Second Law violations in the wake of the Electrocaloric Effect in liquid dielectrics

Andreas Trupp, Fachhochschule der Polizei des Landes Brandenburg
-University of Applied Science-
Private e-mail: atrupp@aol.com

A short version of this article was published in:

AIP Conference Proceedings Vol. 643: Quantum Limits to the Second Law, First International Conference on Quantum Limits to the Second Law, University of San Diego, California, 28-31 July 2002

Abstract: In any textbook on physics, Coulomb's law of the mutual force between two point charges $\mathbf{q_0}$ at a distance $\mathbf{r}$ is modified by the appearance of the term $\mathbf{K}$ if the point charges are embedded in a dielectric:

$$F = \frac{1}{4\pi\epsilon_0} \frac{q_0^2}{K\, r^2} = 4\pi\epsilon_0\, K\, V^2$$

The dimensionless constant $\mathbf{K}$ (≥ 1) denotes the permittivity of the dielectric. According to this formula, the force is either *reduced* by the factor $\mathbf{1/K}$ -if the charges $\mathbf{q_0}$ are kept invariant in amount-, or is *increased* by the factor $\mathbf{K}$ -if the *potential* $\mathbf{V}$ is kept invariant- as a result of the introduction of the dielectric. $\mathbf{V}$ is the potential of the location of *one* point charge as a result of the field generated by the *other* point charge. Feynman argues that the formula is correct only if the dielectric is a liquid, and that it does not work properly with solids. His criticism does not go far enough. Two simple experiments with a liquid dielectric (backed by theoretical reflections) reveal that the formula is correct only if the two point charges have opposite signs (negative and positive). If the signs are equal, the formula reads (when applied to point charges in liquid dielectrics):

$$F = \frac{1}{4\pi\epsilon_0} \frac{q_0^2}{K^2\, r^2} = 4\pi\epsilon_0\, V^2$$

Hence the force is reduced by the factor $\mathbf{1/K^2}$ if the *charges* (of equal sign) are kept invariant, and is left unaffected by the introduction of the dielectric if the *potential* $\mathbf{V}$ is kept invariant. With a so revised formula, cyclic processes can be performed in which the electrocaloric effect (that heats up the dielectric when the electric field is being built, and cools down the dielectric when the field is disappearing) is no longer symmetrical, leading to the conversion of ambient heat to electric work as a net result of the work cycle.

1. Qualitative description of the Second Law violation

It is a well established fact that internal energy in the form of heat, taken from a single reservoir (the ambient) only, can be completely converted to mechanical work without any refuse heat (that would be an unwanted side-product). Such a conversion is, for instance, taking place when an ideal gas, concealed in a cylinder, is expanding isothermally at ambient temperature and is thereby moving a piston. The only heat flow involved is that from the ambient into the gas (to prevent its cooling off), with that heat being totally turned into mechanical work performed by the piston.

Unfortunately, a perpetual motion machine of the second kind (that would convert ambient heat to work without requiring a second heat reservoir of a lower temperture for the reception of refuse heat) can nonetheless not be created thereby. For such a machine to operate, a **cyclic** process would have to be performed. Any means of getting back to the starting point (that of the compressed gas in the cylinder at ambient temperature) would, however, be accompanied by a creation of heat received by the ambient. Moreover, the quantity of heat thus delivered to the ambient would -at least- be as large as the amount of heat that was previously taken from the ambient. With no heat taken from the ambient as a net result of the cycle, no net mechanical work is yielded as a result of the cycle (otherwise the law of conservation of energy would be violated). To put it the other way round: A perpetual motion machine of the second kind would be technically feasible if one could get back to the starting point without delivering heat to the ambient. *The impossibility of a perpetual motion machine of the second kind operating with air as a work medium is hence not rooted in the impossibility of converting ambient heat to mechanical work at a ratio of 1:1, but in the incapability of compressing the gas isothermally without creating heat.*[1]

A similar proposition holds true for electrostatics. Ambient heat can be converted to electric work when the electric field between the plates of a capacitor is disappearing, resulting in an adiabatic cooling of the dielectric material between the plates (electrocaloric effect). After the dielectric has regained its initial temperature (that of the ambient) by means of a heat flow from the ambient, ambient heat has been completely converted to electric work (performed -during the discharge- in the electric circuit the capacitor is part of) as a net result. [2]

As with the gas in the cylinder, a perpetual motion machine of the second could be feasible if one managed to return to the starting-point without creating heat. Simply re-charging the capacitor would, however, not be an appropriate method, as the dielectric is warmed up by the same (now reversed) electrocaloric effect.

In other words: *The task to be solved consists in increasing the potential of a capacitor (that comprises a dielectric) without generating heat in the dielectric as an unwelcome side-effect.*

An attempt worth looking at might be the following: Consider a parallel-plate capacitor filled with vacuum (in order to avoid edge effects, that parallel-plate-capacitor shall be composed of two concentric spheres the diameters of which differ only slightly from each other). The voltage across shall be $\mathbf{V_0}$. The attractive force experienced by each plate shall be called $\mathbf{F_0}$. Let us now replace the vacuum by a dielectric with a relative permittivity $\mathbf{K}$ of well above unity. The voltage across the capacitor shall be kept invariant (at $\mathbf{V_0}$). Will there be a change in the attractive force (now called $\mathbf{F_1}$)? According to any textbook, the force will be increased by the factor $\mathbf{K}$ (permittivity of the

