Where is the Displacement Current in Chemical Reactions?

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Abstract

The current flowing in chemical reactions is governed by electrodynamics, the Maxwell Ampere law, which specifies the magnetic field $\mathbf{B}$. The source for the magnetic field is not its divergence, which is zero, but its curl. Two components of current drive the curl: the usual conduction current of charge transport, and the displacement current proportional to the time derivative of the electric field $\partial\mathbf{E}/\partial t$. The Maxwell Ampere law specifies the properties of the total current made of these components. Maxwell called this true current because it is needed to explain how light propagates in a vacuum devoid of charge or conduction current. The true current forms a divergence-free field with special properties. In series systems, the true current is the same in each series component, although the physics of charge movement is different in each component. The laws of true current are true on the time scale of gamma rays, and during the changes of electron orbitals that define the mechanism of chemical reactions. The displacement current terms are not seen in many models of the mechanism of chemical reactions, although they may be present implicitly. Note that in sets of steady-state measurements, the displacement current is not apparent but it is still significant. Charge is required to change one measurement into another and must be dealt with in theories and simulations. The special property of series systems can be used to decide if a theory of chemical reactions is compatible with the Maxwell Ampere law. Compatibility with electrodynamics is a desirable property of a theory of chemical reactions because electrons changing orbitals produce true current that must flow somewhere without divergence, perhaps from bond to bond or molecule to molecule.

Chemical reactions often involve flows of charged reactants. The current carried by that flow is governed by electrodynamics, including the law of magnetism, the Maxwell Ampere law.

$$\frac{1}{\mu_0}\textbf{Curl B} = \mathbf{J} + \varepsilon_0(\varepsilon_r - 1)\partial\mathbf{E}/\partial t + \varepsilon_0\partial\mathbf{E}/\partial t = \mathbf{J}_{true} \qquad (1)$$

Here $\mathbf{B}$ is the magnetic field; $\mathbf{J}$ is the ordinary conduction current carried by the flux of charges; $\mathbf{E}$ is the electric field. $\mathbf{J}_{true}$ is defined as Maxwell did in Vol. 2, Section 610, p. 232 of [1]; also see section 783 p, 385.

The divergence of the magnetic field has no sources.

$$\mathbf{div\,B} = 0 \qquad (2)$$

The magnetic field is created by the right-hand side of the curl equation (1).

$$\mathbf{J} + \varepsilon_0(\varepsilon_r - 1)\partial\mathbf{E}/\partial t + \varepsilon_0\partial\mathbf{E}/\partial t = \mathbf{J}_{true} \qquad (3)$$

Maxwell emphasized the need to deal with both conduction and displacement components of current and gave examples showing why that was needed. Maxwell evidently chose the name ‘true current’ because ‘total current’ was not emphatic enough.

The true current has three components.

1) It has the ordinary conduction current $\mathbf{J}$ carried by the flux of charges.

Conduction Current	$\mathbf{J}$	(4)

2) It has a material displacement term $\varepsilon_0(\varepsilon_r - 1)\,\partial\mathbf{E}/\partial t$ where ε_0 is the electric constant and ε_r is the dimensionless relative dielectric constant, a single real positive number.

Material Displacement Current	$\varepsilon_0(\varepsilon_r - 1)\,\partial\mathbf{E}/\partial t$	(5)

The dielectric constant ε_r can be viewed as a placeholder for the bewilderingly **complex** properties of the polarization of matter ([2], p. 550-507 of [3]) documented in [4-7]. The amazingly diverse optical properties are revealed ([8], p. 241-275) by many kinds of spectroscopy [4, 9-14].

3) It has a universal exact displacement term that is present in the vacuum of space as well as everywhere else

Universal Displacement Current	$\varepsilon_0\, \partial \mathbf{E}/\partial t$	(6)

The universal term is substantial. It is not a small part of the total displacement current. It is roughly equal to the material displacement current in many molecular dynamics calculations. The universal current is responsible for the propagation of light through a vacuum that contains no dielectrics, charges, or conduction currents.

If we take the divergence of eq. (1) using the identity $\mathbf{div\ curl} = 0$ we get an equation for the true total current

$$\mathbf{div\ curl\ B} = 0 = \mathbf{div}\, \mu_0(\mathbf{J} + \varepsilon_r \varepsilon_0\, \partial \mathbf{E}/\partial t) \quad (7)$$

$$\mathbf{div\ J}_{\boldsymbol{true}} = 0 \quad (8)$$

The identity $\mathbf{div\ curl} = 0$ is easily proven using the definition of the operators in Cartesian form [15]. Mathematicians have studied this identity in many different contexts as they examine divergence-free fields [16-29]. Divergence-free fields are of particular interest because they describe the long-time behavior of approximately incompressible fluids like water.

