1 - \Pi_2$ is the relative Peltier coefficient defined as the difference between the Peltier coefficient Π_1 of the anode and the Peltier coefficient Π_2 of the cathode, R is the resistance of the electrolyte, while ΔU is the overpotential, i.e., the additional voltage required to get the current density $j = J/A$ flowing through the area A of the interface between the electrodes and the electrolyte. In the last form of Eq. (3) the Thomson relation $\Pi = TS$ was used^{5,6}, relating Π to the Seebeck coefficient $S = S_1 - S_2$, and to the absolute temperature T . This relation is a well-known consequence of the second principle of thermodynamics. The T - dependence of S is neglected here.

Finally, the heat given to the engine by the cold source is

$$Q_0 = \Pi_0 Jt = T_0 S Jt, \quad (4)$$

where Π_0 is the relative Peltier coefficient of the two electrodes at the ambient temperature T_0 .

Substituting Eqs. (2)-(4) into Eq. (1), we obtain, after simplifying with Jt

$$\eta = W/Q = \frac{(T-T_0)S + JR + \Delta U}{TS + JR + \Delta U} = \frac{U - U_0}{TS + JR + \Delta U} \quad (5)$$

In the reversible limit defined by $j \rightarrow 0$ we assume that $\Delta U \rightarrow 0$ and obtain from Eq. (5)

$$\eta = 1 - T_0/T, \quad (6)$$

in agreement with the second principle of thermodynamics.

In Eq. (6) we assumed the overpotential $\Delta U = U - U_0 - JR - (T - T_0)(S_1 - S_2)$ to vanish in the reversible limit of small current densities j . The connection between ΔU and j is given by the Tafel law in the implicit form given by Erdey-Gruz and Volmer⁸

$$j = A \{ \exp[-\alpha e \Delta U / kT] - \exp[(1-\alpha)e \Delta U / kT] \} \approx -Ae \Delta U / kT, \quad (7)$$

where A is a factor independent of j and ΔU , $0 < \alpha < 1$ is a fraction distributing the overpotential over the two electrodes, and k is Boltzmann's constant. The last approximation, valid only in the limit of very small j and ΔU values, shows that ΔU can be made arbitrarily small by increasing the area of the electrodes and by reducing the total current J , which also reduces the ohmic voltage drop (reversible limit). Thus, ΔU vanishes indeed in the (reversible) low j limit.

The efficiency η allows us to calculate the excess heat fraction

$$\varepsilon \equiv \frac{1}{\eta} - 1 = \frac{Q}{W} - 1 = \frac{Q_0}{W} = \frac{T_0 S}{[\Delta U + (T - T_0)S + JR]} \rightarrow \frac{T_0}{T - T_0}, \quad (8)$$

which is the perceived excess heat of thermo-electrochemical origin, obtained per unit of applied work W . This quantity is a more convenient indicator of the obtained thermo-electrochemical excess heat than η . The arrow indicates the reversible limit in Eq. (8). *It is remarkable that in the reversible limit the excess heat fraction becomes infinite for $T = T_0$. We conclude that in a flow-through calorimetric experiment with T close to T_0 an infinite amount of thermo-electrochemical excess heat can be obtained from each Joule of expended energy.* Some examples of expected excess heat values are presented in Table 1 below. Table 1 also gives the excess heat fraction ε' obtained by considering the chemically stored energy as a part of W , which is in fact incorrect, but which is necessary in the case of closed cells where the gasses produced in the electrolytic process recombine catalytically in the system. Indeed, in this case the recombination heat becomes indistinguishable from the other heat or enthalpy contributions. One obtains in this case

$$\varepsilon' = \frac{T_0 S}{U} = \frac{T_0 S}{[U_0 + \Delta U + (T - T_0)S + JR]} \quad (9)$$

The presence of the large term U_0 in the denominator of this expression causes it to be very small in a misleading way, and keeps it from going to infinity in the reversible limit. The excess heat fractions are calculated in Table I for three examples of cells at $j = 100 \text{ mA/cm}^2$.

Table 1

Cell Electrodes	T	T ₀	S ₁	S ₂	S	Π	ΔU+JR	ε%	ε'%
	°K	°K	μV/K	μV/K	μV/K	mV	mV		
I. 1)Pt; 2)Pd	301	299	-5.14	-10.7	5.56	1.67	56	2.96	0.1
II. 1)Fe; 2)Ni	301	299	15	-19.4	34.4	10.3	30	34.3	0.7
III. 1)Pt; 2)Ni	301	299	-5.14	-19.4	13.9	4.28	16	26.7	0.28

Table 1.: Thermo-electrochemical excess heat for Pt/Pd, Fe/Ni and Pt/Ni cells.