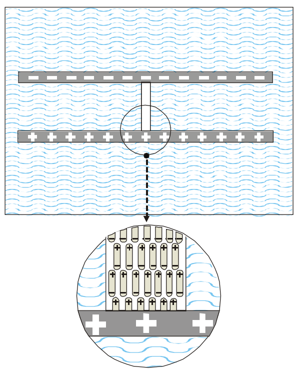
---

[1] See a standard textbook like R.W. Pohl: Mechanik, Akustik und Wärmelehre, 18th edition, Berlin 1983, p. 336 (my own translation):"*The isothermally working air compressor engine is a machine that converts the thermal energy received from the ambient; in an ideal situation the efficiency is 100%.. The conversion occurs while the compressed air is relieved from its pressure. Now we add as a new remark: The relief from pressure increases the entropy of the air. ... This increase in entropy is a permanent and relevant change that the work medium is subject to when isothermally yielding work.*"

[2] One might tend to raise an objection to that description by arguing that all the electric work is the result of the conversion of *energy stored in the electric field* (between the two plates) rather than the result of the conversion of *heat*. However, at least in case we are using a common model dielectric in which the polarization charges are are substituted by regular charges on the surface (with no charges in the interior), that criticism cannot be convincing: With a given voltage across the capacitor, the field between the plates has the same structure and strength as if the dielectric were vacuum, and does hence contain the same amount of energy. Yet the electric work performed by the discharging capacitor can be many times greater than that of the discharging capacitor filled with vacuum. To account for this excess in electric work, the role of ambient heat is indispensable.

dielectric). As Feynman[3] has pointed out, this holds true only in case the dielectric is a liquid. If it is a solid material, the attractive force is counteracted by a virtual pressure exerted on the plate by the solid dielectric in very much the same way as the weight of our bodies is counteracted by the virtual pressure of the ground against our feet. But even with a liquid dielectric (in which the capacitor is immersed), the result is somewhat puzzling: Though a **K** times greater charge sits on each plate, that (free) charge is partly neutralized by polarization charges appearing on the surface of the liquid (in a common model dielectric there are no other charges than these in the whole dielectric). So, when increasing the mutual distance between the two plates, the same *effective* charge is moved as would be moved in case we had not replaced the vacuum by the liquid dielectric. With the effective charge being equal in amount to that in the vacuum-filled capacitor, one would (intuitively) expect $\mathbf{F_1}$ to be equal to $\mathbf{F_0}$. So, how is the increase in force accounted for?

Fig.1

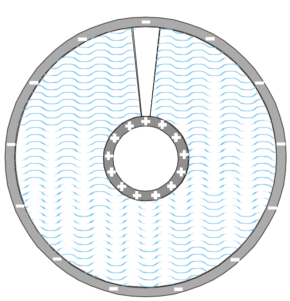


An explanation is revealed in fig. 1. In order to avoid errors by not giving consideration to the effect of the dielectric on itself, a tiny section of both the lower plate of the capacitor and the liquid is cut out and sealed off by vertical walls. The electrostatic force exerted on the free charge that sits on that tiny section of the lower plate is **K** times greater than it would be in case the dielectric were vacuum (at a given voltage $\mathbf{V_0}$). This is due to the fact that the external field (that is the field generated by all charges outside of that section) acting on the depicted free charge is the same as it would be in case the dielectric were vacuum, with the depicted free charge itself, however, being **K** times larger in amount.

This result is not modified by the presence of the dielectric inside the section. The net force exerted on the column of dielectric (enclosed in the cut-out volume) by the external field is zero: As the external field inside that volume is homogeneous, all the dipoles (the dielectric is made up of) experience a torque only, and no translational force. As a consequence, the contribution (made by the column of dielectric) to the total force exerted on the cut-out section of the capitor plate is zero (we neglect the hydrostatic force generated by *gravity*).

Thus, when increasing the potential energy of the charges by doubling the mutual distance between the plates (with the charging wires disconnected), **K** times more mechanical work has to be spent (compared to a capacitor filled with vacuum). Since the *increase* in potential energy (= capacity of yielding electric work when eventually discharging the capacitor) brought about by that widening of space between the plates is also augmented by the factor **K** (compared to a capacitor filled with vacuum) due to a **K** times greater amount of free charge sitting on the plates, the quantity of electric work yielded (during the eventual discharge of the plates) matches the sum of electric and the mechanical work invested. This is why the work cycle does *not* represent a perpetual motion machine of the second kind, and the total account of heat added to and taken away from the dielectric must break even. As the electrocaloric effect of adiabatic *cooling* (during the discharge), due to the doubled volume of the dielectric between the plates, was twice as great in amount as had been the electrocaloric effect of adiabatic *heating* (during the charging of the capacitor), nothing else but the generation of heat during the process of moving the plates away from each other can be responsible for the balanced heat account.

Fig.2



Things turn different if we consider fig. 2, which shows a spherical capacitor consisting of two concentric spheres of extremely unequal diameter. The

[3] Lectures on Physics II, 10-5

outer sphere is grounded. The voltage across that capacitor shall again be $\mathbf{V_0}$. We will start with vacuum as a dielectric. Analogous to the parallel-plate capacitor, a tiny sector of the inner sphere's surface (and of the adjoining liquid dielectric) is cut out and sealed off by radial walls reaching to the outer sphere. The radial and outward (electrostatic) force experienced by the tiny section of the inner sphere shall again be called $\mathbf{F_0}$.

