pH is a nonideal property that requires a consistent variational treatment

1 message

Bob Eisenberg <bob.eisenberg@gmail.com> Wed, Jan 29, 2014 at 6:29 AM
Reply-To: bob.eisenberg@gmail.com
To: Troels Ring <tring@gvdnet.dk>, Bob Eisenberg <beisenbe@rush.edu>, Chun Liu <liu@math.psu.edu>

Dear Troels

I am afraid you have much more patience with our catastrophic political system than I do. Obama is indeed a fine speaker and a wonderful symbol.

But the system (designed by Madison and Jefferson to be very inefficient so the Federal government could not interfere with their prosperity and life, including slavery) does not work.

Most Europeans are unaware, for example, that the budget proposed by our executive (i.e., President) is NEVER accepted by Congress, but rather is argued about with enormous participation by paid lobbyists (who are allowed to make essentially unlimited contributions to the personal campaign funds of members of congress) for at least one year.

To science:

I recently spent nearly a week at Purdue as I may have told you and gave seminars in Chemistry and separately Math (and engineering as well on a different subject). The point of the Chemistry seminar was that nonideal properties dominate physiological chemical reactions and ionic movements. The point of the Math seminar was to show that such nonideal properties (of SPHERICAL IONS with a definite diameter) can be dealt with rigorously by the new variational methods we call EnVarA (or its equivalent) using (from the math point of view) a slight change in math methods.

The response of the chemists can be summarized by the comment of Steve Adelman (and old timer who has contributed to stat mech for several decades): "we have to redo all of chemistry [in the liquid phase". The response of Jie Shen (senior mathematician and numerical analyst) was "Now,we know what to do"

The problem with your questions about pH is that the main species involved is NOT (known to be) a sphere. Thus, we do not have a well defined way to include "protons" into the EnVarA scheme. (and of course we do not know yet how to include the chemical reaction which buffers pH, or the nonionized species, or the hydroxyl ion).

Thus, I would not know how to proceed with what you want to do.

I do know the only approach that (in my opinion, others will disagree for sure) will work.

1) DEFINE pH by an experiment NOT a theoretical discussion

2) IDEALIZE the experiment

3) WRITE a variational description of the experiment

4) SOLVE the EnVarA description to provide an OPERATIONAL definition
of pH, proton activity, hydroxyl activity, unionized buffer activity etc. OPERATIONAL
means that the dependent variables just listed are written as functions (ONLY)
of measurable quantities (no theoretical constructs).

5) USE the EnVarA analysis to address practical issues like you raise.

About your (understandable) desire to use an incremental approach.
I wish (a) I could do it (b) it would work.

(a) I am unable to do that because I do not have the "finger feel" for pH
that I (more or less) have for ion channels.

(b) the attached papers show that for a closely related subject (the 'law of
mass action') NO FIX UP IS POSSIBLE. Rather, the entire definition of
the law of mass action must be replaced by an analysis which deals
consistently with ALL the energies and forces involved, namely with
the GLOBAL electric field, nonideality of various types, and electrodiffusion
which is ALWAYS involved away from equilibrium when chemical reactions
actually occur.

In my view, no fix up of pH will be successful.

If you view this as unnecessarily pessimistic, I urge you to look at

Hünenberger, P. and M. Reif (2011). Single-Ion Solvation. Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities. London, Royal Society of Chemistry.

This fantastic book shows that after something more than a century we do not know
how to define the property of sodium in a sodium chloride solution. This is completely
understandable in the view of a variational approach. There we see that "everything
interacts with everything else" and the idea that NONconsistent NONvariational
models could define a single ion property is laughable. One obviously cannot describe
water flow from a shower, or airflow over a wing of an airplane, or sound distribution
in a concert hall by such nonconsistent models. Every model would give a different
answer which is exactly what happens with ions in ionic solutions.

and what happens with pH (in my opinion)

I do not believe a fix up will work.

MUSIC
I will listen with pleasure, later today

As ever

Bob

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On Wed, Jan 29, 2014 at 3:20 AM, Troels Ring <tring@gvdnet.dk> wrote:

> Dear bob - just heard this after hearing your president and thought you might enjoy. Also, while I'm strengthening myself to make the approach you suggested I wonder whether in two words you find my previous attempts totally useless? I know we have to go quite far to get a proper and meaningful picture - but it would be nice to - sort of - know from where to take the first step. As a clinician I would like to start approximately where our current most likely misdirected thinking has brought us. I remember an old saying from Danish philosopher, Søren Kierkegaard - in my translation - "if you really want to help someone move somewhere, you better try to find him where he is and start there" -
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> All best wishes
> Troels