Bob Eisenberg <bob.eisenberg@gmail.com>

Re: Law of Mass Action does not conserve charge

Bob Eisenberg <bob.eisenberg@gmail.com> Mon, Jan 19, 2015 at 12:09 AM
Reply-To: bob.eisenberg@gmail.com
To: jinnliu <jinnliu@mail.nhcue.edu.tw>, "Bob Eisenberg beisenbe@rush" <beisenbe@rush.edu>

Dear Jinn

Good idea!
and if you find some mistakes are faults
do not be shy. I am very capable of doing
silly things.

There are a few comments I should make.

1) I purposely did not do a general case. I wanted
to take the simplest case and show the issue.
Every particular chemical reaction will have
situations in which the law of mass action is
compatible with Kirchoff's law. Furthermore,
most chemical or anyway biochemical reaction
can be studied in such a restricted range of conditions
that the law of mass action is more or less true.

My point is that ROBUST transferable "laws"
are obviously impossible if they violate Kirchoff's
law.

1a) Because I tried to keep things simple, I consider
only the case where rate constants are constant.
I purposely avoid discussing how to generalize
rate constants to deal with some of the problems
BECAUSE it is obvious that the rate constants
must be GLOBAL functions in general.

**If I gave the chemists some way to get out of the
general problem, they would grab it and avoid
the main issue.**

2) I purposely was vague about the difference
between conservation of charge and Kirchoff's current
law. If one simply BALANCES charges, the way chemists
sometimes do (but not always), the charge in the various
stages of the reaction will be the same. But the key
idea is that the electrical currents themselves MUST
always under all conditions and times etc etc be the
same no matter what, if displacement current is included.

3) I am not familiar enough or good enough with Maxwell's
equations to reduce them to Kirchoff's current law rigorously
so some of what I say may be approximate and only valid
when circuits do not radiate energy.

4) I VERY purposely avoided anything except series circuits
because I am fully aware that the 3D world is much more complex
and must be dealt with by pde's (at best, sometimes integrodifferential
equations, sometimes even stochastic de's coupled to pde's).
Fortunately, nearly all of chemistry and biochemistry is analyzed
with 'graphs' that look like circuits, i.e., can be made by a combination
of series and parallel circuit elements. Indeed, most of chemistry
and biochemistry considers a series or sequence of reactions.
So I can illustrate the issue with just this case without oversimplifying.

5) If one considers chemical reactions in general, in three dimensions,
the situation is actually terrifying. Consider the following example
which is realistic but not necessarily typical.

Consider a reaction in a liquid which is a steep function of concentration.
(There are many many such reactions but certainly not all).
Consider a reaction in which the electron rearrangement which IS
the chemical reaction (i.e., the change in covalent bonds) is very fast
like 1e-18 sec. (This is realistic.)

Now consider electrodiffusion.
Electrodiffusion creates regions of concentration of some size
(I do not know what size, but certainly we are talking about many
angstroms and maybe MUCH larger) that have concentrations far
from the mean FOR TIMES THAT ARE OF THE ORDER OF NANOSECONDS
TO PICOSECONDS.

These times are "infinite" compared to the time needed for the electron
rearrangement.

Because these regions have large concentrations for a very long time
(on the time scale of the chemical reaction) a large fraction of the
chemical reaction will occur there.

THUS A LARGE FRACTION OF THE CHEMICAL REACTION WILL
OCCUR AT CONCENTRATIONS THAT ARE NOTHING LIKE THE
AVERAGE CONCENTRATIONS used in chemical models.

The reason this is frightening is that such reactions can only be simulated
or studied by a fully coupled model in space and time including
quantum chemistry.

I look forward to benefitting by your checking!

As ever
Bob

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New hospital tower at Rush

On Sun, Jan 18, 2015 at 11:12 PM, jinnliu <jinnliu@mail.nhcue.edu.tw> wrote:

> Dear Bob,
>
> Thank you for sending me your important work on the Law of Mass Action. I'll take a good look at the paper. I may repeat in detail of your proof of the theorem to fully understand conservation of charge.
> Best,
>
> Jinn
>
> > ※ 引述《"Bob Eisenberg" <bob.eisenberg@gmail.com>》之郵件內容：
> > Dear Jinn
> >
> > 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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