We are interested in finding out whether or not this force will be affected by filling the -previously empty- interior of the spherical capacitor with a liquid dielectric. (The inner sphere shall be kept connected to the battery, so that the voltage $\mathbf{V_0}$ stays invariant.) After the capacitor has been completely filled, the free charge in the tiny sector (on the surface of the inner sphere that is cut out by the radial walls) is **K** times greater in amount than it was prior to the insertion of the liquid dielectric, while the external field is invariant. Does this result in an **K** times greater outward force (which we call $\mathbf{F_1}$) experienced by the tiny part of the surface of the inner sphere (that is cut out by the radial sector walls)? The answer is in the negative. The external field acting on the dielectric (within the sealed-off volume) is inhomogeneous. This is why every dipole is experiencing a radial force toward the center of the spherical capacitor. The individual forces sum up to build an inward pressure against the tiny part of the surface of the inner sphere, thereby counteracting the outward radial force experienced by the free charge. Thus, when reducing the diameter of the inner sphere to ½ (after having disconnected the charging wire), the mechanical work spent on the shrinking process is *less* than **K** times greater than it would be in case the capacitor were filled with vacuum. The *increase* in potential energy (= capacity of yielding electric work when eventually discharging the capacitor) brought about by that reduction of diameter is, however, augmented by the factor **K** (compared to the case in which the capacitor undergoes the same procedure while being filled with *vacuum*). Hence the quantity of electric work yielded in the cycle (consisting of charging the capacitor as a first step, making the inner sphere shrink -with the charging wire disconnected- as a second step, discharging the capacitor as a third step, and making the inner sphere expand to its original size as a fourth step) does no longer match the sum of electric and the mechanical work invested, but is in excess of that sum. This excess has to be at the expense of heat (otherwise the law of conservation of energy would be violated). That is to say: When charging the capacitor and reducing its diameter thereafter, the total amount of heat produced (and transferred to the ambient) must be smaller than the amount of heat converted to electric work during the eventual discharge. The electrocaloric effects are no longer symmetrical, and we are facing a Second Law violation.

This has been verified experimentally. By an arrangement described further below, the outward pressure of the inner sphere of a spherical capacitor (at a given voltage across the capacitor) was found to be the same no matter if the capacitor was filled with a liquid dielectric or with air, provided the diameter of the outer sphere is great enough. Thus it has been proved that physics textbooks are incorrect in asserting that all forces between charged conductors, at a given voltage, are increased by the factor **K** if these conductors are immersed in a liquid dielectric, independent of their arrangement.

It should be noted that for a Second Law violation to be avoided, the radial (inward) force experienced by the liquid dielectric in the sealed-off volume (as an effect of the external field) would have to be *zero* - which, however, would be incompatible with the undisputed fact that every single dipole is subject to a radial, inward force.

2. Quantitive description of the Second Law violation

A. Preliminary considerations: Quantitative description of the Electrocaloric Effect

a) If, for a short period of time, a single dipole is subject to a homogeneous electric field, its kinetic

energy can either be increased or reduced: It is *increased* in case ist random rotary motion (which, in turn, is due to the distribution of the thermal motion among more than three degrees of freedom) is performed in accordance with the torque created by the field. It is *reduced* in case its rotary motion is performed against the torque. The increase or decrease in kinetic energy shall be called $\mathbf{dW_{dipol}}$. The term $\mathbf{q_{di}}$ denotes the charge at each end of the dipole. The scalar $\mathbf{p_E}$ denotes that component of the dipole moment $\vec{p}$ (vector) which is parallel or anti-parallel to $\vec{E}$ (vector), with the dipole moment $\vec{p}$ (vector) being defined as the product of $\mathbf{q_{di}}$ and the distance $\vec{r}$ (vector) between the two ends of the dipole (pointing from the negative charge to the positive charge). Each end of the dipole undergoes a displacement, but only that component of the displacement which is parallel or anti-parallel with the field $\vec{E}$ is what matters when the work shall be determined. That displacement is denoted as $\mathbf{1/2\ r_E}$. **F** (taken as a scalar) denotes the force acting on each end of the dipole. It is always parallel or anti-parallel to the field $\vec{E}$. Then we have:
(1)

$$dW_{dipole} = 2\ F\ d(\frac{1}{2}\ r_E\ )$$

$$= \frac{F}{|q_{di}|}\ |q_{di}|\ dr_E = \frac{F}{|q_{di}|}\ dp_E = E\ dp_E$$

The term $\mathbf{dW_{dipole}}$ is defined as positive if the dipole is rotating *with* the field; it is defined as negative if the dipole is rotating *against* the field. The term $\mathbf{dp_E}$ might be different for every single dipole. The field **E** within the sealed-off section in fig. 1 can be separated into an external field $\mathbf{E_{ext}}$, and a local field $\mathbf{E_{local}}$ the sources of which are located within the sealed-off section. The internal work within the dielectric (in the sealed-off section of fig. 1) would then be:
(1a)

$$dW_{intern} = \Sigma dW_{dipole} = E_{ext}\ \Sigma dp_{E_{ext}} + \Sigma E_{local}\ dp_{E_{local}}$$

The last sum (which can be defined as a function of $\mathbf{E_{ext}}$) can be neglected, as it is zero for any value of $\mathbf{E_{ext}}$.

The sum of all dipole moments $\vec{p}$ (vector) within a unit volume is called $\vec{P}$ (vector). That vector is always parallel and proportional to the external electric field.. For $\vec{P}$ we thus have (as an empirical law):
(2)

$$\vec{P} = (K - 1)\epsilon_0\vec{E}$$

The term ϵ_0 denotes the dielectric constant. Thus (1a) can be converted to
(2a)

$$dW_{intern} = \Sigma dW_{dipole} = E_{ext}\ dP_{E_{ext}}$$

which (by making use of Equation 2) turns into:
(3)

$$dW_{intern} = E_{ext}\, dP_{E_{ext}} = \vec{E}_{ext} \cdot d\vec{P}$$

$$= \vec{E}_{ext} \cdot d[(K-1)\epsilon_0 \vec{E}_{ext}] = (K-1)\epsilon_0 E_{ext}\, dE_{ext}$$

giving the internal work per unit volume [4] . Thus the total amount of internal work due to a change in the external field is given by the following integration:
(4)

$$W_{intern} = \int_0^E (K-1)\epsilon_0 E\, dE + \Sigma E_{local}\, dp_{E_{local}} = \frac{(K-1)\epsilon_0}{2} E^2$$

The integral is formed from **E** to 0 (rather than from 0 to **E**) if the field is fading. Then Equation 4 gives the amount of kinetic energy of the dipoles that disappeared as a result of the disappearance of the field.

