Bob Eisenberg <bob.eisenberg@gmail.com>

RE: Law of Mass Action does not conserve charge

1 message

Stuart A. Rice <sarice@uchicago.edu> Mon, Jan 19, 2015 at 1:42 PM
To: "bob.eisenberg@gmail.com" <bob.eisenberg@gmail.com>

Dear Bob,

I have quickly scanned the paper you sent to get an overall impression of the arguments you make. The major thrust of your argument is that when charge flow is involved in a process it is necessary to account for displacement currents, and that conventional treatments do not do so. Ultimately, the inclusion of the displacement current requires a proper treatment of the boundary conditions that define the system. These general observations are, as you observe, fundamental to electromagnetic phenomena. They are, as far as we know, unchallengeable and universally applicable. But then, the way in which you present the argument with respect to successive chemical reactions seems to me to cobble together several notions without addressing their limitations, and it obscures the strength of your major observations.

The following remarks are "off the top of my head" and incomplete, but give the spirit of what I find confusing or wrong in the draft paper. I have not thought them through carefully so not everything below may be pertinent.

Consider first your statement that the law of mass action does not conserve charge. That is not correct. In my language, the law of mass action is a different set of words describing the equilibrium constant in a chemical reaction: it describes the relationship between the activities […] of the products and the reactants, the familiar form being for the reaction aA + bB $\rightarrow$ cC + dD. It is important that the stoichiometry be correct (the numbers of the atoms of each species and the net charges of the reactants and products be the same). The equilibrium constant is determined by the differences in chemical potentials of the products and reactants, and it accounts for all interactions between species and charges at equilibrium. In making this statement I am assuming that approximate representations of the chemical potentials are not used. Moreover, the equilibrium constant appropriately accounts for the reaction stoichiometry and it is independent of the mechanism by which the reaction occurs. There can be any number of intermediates unmentioned in the stoichiometric balance, and the rates with which they are formed and destroyed can follow peculiar kinetics, but that does not influence the form of the equilibrium constant between reactants and the designated products. The widely used definition of an equilibrium constant as a ratio of rate constants is only applicable for direct transformations; it cannot describe the equilibrium constant when there are intermediates. And the rate constant ratio definition does not account for the interactions between species at equilibrium, those that renormalize the concentration to the activity.

In fact, you are not interested in equilibrium states of the system; you are interested in (possibly stationary) states of the system with current flow. When you write X $\rightarrow$ Y $\rightarrow$ Z you wish to determine he current flow along that reaction path. As written, with X, Y and Z chemical species, this sequence corresponds to successive isomerization reactions and you assume unimolecular kinetics for the rate of growth/decay of each species; if the reactions are not isomerizations the stoichiometries are wrong and the kinetic equations are wrong. But most important, if a net current flows the system cannot be at equilibrium, and the mechanism of current flow must depend on the intermediate pathway, unlike the case of equilibrium. Using the equilibrium relationship between reactants and products to ascertain the current in one direction is not appropriate.

Your discussion of Fig. 2 is good, and without using the words it emphasizes the role of boundary conditions, e.g, the condenser and displacement current are defined by the confining plates. That is the point I think you should emphasize, since it is certainly applicable in a membrane channel.

I will send this now rather than sit and refine arguments.

Stuart

From: Bob Eisenberg [bob.eisenberg@gmail.com]
Sent: Sunday, January 18, 2015 9:09 AM
To: Stuart A. Rice
Subject: Law of Mass Action does not conserve charge

Dear Stuart

I have been working hard on the attached and would greatly appreciate your comments.

The gist of the story is this

> Chemists have been interested in making molecules, not in signals or interactions with the environment, not in charge, and so they have not noticed that their standard formulation of chemical reactions does not conserve charge.
>
> Mathematicians often do not notice that accumulation of charge at a node is fundamentally different from accumulation of mass, because of the existence of displacement current, which automatically and exactly charges the electrical potential by $ i_{displacement} = \partial V/\partial t $ so the current entering a node EXACTLY equals the current leaving the node, when current is defined to include displacement current. Current MUST be defined this way if it is to be the source of the magnetic field that allows light to propagate through a vacuum.
>
> Mass accumulating at a node does not satisfy any simple universal law. It accumulates and has effects that depend on the details of the constitutive equations and system. No generalization of mass flow equivalent to Maxwell's generalization of current flow is known.

All comments, questions, suggestions, and criticisms are most welcome.

As ever
Bob

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