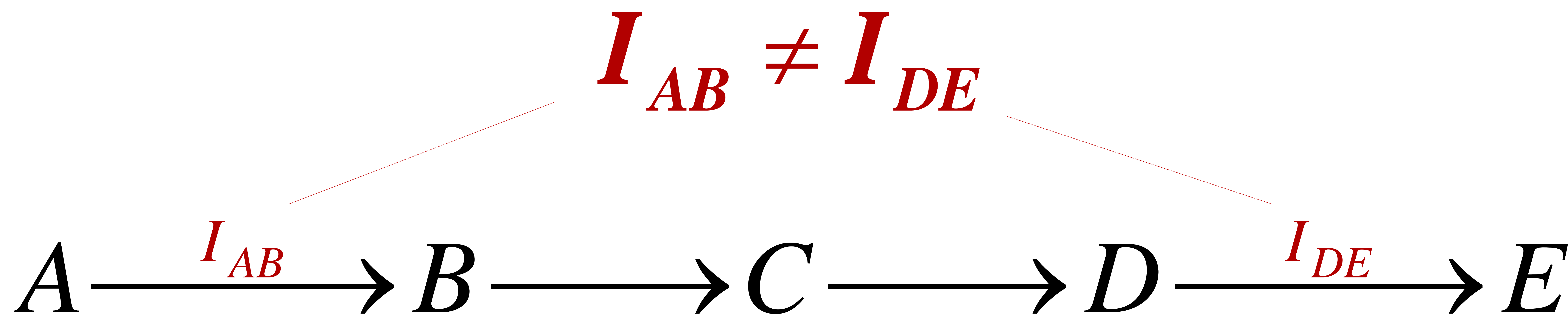


Bob Eisenberg, Rush University, Chicago IL USA beisenbe@rush.edu

Current Flow is NOT the Same in a Series of Mass Law Reactions



Abstract

Rate Models do Not Conserve Current

Rate constant models built on laws of mass action are used widely to describe ions moving 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 0.999 999 999 999 999.

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



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

$$I_{XY}/F = z_X k_{XY}[X] - z_Y k_{YX}[Y]; \quad I_{YZ}/F = z_Y k_{YZ}[Y] - z_Z k_{ZY}[Z]$$

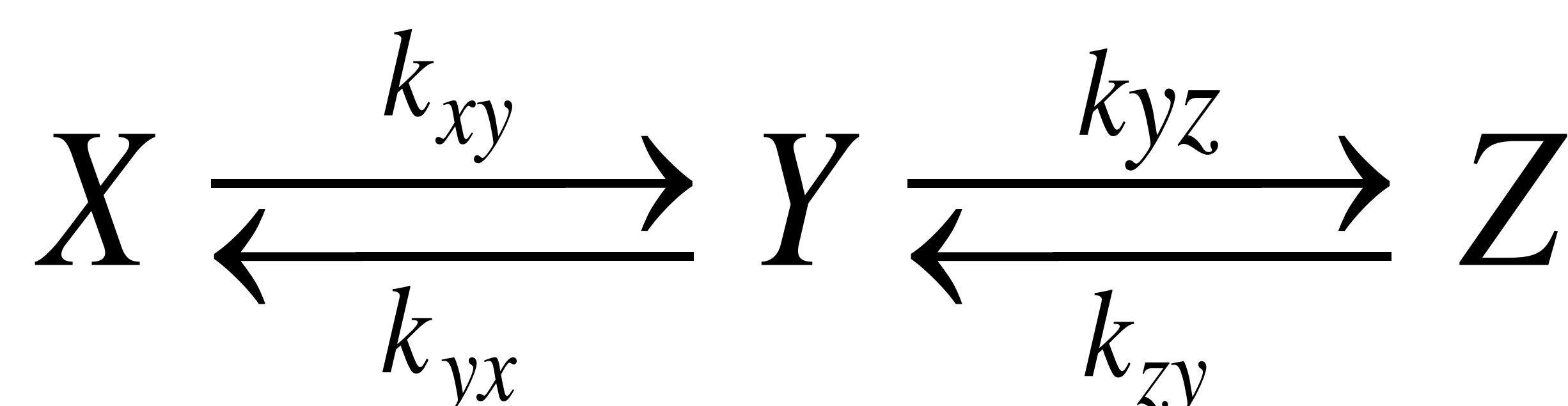
Kirchoff's current law requires $I_{XY} = I_{YZ}$ under all circumstances and conditions.

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

The artifactual 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 unforgettably in p.1-1, of

"Feynman's Lectures on Physics, Vol. 2, Mainly Electromagnetism..."
http://www.feynmanlectures.caltech.edu/II_toc.html.