If **K** is great enough, almost all of the energy provided by the battery (that energy being $\mathbf{1/2\ K\ \epsilon_0 E^2}$) is converted to heat. By the same token, almost all of the electric work done when a capacitor (filled with a dielectric) is discharged is at the expense of heat!

b) A cross-check shall confirm this result. When a capacitor (filled with a dielectric) is being charged, the bound charges within the dielectric undergo slight displacements that sum up to form a real current $\mathbf{I_{pol}\ (t)}$, the reality of which becomes obvious as it makes a magnetic field as does as wire current (thus superposing and increasing the magnetic field brought about by the change in the electric field between the capacitor plates). With that current being a real current, it obeys Ohm‘s law. In order to apply Ohms‘ law, the dielectric is considered to be a resistor. For that resistor, we get:

---

[4] The same result is arrived at by Georg Joos: Theoretical Physics, Dover Publ., New York, 3rd edition, 1986, chapter XIII, par. 2, p.289/290, who also, when describing the energy density **u** in space filled with a dielectric, distinguishes between the change in energy of the vacuum and the change in the energy of a material body (dielectric). Starting from:

$$\mathbf{u = 1/2\ K\ \epsilon_0\ E^2}$$

he proceeds by developing **du/dE**. The result is multiplied by **dE**. He gets

$$\mathbf{du = K\ \epsilon_0\ E\ dE = (\chi+1)\ \epsilon_0\ E\ dE}$$
$$\mathbf{= \epsilon_0\ E\ dE + P\ dE = \epsilon_0 E\ dE + E\ dP}$$

with χ being equal to **K-1**, and with dipole moment density **P** being equal to **E** times $\chi\ \epsilon_0$. The last term **EdP** on the very right side (which matches with the expression of the change in internal energy found in our Equation 3) is labeled as „change in the energy of the material body“, while the first term is labeled as „change in the energy of the vacuum“.

(4a)

$$\frac{dW_{electr}}{dt} = I_{pol}(t)\ V(t)$$

which can be turned into [5]

(4b)

$$dW_{electr} = \frac{dq_{pol}}{dt} V(t)\ dt = dq_{pol}\ V(t)$$

Since the voltage **V** across the capacitor is proportional to the amount of polarization charge $\mathbf{q_{pol}}$ that has passed through the sectional area of the dielectric, **V** can be substituted by the product of $\mathbf{q_{pol}}$ times a constant $\mathbf{C_1}$. Thus (4b) turns into

(4c)

$$W_{electr} = \int_1^2 dW_{electr} = \int_0^{q_{pol}} C_1 q_{pol} dq_{pol} = \frac{1}{2} C_1 q_{pol}^2 = \frac{1}{2} V q_{pol} = \frac{1}{2} Eh\ q_{pol}$$

The term **h** denotes the distance between the two capacitor plates. Multiplying and dividing by the surface area **A** of each plate results in
(4d)

$$W_{electr} = \frac{1}{2} \frac{q_{pol}}{A} E\ hA = \frac{K-1}{2} \frac{q_{eff}}{A} E\ hA = \frac{(K-1)\epsilon_0}{2} E^2\ hA$$

The term $\mathbf{q_{eff}}$ denotes the effective charge (formed by the free charge plus the polarization charge). Dividing the last term of (4d) by the volume **hA** of the dielectric gives the electric work per unit volume just as in (4).

B. Absence of heat generation in a liquid dielectric (while increasing the potential of a conductor) as a consequence of Maxwell's Laws

As pointed out above, a Second-Law-violation would materialize if one managed to increase the potential of a charged conductor (immersed in a liquid dielectric) without generating heat in the dielectric as an unwelcome side-effect.

When making a spherical conductor shrink that is immersed in a "sea" of liquid dielectric, no

[5] In order to apply Ohm's law, it is, in addition, required that no form of energy other than heat is generated by the current. This is, of course, not true for the polarization current, which is building up its own magnetic field. But the energy stored in that field is turned into heat when the polarization current, at the maximum state of polarization, is dying out. This is why the error is being corrected „automaticly".

magnetic field **B** can emerge -simply for reasons of symmetry-, though the electric field is changing and charge is moving. Any magnetic field would define a privileged direction, for which there is no justification in a radial-symmetrical "world". The two mathematical "sources" of a magnetic field (see the right side of Maxwell's fourth equation as displayed below) just cancel.

Considering a surface section **A** (cut out by the closed path **s**) of a thought sphere concentric with the spherical conductor, we have:
(5)

$$\oint_s \vec{B} \cdot d\vec{s} = 0$$

Then, according to Maxwell's fourth law, which is
(6)

$$\nabla \times \vec{B} = \frac{\vec{j}}{\epsilon_0 c^2} + \frac{\delta \vec{E}}{c^2 \, \delta t}$$

(E denotes the electric field or the electric flux per unit area, **j** denotes the current density, that is charge per second and per unit area, **c** denotes the speed of light), we get:
(7)

$$\left|\frac{I}{\epsilon_0}\right| = \left|\frac{\delta\left(\int_A \vec{E}\, d\vec{A}\right)}{\delta t}\right|$$

The term **I** denotes the current through that surface section **A.** Replacing **I** by **dq/dt**, and the surface integral of **E** by **EA**, (7) turns into:
(8)

$$\left|\frac{\delta q}{\epsilon_0}\right| = |A \;\delta E|$$

An integration of (8) leads to
(9)

$$\left|\int_1^2 \frac{dq}{\epsilon_0}\right| = \left|A \int_1^2 dE\right|$$

$$\left|\frac{q}{\epsilon_0}\right| = |A \;\Delta E|$$

The charge **q** denotes the amount of charge that passed through **A** during the increase or decrease of the field.