The values of the thermopower S in this table have been taken from Landolt-Börnstein⁹ and are for metals of high purity. Impurities usually present in the electrodes can cause S to differ by as much as two orders of magnitude.

III. Comparison with the Experimental Evidence

The excess heat percentages in Table 1 are referred to the total energy input W into the cell from the time when the current has been first applied to the cell. On the other hand, the observed heat release from electrolytic cells is very non-uniform in time and reflects the presence of other terms in the heat balance equation, such as the heat of solvation (which changes sign in hydrogen-absorbing materials at high concentrations of hydrogen or deuterium, the process becoming endothermic), exothermic release of deuterium (often initiated when the temperature is changed), or even partial catalytic oxidation with water formation in open cells. Thermo-electrochemical excess heat can be stored and used to provide for solvation heat at high

deuterium concentrations, remaining entirely unnoticed, while the heat emission connected with a sudden deuterium release, or release during several hours or days, can be mistaken for genuine excess heat, and considered too large to be explained by Eqs. (8) - (9). Therefore, only an energy balance extended over the entire period of operation of the electrolytic cell, with all terms included for the duration of the entire experiment, can be used as a basis for identifying true excess heat.

The main earmark of the thermo-electrochemical excess heat ($\Pi_0 It$) concept introduced in this paper is its proportionality with the total electric charge (It) which has passed through the electrolytic cell, or the proportionality of the excess power produced (ΠI) with the average current I . This characteristic proportionality was present from the beginning¹, as we see in Table 2, and can be expressed with the help of an effective Peltier coefficient Π_{eff} . In Table 2 below we list the current densities j , the measured¹ excess heat percent ϵ , the corresponding cell voltages U implied by the listed current and excess heat values¹, and the effective Peltier coefficient $\Pi_{eff} = T_0 S_{eff} = (U - U_0)\epsilon / 100$ obtained from Eq. (8) above.

Table 2

Current Density	Excess Heat ¹	Cell voltage	Eff. Peltier Coefficient
j	ϵ	U	$\Pi_{eff} = T_0 S_{eff}$
<u>mA/cm²</u>	<u>%</u>	<u>V</u>	<u>mV</u>
8	23	3.22	390
64	19	3.65	390
512	5.5	8.9	400

Table 2.: Measured¹ values of the excess heat percent and cell voltage for various current densities, indicate the presence of a constant effective Π .

The observed values of Π and S are more than 200 times larger than the values calculated in Table 2 assuming constant excess heat power all the time. They are of the order of values measured in semiconductors, rather than in metals. This is primarily because excess heat appears over a shorter period, only intermittently, while the action of the thermo-electrochemical effect is always present. If the excess heat was noticed only for a fraction f of the total time during which the constant current was flowing through the cell, we should compare Π and S with $f\Pi_{eff}$ and fS_{eff} respectively. In Table 2, we may have $f=0.5$ %.

The proportionality of excess power with the constant current applied to the cell is evident in most if not all excess heat measurements to date. A particularly clear example is on page 15 of the last Conference Proceedings¹⁰ in this series, which allows to define $\Pi = 150$ mV/K. More research is needed to separate true fusion heat.

It is important to note that the thermo-electrochemical excess heat introduced

here can be automatically compensated by enclosing the connection of the electrodes with identical (e.g., copper) wires in the calorimeter together with the electrolytic cell itself, as indicated by the dotted adiabatic surface B. We have to consider the use of configuration B as the likely cause of the negative results, and the use of both A and B by different investigators as the likely cause of the well-known irreproducibility of cold fusion results.

The above discussion should not be interpreted as a claim that excess heat from cold nuclear fusion does not exist. The present paper only introduces a new mechanism of excess heat, which was never considered before in electrochemistry and in cold fusion research, and suggests a careful reexamination of all previous measurements and a careful planning of all future experiments on this basis.

IV. The Main Paths to Cold Fusion

The main difficulty in cold fusion is expressed by the extreme smallness of the fusion cross sections at low energies, and even at energies in the KeV range. This causes more losses of energy than can be recovered from the fusion reactions. As long as we are unable to recover this large lost energy, the only way to improve the energy balance is to increase the fusion cross sections.

The fusion cross sections are small because of the large Coulomb barrier. This barrier can be reduced with the help of negatively charged mesons, such as μ -mesons, binding together a pair of hydrogen isotope nuclei. After catalyzing a fusion, the muon continues to catalyze other fusions with large probability. Experiments at the Los Alamos Meson Physics laboratory have demonstrated yields of 150 fusions per muon, with energy liberation close to 3 GeV per muon. There are indications that 300 fusions per muon are possible. The present estimate of the average accelerator beam energy needed to produce a muon is about 5 GeV, although the theoretical limit is below 2 GeV.