Law of Mass Action



In equations

$$J_{xy}^{net} = k_{xy}[X] - k_{yx}[Y]$$

$$J_{yz}^{net} = k_{yz}[Y] - k_{zy}[Z]$$

which implies

$$I_{XY} = Fz_X \cdot k_{xy}[X] - Fz_Y \cdot k_{yx}[Y]$$

$$I_{YZ} = Fz_Y \cdot k_{yz}[Y] - Fz_Z \cdot k_{zy}[Z]$$

Obviously,

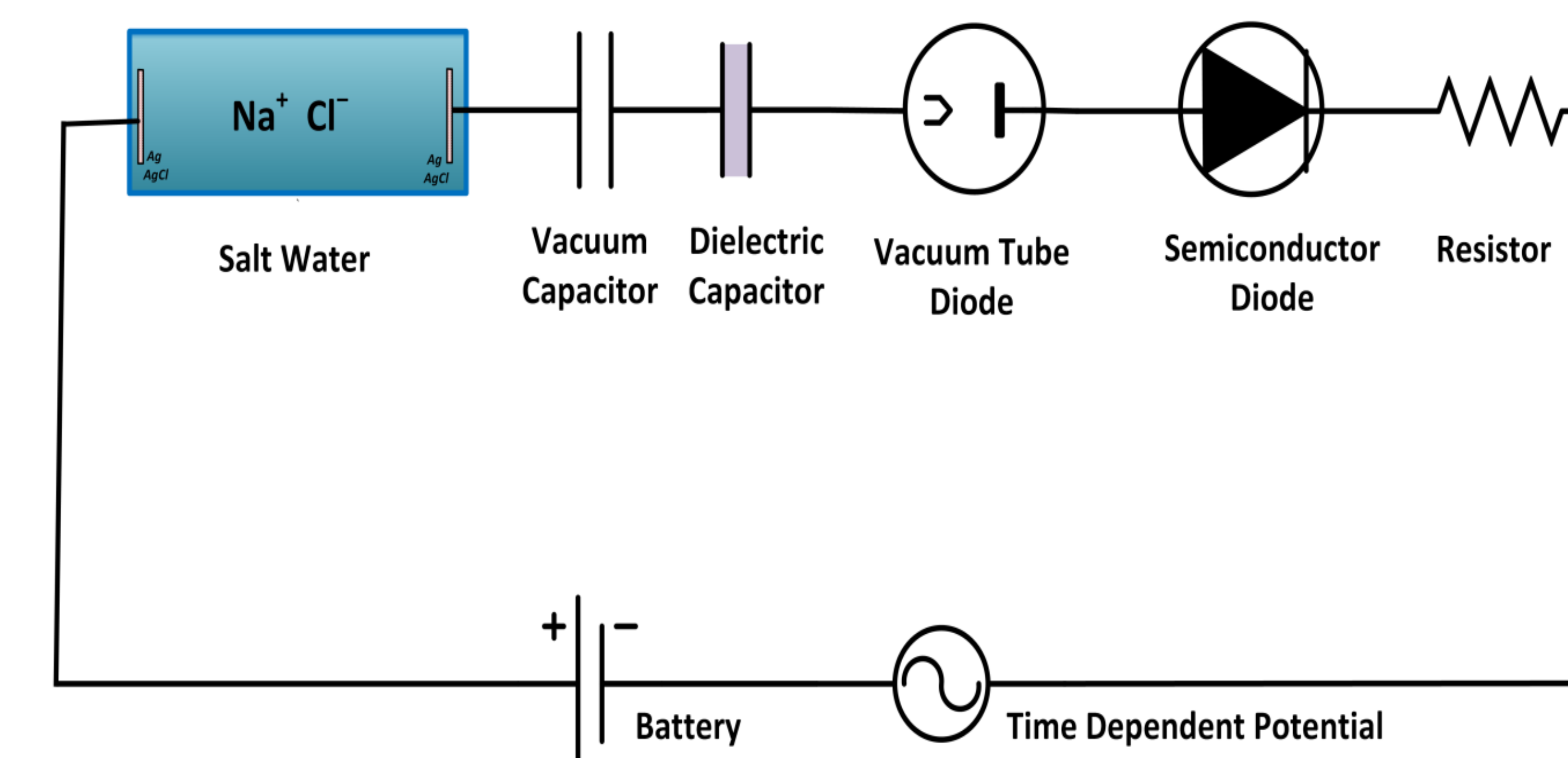
$$I_{xy} \neq I_{yz}$$

Except in artificially special symmetrical situations, like

$$I_{xy} - I_{yz} = 0 = z_X k_{xy} - z_Y k_{yx} - z_Y k_{yz} + z_Z k_{zy}$$

$$\text{with } [X] = [Y] = [Z] = 1 \frac{\text{mole}}{\text{liter}}$$

Conservation of Current CURRENT IS THE SAME EVERYWHERE in a series system



CONCLUSION Law of Mass Action Does NOT Conserve Current in general

SIZE OF EFFECT

Electrical Field Dominates
1% charge imbalance
at one meter distance
lifts the earth

Feynman:
p.1-1 of "Mainly Electromagnetism"

1% concentration gradient
does
almost nothing