Several of those thought surface sections **A** shall be „installed“ in the cut-out volume filled with liquid dielectric (as shown in fig. 2) at different distances from the center of the sphere. Let us see why: The (macroscopic) external work yielded by a translational move of all the dipole-ends ($\mathbf{dq_{di\,-}}$ or $\mathbf{dq_{di\,+}}$) inside the sealed-off quantity of the liquid dielectric (when the inner sphere of fig. 2 is shrinking) amounts to:
(10)

$$|W_{ext}| = \left| \int_1^2 \int_{q_{di-}} \vec{\boldsymbol{E}}_{\boldsymbol{ext}}\, dq_{di-}\, \vec{\boldsymbol{dr}} - \int_1^2 \int_{q_{di+}} \vec{\boldsymbol{E}}_{\boldsymbol{ext}}\, dq_{di+}\, \vec{\boldsymbol{dr}} \right|$$

$\mathbf{E_{ext}}$ denotes the field created by charges outside the cut-out volume in fig. 2, $\mathbf{q_{di\,-}}$ and $\mathbf{q_{di\,+}}$ denote the total amount of negative or positive dipole charge in the volume considered. As long as **A** is situated in the interior of the liquid dielectric (at an invariant distance from the center of the sphere), the flux through **A** stays invariant though the spherical conductor is shrinking, resulting in a zero flow of charge through **A** according to (9). Obviously, in the interior of the dielectric the move of negatively charged dipole-ends is neutralized by a move of positively charged dipole-ends [6]. A change in flux through **A** is only taking place when the *interfaces of the dielectric* pass through **A** during the shrinking of the conducting sphere. Thus (10) converts to:
(11)

$$|dW_{ext}| = \left| \vec{\boldsymbol{E}}_{\boldsymbol{ext}\ (\boldsymbol{interface}\ 1)}\, q_{pol\ (interface\ 1)}\, \vec{\boldsymbol{dr}} - \vec{\boldsymbol{E}}_{\boldsymbol{ext}\ (\boldsymbol{interface}\ 2)}\, q_{pol\ (interface\ 2)}\, \vec{\boldsymbol{dr}} \right|$$

Interface 1 is the inner interface (dielectric/conducting sphere), interface 2 is the outer interface of the dielectric at an indefinite distance. The term $\mathbf{q_{pol}}$ denotes the polarization charge on the interfaces of the dielectric. As the external field $\mathbf{E}_{ext}$ reduces to zero at interface 2 (with the polarization charges being equal in amount to those at interface 1), the second term of (11) reduces to zero, too.[7]

$\mathbf{E_{ext\ (interface\ 1)}}$ equals **1/2 E**, with **E** denoting the field just above the surface of the sphere (in a hypothetical slot within the dielectric parallel to the field lines). This can be proved by some simple reflections: It is well known that, at a given charge density, the field just above or below an evenly charged plane is the same no matter how large the plane is, and no matter what special height above the plane is considered. With the field between *two* charged planes of opposite signs (inside a

---

[6] One might pose the question as to whether or not volume polarization charges exist in the interior of the (isotropic) dielectric. The answer is in the negative. The shortest proof of the absence of volume polarization charges is found in the fact that the increase in capacitance of a condenser filled with some dielectric depends on the material only, and not on the shape of the condenser. Therefore no field lines can originate or terminate in the interior of the dielectric (this is pointed out by Leonard Eyges: The Classical Electromagnetic Field, New York -Dover Publ.- 1980, p. 104).

[7] Equation 11 matches with the result found by L. Eyges (The Classical Electromagnetic Field, New York - Dover Publ.- 1980, p. 163): „This is the desired result: the force on the body is *as if* the external field acted on the polarization charges.“ See also another derivation of this result in A. Trupp: A Theoretical Paradox Related to Solid Dielectrics that Cannot be Resolved even after a Computer Simulation Using Finite Element Analysis, in: Proceedings ESA (Electrostatic Society of America) Annual Meeting 1999, p. 100-102.

parallel-plate-capacitor) being equal to the full charge density (divided by ϵ_0), the field above or below one single plane is equal to 1/2 of the charge density (divided by ϵ_0).

When considering a location in the interior of a charged sphere just below an arbitrarily chosen point on its surface (at a differentially small distance from the surface), the field at this location is zero (as it is in the interior of *any* conductor). But the field generated by the differentially tiny and therefore flat surface zone around the depicted point equals 1/2 of the surface charge density divided by ϵ_0. Obviously, this field is superposed and exactly neutralized by the field created by the vast rest of the sphere.

When considering a location just *above* that arbitrarily chosen point on the surface of the charged sphere (at a differentially low altitude), the field equals the full charge density divided by ϵ_0 according to the properties of the field geometry. It is as if all charge were concentrated in the center; so the field -which can be expressed as Coulomb force per unit charge- is
(12)

$$\frac{1}{4\pi\epsilon_0}\,\frac{q_0\,q}{r^2}\,\frac{1}{q_0} = \frac{q}{\epsilon_0 A_{sphere}} = E$$

With the flat surface zone (of differential size) around the depicted point being responsible for half of the magnitude of **E**, it is obvious that the field created by the vast rest of the sphere ($\mathbf{E}_{\mathbf{restsphere}}$) is again equal to 1/2 of the surface charge density ($\mathbf{q/A_{sphere}}$) divided by ϵ_0, that is $\mathbf{E}_{\mathbf{restsphere}} = \mathbf{E}_{\mathbf{ext\ (interface\ 1)}} = 1/2\ \mathbf{E}$. Moreover, $\mathbf{dE}_{\mathbf{restsphere}}/\mathbf{dr}$ must be zero at the surface.

