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Covalent Bond changes in a three dimensional world

Bob Eisenberg <beisenbe@rush.edu> **Fri, Aug 26, 2011 at 11:37 AM**
Reply-To: beisenbe@rush.edu
To: Chun Liu <liu@math.psu.edu>, Yoichiro Mori <ymori@umn.edu>, Bob Eisenberg <beisenbe@rush.edu>

Dear Chun and Yoichiro,

I fear I was far too cryptic in my previous emails
and paper on mass action about the issues in
classical chemistry, which for this purpose excludes
enzymes, and even solid catalysts. I also am describing
ONLY chemical reactions that involve substantial changes
in electron orbitals, i.e., covalent bond changes. In other
words I am talking about the meat and potatoes of classical
chemistry, without the vegetables and dessert of biochemistry.

The issue here is really quite fantastic:

1) All of classical chemistry ignores spatial gradients of concentration.

2) All of chemistry interprets experimental results using the law of mass action
with the concentrations of the bulk solution.

3) Changes in electron orbitals (i.e., changes in covalent bonds) occur very
rapidly (say 10${-18}$sec or faster.

4) In many (but not all) cases, the changes in orbitals are likely to occur in
a region in which local concentrations of reactants is high for a period of time
much (i.e, 10x) longer than a typical reaction time 10${-18}$sec

5) Electrodiffusion and even stirring is not very effective on the 10${-18}$sec time
scale. On this time scale, spatially local fluctuations in concentration will be unavoidable.

6) In the kind of situation I just described

7) the local concentrations that actually do the reacting far exceed the average
concentrations in the bulk.The reactants are not ideal so The law of mass action is valid only
with
rate constants that depend on 'everything'. Flow into the reaction region is intimately involved

in
everything that happens.

8) A coupled treatment of electrodiffusion, stirring,
and the chemical reaction itself is needed to get even the spirit of the analysis right
because "Everything" is coupled to everything else.

9) Covalent bond changes act as sources (and potentially sinks) for the rest of the system of great strength.
The coupling of covalent bond changes to existing EnVarA formulations requires thought. In present analysis,
these issues should be identified, but skirted. **First we need to incorporate the universal formalism of chemical**
reactions into our EnVarA schemes. Then we will need to learn how to deal with energies DOMINATED BY the
chemical reactions themselves.

In my opinion, **we must not let the perfect undermine the good** (enough). We must push on
(in my view) with the phenomenological description of chemical reactions even though we know this eventually
will need to be rebuilt. We must do this because we must communicate with chemists . We must do this
so we ourselves can learn to understand the chemical literature. How much of chemical formalism will actually survive a fully coupled treatment
is hard to say.

As ever
Bob

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