**Bob Eisenberg’s Recent Work in Physical Chemistry**

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Bob Eisenberg has recently been working mostly in physical chemistry because he rediscovered what has been known for a long time, since the 1800's: the law of mass action is derived and applies to infinitely dilute gases without electrical charge. ONLY in that case are the equilibrium constants chemists are taught actually constant! Otherwise, they vary a great deal, and depend on the concentration of everything in the solution, and the shape of the system, and properties of its boundaries.

Biology occurs in ionic solutions, ionic plasmas in fact, that are charged and not at all dilute. The law of mass action has been consistently misused in this situation because equilibrium and rate constants have been assumed constant. That means that interactions of the ions themselves have been mistakenly attributed to interactions with proteins, channels or enzymes (or binding proteins).[[14](#_ENREF_14)] Since much of biology is produced by these interactions, the implications are serious and general.

The crucial fact is that equilibrium and rate constants change when the concentrations of  EVERY species in a biological 'Ringer' solution is changed and they change a lot. This crucial property of ionic solutions has always been known to experimental physical chemists (i.e., since the 1920's or earlier) but escaped the notice of the key biophysical chemists Edsall [[4](#_ENREF_4)]  and Tanford.[[32](#_ENREF_32), [33](#_ENREF_33)]

These facts were presented at the Gordon Conference on Water in the summer of 2010 and led to an invitation to write a Frontiers article that appeared on the cover of Chemical Physics Letters.[[10](#_ENREF_10)] See also [[11](#_ENREF_11)]. This article was invited by Rich Saykally a physical chemist at University of California at Berkeley and a member of the National Academy of Sciences (USA). At the same time, Mark Ratner and George Schaatz, also members of the National Academy in physical chemistry, invited Bob to write an article showing why the simulations of molecular dynamics have so far not been able to deal with the solutions that life exists in.[[9](#_ENREF_9)]

The key challenge here is that in ionic solutions everything interacts with everything else and a mathematics is needed that will accommodate interactions in a constrained way without an indefinite number of unknown parameters. The energetic variational method of Chun Liu [[3](#_ENREF_3), [20](#_ENREF_20), [22](#_ENREF_22), [25](#_ENREF_25), [27](#_ENREF_27), [28](#_ENREF_28), [30](#_ENREF_30), [31](#_ENREF_31), [34](#_ENREF_34)] applied to electrolyte solutions [[13](#_ENREF_13), [21](#_ENREF_21), [23](#_ENREF_23), [24](#_ENREF_24), [26](#_ENREF_26), [29](#_ENREF_29), [30](#_ENREF_30)] does this. Mathematical problems that prevented such treatments [[18](#_ENREF_18), [19](#_ENREF_19)] have been solved by Chun and his community.

The importance of these questions has been recognized by the physical chemistry community, along with the (so far unproven) possibility that the variational method may actually solve problems outstanding for a century or so. Bob was invited to write a long review about how he approaches problems of ions in solution and channels and it has recently appeared.[[12](#_ENREF_12)] This article was invited by Stuart Rice, a recent recipient of the Wolf Prize and the National Medal of Science.

The physical chemistry community evidently wants to learn more of this variational approach and so nominated Bob to be a Visiting Professor (four months) in the Miller Institute of the University of California at Berkeley and the Department of Chemistry. This position is highly competitive between Departments many of which at Berkeley are among the best anywhere, including Chemistry. Awards have rarely been given to people ‘unqualified’ in their field. (Bob is biophysicist and biomathematicians somewhat, not a physical chemist by training.) So it was a pleasant surprise to hear that Bob received the award. It was particularly pleasant in a personal way to have critical thoughts well received by the targets of the criticisms, since the biophysical community in which Bob was raised (Ph.D. in Biophysics, Univ. of London 1965; A.B. summa in Biochemical Sciences, Harvard College, 1963) had not responded kindly to an equally serious criticism published some 25 years ago [[1](#_ENREF_1), [2](#_ENREF_2), [5-8](#_ENREF_5), [15-17](#_ENREF_15)] despite the general acceptance of the criticism nowadays. (The earlier criticism is a subset of the recent work.)

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