It is only the field created by the vast rest of the sphere that counts (for determining the radial force acting on the cut-out volume of the sphere in fig. 2), since the field created by the (differentially) small amount of free charge on the cut-out part of the inner sphere (within the cut-out volume) is not able to set the contents of that volume in motion.

Not only the polarization charge, but also the free charge on the cut-out part of the inner sphere is subject to **1/2 E**. So the total work invested when making the inner sphere shrink amounts to
(12a)

$$dW_{mech} = \frac{E(q_{pol}+q_{free})}{2}dr = \frac{E\,q_{eff}}{2}dr = \frac{E}{2}\,\frac{q_{eff}}{A_{sphere}}\,A_{sphere}\,dr = \frac{\epsilon_0}{2}\,E^2\,A_{sphere}dr = \frac{\epsilon_0}{2}E^2\,dV$$

which is equal to the work required in case the dielectric were vacuum or air (**V** denotes volume, not voltage).

Now it can be realized that no creation of heat can occur within the dielectric: The *net electrocaloric effect* (as regards the charging and the decharging of the spherical capacitor) amounts to (see Equation 4):
(13)

$$\Delta W_{intern} = \int_{\Delta V} \frac{(K-1)\epsilon_0}{2}\,E^2\,dV$$

with ΔV denoting the space „abandoned“ by the sphere as a result of its skrinking (**V** denotes volume). The *net electric work* yielded in the cycle amounts to:
(14)

$$\Delta W_{elect} = \int_{\Delta V} \frac{K\epsilon_0}{2} E^2 \, dV$$

The *mechanical work* of making the inner sphere shrink amounts to:
(15)

$$W_{mech} = -\int_{\Delta V} \frac{\epsilon_0}{2} E^2 dV$$

The net gain in (technically usable) energy amounts to
(16)

$$\Delta W_{elect} + W_{mech} = \int_{\Delta V} \frac{(K-1)\epsilon_0}{2} E^2 \, dV$$

That net gain is equal to the net electrocaloric effect. In case a creation of heat took place during the shrinking process, the law of conservation of energy would be violated.

3. Description of the Experiment Conducted

A. The experiment was conducted by Ben Wiens Energy Science Inc., Coquitlam BC, Canada, on contract. The following equipment was used:

(1) Outer sphere 30.5 cm OD, aluminum, both halves grounded to electrical outlet ground wire
(2) Inner sphere 5.5 cm OD, brass
(3) Inner upper half-sphere support hardware, plastic
(4) High voltage power supply, Bertan, 15,000 volts at 3 volts monitor
(5) Scale, 4 beam balance 1/100 gram accuracy
(6) Dielectric fluid, DC-100, 99.9% paraffin
(7) 80 liter bucket to catch dielectric fluid spill
(8) Plastic outer sphere support stand, in bucket
(9) Dielectric fluid hand pump, plastic construction
(10) Inner lower half-sphere connected permanently to high voltage with thin copper wire
(11) Inner upper half-sphere connected permanently to high voltage with thick copper wire
(12) Outer sphere grounding wire connected to electrical plug ground

Tests:
(1) Monitor voltage=2.72
(2) Actual voltage=13,600 Volts

(3) Net force change in air=0.30 „grams“=0.0030 Newton
(4) Net force change in DC100 dielectric fluid=0.50 „grams“ (=0.0050 Newton) or more to start, down to 0.30 „grams“ (=0.0030 Newton) after 20 minutes.

The inner sphere of the spherical capacitor was divided into a lower and an upper half, with the upper half firmly connected to the outer sphere by plastic struts, and with the lower half suspended by a string that was attached to scales above the spherical capacitor. A hole at the „North Pole“ of the (grounded) outer sphere allowed the string to penetrate the wall of that sphere. Both halves of the inner sphere were permanently in contact with a high voltage power supply of 13,600 Volts. In air, the electrostatic repulsive force which the lower half was subject to was 0.30 „grams“, that is 0.003 Newton. The force in air with the charging wire removed was basically the same as with charging wire connected permanently, so this method produced just as reliable results. In the dielectric liquid, the electrostatic repulsive force (which the lower half was subject to) was 0.30 „grams“, that is 0.003 Newton (just as in air), after a state of equilibrium had been attained.

In a second experiment, the attractive force between two parallel plates charged with electricity of different signs was measured in air and in paraffin oil (at an identical voltage).

1. Experimental Apparatus
(a) 80 liter plastic bucket
(b) 1/100 gram accuracy 4 beam balance
(c) Stainless Steel disks with sharply upturned edge about 210 mm diameter
(d) Rod to connect upper Stainless Steel disk to scale was brass threaded rod and wire hook to scale
(e) Grounding to upper Stainless Steel disk via grounding of all metal balance and linkages to upper disk.
(f) High voltage supply to lower Stainless Steel disk via insulated wire to Bertan high voltage supply
(g) Monitoring voltage was 2.72 volts=13,600 volts (3 volts=15,000 volts)
(h) Distance of flat portion of disks apart in tests in air and paraffin oil was identical and about 40 mm.
(i) Paraffin oil was DC100 and covered the upper disk completely in the test
(j) Upturned edges of disks were facing away from each other

2. Test in air
Attractive force=4.70 „grams“ and steady over many minutes.

3. Test in paraffin oil
Attractive force=10.00 „grams“ at 1 minute, 12.00 „grams“ at 10 minutes, 12.80 „grams“ at 120 minutes. Hence the equilibrium force was about 2.7 times greater in paraffin oil (as a liquid dielectric) than in air. This matches with the relative permittivity of paraffin oil, which ranges from 2.2 to 4.7 .

