Rate Constant Models cannot Describe Movement of Charged Atoms or Molecules

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Summary

Rate constant models built on laws of mass action are used widely to describe movement of ions and electric current through channels, and chemical reactions of charged substrates. But mass action laws are derived from conservation of mass and say nothing about electric charge. Laws of electricity (Maxwell’s equations: a generalization of Kirchoff’s current law) are about conservation of charge, not mass. In classical rate models, flows of ions are not correlated by laws of electricity. But Maxwell’s equations strongly correlate flows of charge (including displacement current), without known exception, within one part in $10^{18}$ or so. Correlation coefficients (describing correlated flows of charges in rate models) should then be nearly one, something like $0.9999999999999999999$. Correlations of charge movement are ignored in classical rate models, so classical rate models cannot describe movements of charged atoms or molecules with one set of rate constants over a range of conditions.

A proof goes like this:

Consider the spatial series of reactions

$$X \rightleftharpoons Y \rightleftharpoons Z$$

Currents in a series of reactions analyzed by mass action are not (in general) equal:

$$I_{XY} = z_x k_{XY} [X] - z_y k_{YX} [Y]; \quad I_{YZ} = z_y k_{YZ} [Y] - z_z k_{ZY} [Z]$$

Kirchoff’s current law requires $I_{XY} = I_{YZ}$ under all circumstances and conditions.

Details can be found at http://arxiv.org/abs/1409.0243 on the physics archive.

The artificial difference $I_{XY} - I_{YZ}$ can have large effects. It can produce net charge and electric fields strong enough to break down membranes, proteins, chemical bonds, and even ionize atoms, because of the enormous strength of the electric field, as described unforgettable in p.1-1, of "Feynman’s Lectures on Physics, Vol. 2, Mainly Electromagnetism..."

http://www.feynmanlectures.caltech.edu/III_toc.html.

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