Various forms of muon-catalyzed fusion reactors are presently envisioned. Although pure fusion is not energetically solvent today, fusion-fission hybrids combined with a spallation breeder would require only 100 fusions per muon and would yield net energy gain today even if the energy expenditure per muon stays as high as 5 GeV. Modern concepts try to avoid the need to produce intermediate pi-meson and muon beams. Synergetic systems of this kind use the deuterium-tritium mixture both as the target for muon production and as the fuel for the subsequent muon-catalyzed fusion process.

Many-body effects can also be used to enhance the ridiculously low natural fusion rates. As was shown previously, the very large effective masses of electrons in some rare-earth combinations are similar to the mass of the muon, although this similarity neglects the anisotropy and is limited to the less important long wavelength region. Nevertheless, it leads to a large increase of the hydrogen binding energy in metals with increased electronic effective masses⁴. This shows that the large effective masses have a considerable effect in bringing the hydrogen nuclei closer.

We conclude that cold fusion research is not less likely to lead to a solution of our energy problems than magnetically confined hot fusion, or inertial fusion.

V. References

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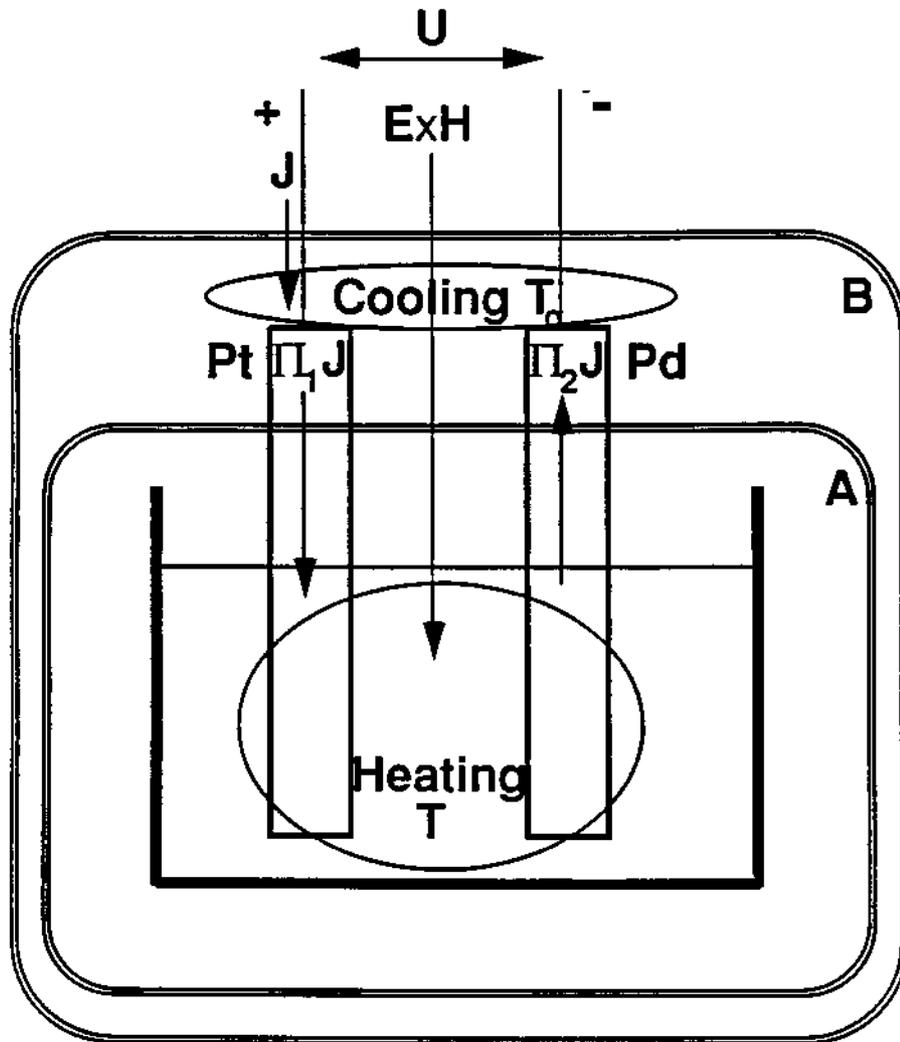


Fig. 1. Thermo-electrochemical effect in a Pt/Pd cell: The work input $UJ = \int \mathbf{E} \times \mathbf{H} da$ and the heat transport ΠJ from the environment into the electrolytic cell. U is the applied voltage, J the current, and $\Pi = \Pi_1 - \Pi_2$ a Peltier coefficient. Excess heat is observed if no enclosure is used, or if enclosure A is used. No excess heat is observed when enclosure B is used, encompassing both the hot and cold source.