Special Properties of True Current: Divergence-free Fields that form Circuits.

The total true current equation (8) specifies a solenoidal field divergence-free at all times. The total true current is truly incompressible [30]. Such fields have special properties that produce streamlines that never end in finite two-dimensional systems [31]. These streamlines are generalized circles forming circuits that close on themselves and so end where they begin. Circuits are responsible for a substantial part of our modern technology, from power distribution in our cities, to information processing in our computers and smartphones.

Solenoidal currents have no end or beginning. Thus, they do not accumulate. Solenoidal currents must balance at every instant of time without delay, i.e., 'instantaneously'. They cannot accumulate even briefly.

The special properties of true total current are very different from the properties of the conduction current and the ionic components of conduction current. The ***conduction current does accumulate.*** It can accumulate and be 'paid back' later. The conduction current is the sum of the conduction currents—the fluxes—of individual chemical species. The fluxes of individual species do accumulate, often to be paid back later.

The true total current follows its own conservation law of no accumulation at any time. This law is a powerful determinant of qualitative as well as quantitative behavior. It forces a universal coupling of the components of true total current arising from global properties of electric and magnetic fields, not from local interactions of microphysics.

If one component gets larger, another component must get smaller. The mathematical properties of true total current guarantee that the conduction current of one component depends on the conduction current of another component. The components are coupled by the conservation law (8) itself. The coupling is not mechanical. The coupling is global not just local. Physical contact of the components is not directly involved in the coupling. A plot of one component vs. another component will show a single definite curve—perhaps a straight line—as conditions change.

Chemical Reactions in Series.

In series systems, the total true current is identical in every component of the one-dimensional series system. If the series system consists of chemical reactions one after the other, the total true current is the same in all the chemical reactions. The chemical reactions are coupled by the conservation law of no accumulation.

The universal component $\varepsilon_0\, \partial \mathbf{E}/\partial t$ of displacement current inherits its properties from the Maxwell Ampere law. It is derived from the Maxwell Ampere law by mathematics without approximation or assumption and is true whenever the Maxwell Ampere law is true. Thus, the true total current in a series of chemical reactions is equal in every one of the chemical reactions. At any time, the true total current is the same in every reaction in the chain of reactions. Of course, the true total current flowing throughout the series of components can change with time.

The Maxwell Ampere law certainly applies on the 10^{-21} second time scale of gamma rays and at shorter times than that. The Maxwell Ampere law is thus valid during the time in which electrons move to change chemical bonds. The Maxwell current law eq.(8) applies to the mechanism of chemical reactions. The true currents that flow as electrons change orbitals are an important part of chemical reactions and cannot be ignored. They must flow somewhere without divergence, perhaps in circuits linking bonds or molecules.

Steady-State Measurements of Reaction Mechanisms.

The time derivative is not present when steady-state measurements of reaction mechanisms are made. The displacement current is invisible when $\partial \mathbf{E}/\partial t = 0$. ***But its effects are still present.***

Experiments are performed in sets. Each measurement usually involves different conditions and **E** is usually different in each one. One measurement is different from the next because conditions are changed. When conditions are changed, charge is added to the system. The electric field changes when switching from one measurement to the next even if the electric field is the same during each measurement. In other words, $\partial \mathbf{E}/\partial t \neq 0$ from one measurement to another. That means that displacement current flows as one measurement is ended and another started. Charge is stored as measurements are switched from one to another. That charge must be predicted. That charge is part of the mechanism of a chemical reaction.

Is Displacement Current Implicit in a Calculation?

Displacement current may be present implicitly in a theory even if a $\partial \mathbf{E}/\partial t$ term is not apparent because of conservation of charge, see p. 8 of [32] and [33]. For example, the displacement current may be present implicitly in quantum mechanical theories that include charge movements [23-25, 34], even though $\partial \mathbf{E}/\partial t$ terms are not seen.

In these cases, answering the question that is the title of this paper—where is the displacement current in chemical reactions—can be difficult. It may be useful then to check whether a series of chemical reactions obeys eq. (8). One way to check is to see if the total true current is in fact equal in each chemical reaction in the series system as eq. (8) requires.

If true total current is not found to be equal in each reaction, the theories and simulations can be modified to include charge storage terms. The modified chemical theory or simulation then becomes compatible with the Maxwell Ampere Law eq.(1). Compatibility with electrodynamics is a desirable property of a theory of chemical reactions because electrons changing orbitals produce true current that must flow somewhere without divergence, perhaps from bond to bond or molecule to molecule.

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