B. As with most liquid dielectrics, conductivity is much higher in paraffin oil than in air. Thus paraffin oil is far from being a perfect insulator, and can be considered to be a resistor. Does this imply an accumulation of free charge in the dielectric and hence an error in measuring the force of repulsion? The answer is in the negative. According to Ohm‘s law we have
(17)

$$I = \frac{\Delta V}{R} = \frac{\Delta V\, A}{R_{specif}\, L} = \frac{\Delta V\, A}{L}\, \sigma$$

I denotes the current of free charge, **ΔV** the voltage drop along a bundle of stream lines within a resistor, **L** the length of the bundle of stream lines, **A** the average cross-sectional area of that bundle, **R** the resistance, $\mathbf{R_{specif}}$ the specific resistance, **σ** the specific conductivity (which is the reciprocal of the specific resistance). Since Ohm‘s law is still valid when all terms have differential dimensions only, (17) can be expressed as:
(17a)

$$\frac{d\vec{I}}{dA} = \frac{d\vec{V}}{dL}\, \sigma$$

With the current density **j** being defined as **dI/dA**, and with the field **E** being **dV/dL**, we get
(18)

$$\vec{j} = \sigma\, \vec{E}$$

The current density is proportional to the field inside the resistor at any spot considered.

As the divergence of $\vec{j}$ is zero *as soon as the current is steady* (the same amount of charge that enters a volume element per temporal unit must leave that element per temporal unit), the divergence of $\vec{E}$ must, too, be zero. Hence, as a consequence of Gauss' law, there can be no accumulation of charge in the interior of the resistor. This has been labeled as a „fundamental law of electricity" in standard textbooks. [8]

Things are different only if **σ** varies along the electric circuit. At the interface of two different resistors, **j** has to stay invariant, while **σ** is undergoing a change. This implies a reciproke change in **E** according to (18). Thus, when imagining a right-angled volume element that comprises both resistors so that the current enters through the left side and leaves through the right side, the divergence of **j** is still zero, but the divergence of **E** is different from zero. Therefore, according to Gauss' law, some accumulated charge must sit in that volume element.

That charge is the same in amount as if the dielectric were vacuum: With the high specific conductivity of the brass (the inner sphere is made of) as the conducting material on the one hand, and with the weak current density provided for by the liquid paraffin (as a fairly good resistor material) on the other hand, the field **E** inside the brass is practically zero according to Equation 18. Therefore the flux of **E** through the inner side of a (thought) right-angled volume element that comprises both the brass and the dielectric is zero. Since the radial geometry and the strength of the field between the two spheres of the capacitor are the same as if the dielectric were vacuum (due to the absence of free charges in the interior of the dielectric), the flux through the *outer* side of the volume element is also the same as if the dielectric were vacuum. Then, according to Gauss' law, the effective charge within the volume element, too, has to be the same in amount as if the dielectric were vacuum.

The absence of free charges in the interior of resistors, and the fact that the distribution of effective charge on the surface of a metal body (when permanently connected to a pole of a battery and immersed in a liquid of high resistance) is the same as if the metal body were embedded in vacuum, entails a spatial distribution of the potential (in an entirely resistor-filled space surrounding the conductor), which, at a given potential of the conductor, is identical to the spatial distribution (of the potential) generated if the space were filled with vacuum. This property is being used in experimental physics to determine the spatial distribution of the electrostatic field generated by irregularly shaped bodies in space [9]: A model of the body made of metal is immersed in a bath containing an electrolytic liquid. The metal body is connected to one pole of a power supply, and the far away (metal) container that holds the liquid is connected to the second pole of the power supply. A probe with an insulated wire is introduced into the liquid, with the other end of the wire connected to the container. The voltage given by a dynamic voltmeter is an expression of the potential of the probed

---

[8] See G. Bruhat: Cours d'Electricite, 3rd edition, Paris 1934, p. 223 (my own translation): *„We have already stated that the vector i satisfies the condition div i=0 under a permanent regime. It follows from Ohm's law that one also has div E=0, and since, according to Poisson's law, one has div E=...=4pi q, it follows as a fundamental law that the electric volume density, when a system of conductors has arrived at a permanent regime, is zero at all points of the conductors; the electrification of the conductors is purely superficial*". See also Georg Joos: Theoretical Physics, Dover Publ., New York, 3rd edition 1986, chapter XIV, par. 1, p. 294/295.

[9] See Georg Joos, op. cit.; Grimsehl: Lehrbuch der Physik, Vol. 2, 13th edition, Leipzig 1954, p. 170; standard experimental devices for two-dimensional electrostatic problems that use thin sheets of solid resistor material in connection with probes and voltmeters are being sold by companies that supply lab equipment to schools, colleges and universities, see for instance the catalogue of „PHYWE", based in Goettingen, Germany.

location.

C. It can be realized that it is the *state of a steady currents* -and not the initial state of time varying currents- which counts when determining the electrostatic force of repulsion. Only the state of steady currents is a state that guarantees the absence of free charges in the interior of the resistor (dielectric). The fact that an equilibrium (steady current through the dielectric) is arrived at only after some time has elapsed can be accounted for as follows: When undergoing a fast increase in voltage by a power supply, capacitors can accumulate some excess charge (= more than in a state of equilibrium) for a short time -during which the surface of the conducting material (plates and wires) does *not* form an equipotential surface- in very much the same way as the surface of a liquid may temporarily rise above normal (=equilibrium) height by the action of a wave. This can be illustrated by considering two vacuum-filled capacitors (of identical capacitance) in a serial arrangement, with only one of the two being charged. As soon as the gap in the connecting wire between the two capacitors is being closed by a switch, charge is flowing from the first to the second capacitor through an ideal wire with no resistance. If the flow came to a standstill as soon as the charge is evenly distributed among the two capacitors, the law of conservation of energy would be violated: Each of the two capacitors would contain only 1/4 of the energy previously stored in the first capacitor, since the energy of the field between the plates is proportional to the *square* of the charge density. In order to avoid a violation of the law of conservation of energy, the charge is oscillating from one capacitor to the other and vice versa, and the divergence of the current density **j=I/A** is different from zero. As real wires *do* have a resistance different from zero, the oscillation is dampened until it fades out [10].

Back to the spherical capacitor filled with a dielectric: When there is a charge wave (making **div** $\vec{j}$ differ from zero) which travels along the circuit, that wave of accumulated charge is only partly reflected at the interface sphere/dielectric. Some charge (say, negative charge) enters the dielectric and is pushed forward by the existing field as long as the sphere is still charged with electricity of the same negative sign. As soon as the electricity on the sphere changes to positive, the charge that had entered the dielectric is drawn back by the (then existing) field. However, since the wave is dampened both by the resistance of the conductor and by the previous loss of negative charge to the dielectric, only a fraction of the negative charge inside the dielectric manages to leave the dielectric during the phase in which the charge on the sphere is positive. Thus some residual negative charge remains in the dielecric after a full wave (2π) has been completed. That residual accumulation of charge will migrate along the steady field which is established as soon as the oscillation in the conductor has come to a standstill. Due to the poor conductivity of the dielectric, it may take several minutes or more for that cloud of accumulated charge to traverse the dielectric.[11] Not before the disappearance of that charge will a state of dynamic equilibrium be attained.

d) The permittivity of paraffin oil **K** ranges from 2.2 to 4.7. Hence, in order to avoid a violation of the Second Law, the repulsive force would have to be at least 2.2 times 0.0030 = 0.0066 Newton rather than 0.0030 Newton (which is the force in air). Only then would the result match with the textbook version of Coulomb‘s law in dielectrics, which postulates an increase in forces between

---

[10] See A.D. Moore: Electrostatics, 2nd edition, Morgan Hill 1997, p.106: “*When a capacitor discharges by way of a spark the current in the spark is typically oscillatory. It surges back and forth quite a few times at high frequency before it dies out.*”

[11] Conductivity in highly insulating liquids is caused mainly by „foreign“ ions that are present due to the impurity of the liquid; in order to remove *those* ions, electric fields have to exert their influence on the liquids over a period of several days. See: R.W. Pohl: Elektrizitätslehre, 18th edition, Berlin 1983, p. 177. So it is no surprise to find an equilbrium only after several minutes or even hours.

conductors by the factor **K** (=the relative permittivity of the dielectric) as a result of the presence of the liquid dielectric.

The drag created by the stationary current of free electrons or negative ions that “bump” against the molecules of the dielectric does not give rise to a modification of the expected result. It is just to the contrary: Without those “bumps”, the positively charged ions in the dielectric would transmit a net force to the liquid no matter if they are immobile or being dragged through the liquid themselves. It is by the effect of those “bumps” that this force on the liquid is neutralized.

A slight modification of the expected result is, however, brought about by the fact that the diameter of the outer sphere is not infinite, but only 5.5 times greater than the diameter of the inner sphere. Hence the expected force is about 4% greater than in case of air as a dielectric, that is 0.0031 Newton.

In order to measure forces by the scales used, the object (lower half of the inner sphere, upper plate of the parallel plate capacitor) had to undergo a (slight) vertical displacement within the liquid. Dynamic viscosity of the liquid was nothing to worry about, since internal friction is proportional to the velocity of the object, so this effect can be evaded by simply reducing the speed of motion through the liquid. But sheer forces, which are zero in a liquid when the relative speed of the object and the liquid is zero, can (in principle) be different from zero -even if everything is at rest- due to electric forces between the dipoles of the dielectric (resulting in the phenomenon of pressure being dependent on direction). So it was not certain *a priori* whether or not the object would resist a displacement unless a minimum force of considerable amount (in the order of the expected force of electrostatic repulsion) would be applied. This did not happen.

Review of

"Second Law violations in the wake of the Electrocaloric Effect in liquid dielectrics", by Andreas Trupp

This paper is unacceptable for ***Physical Review E****.*

The reasons for this assessment are as follows:

1) The vast majority of the paper is a narrative which is alternately pedagogical and speculative. Large parts of the narrative describe basic and/or textbook physics. Such substantial pedagogical treatments are inappropriate for journals devoted to research into new or previously unexplained phenomena. Other portions of the narrative are speculative discussions of possible physical phenomena which might be at play. This is also inappropriate for a research journal.

2) The author provides an unacceptably brief experimental section 3A. The level of this work is not suitable for Physical Review. The experimental scientists who completed the work should be identified. Dielectric materials of undetermined properties are utilized. Systematic measurements using the same apparatus for a variety of conditions (voltages, timing of variations, dielectrics) have not been made (at least not reported) to allow separation of geometrical errors or apparatus flaws to be distinguished from physical phenomena. There is inadequate experimental *information to support the speculative analysis.*

N. B. A.
Editorial Board Member
Physical Review E

Any lab interested in repeating the experiments will be provided with the experimental apparatus free of any charges or costs. Please contact me under my private email address:

atrupp@aol.com

Phone: (011)49-3338-760937