Electric Field is Strong

The Electric Field is Special

The Electric Field is Strong

"If you were standing at arm's length from someone and each of you had

***One percent* more electrons than protons,**

**the force
would lift the**

Entire Earth!"

**slight paraphrase of third paragraph, p. 1-1 of
Feynman, R. P., R. B. Leighton, and M. Sands. 1963. *The
Feynman: Lectures on Physics, Mainly Electromagnetism
and Matter.* New York: Addison-Wesley Publishing Co.,
also at *http://www.feynmanlectures.caltech.edu/II_toc.html.***

The Electric Field is Special

The Electric Field is Strong

Electrons are points < 10^{-22} m
Maxwell Equations are Universal,
true on all known time scales and distances, with
quantum interpretations, e.g., Casmir effect

Electrostatics and Chemistry

"...**all forces**
on atomic nuclei in a molecule
can be considered as
purely classical attractions
involving
Coulomb's law"

"The electron cloud distribution is prevented from
collapsing by obeying Schrödinger's equation."

R.P. Feynman (1939)
Forces in Molecules.
Physical Review 56: 340.

Maxwell Equations are Special

Continuity of Current is Exact
no matter what carries the current

even though

Physics of Charge Flow
Varies Profoundly
even Creating Plasmas!

> **'Charge' is an Abstraction**
> **with**
> **VERY different Physics**
> **in different systems**
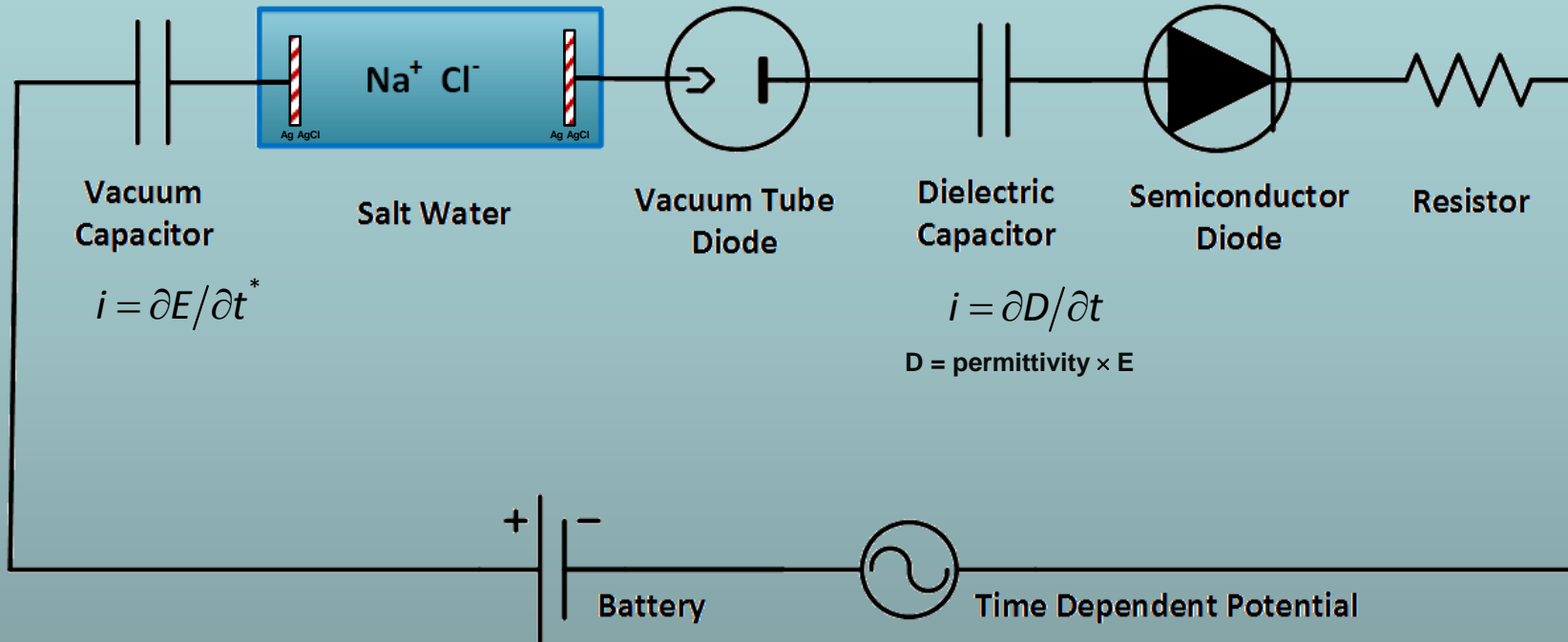
Maxwell's Equations

are about

Conservation of Charge

and continuity of current, including displacement current

'Charge' is an Abstraction

with different Physics
in different systems

'Charge' is an Abstraction with different Physics in different systems

Vacuum Capacitor

$$i = \partial E / \partial t^*$$

Salt Water

Na^+ Cl^-

Ag AgCl   Ag AgCl

Vacuum Tube Diode

Dielectric Capacitor

$$i = \partial D / \partial t$$

D = permittivity × E

Semiconductor Diode

Resistor

+ − Battery

Time Dependent Potential

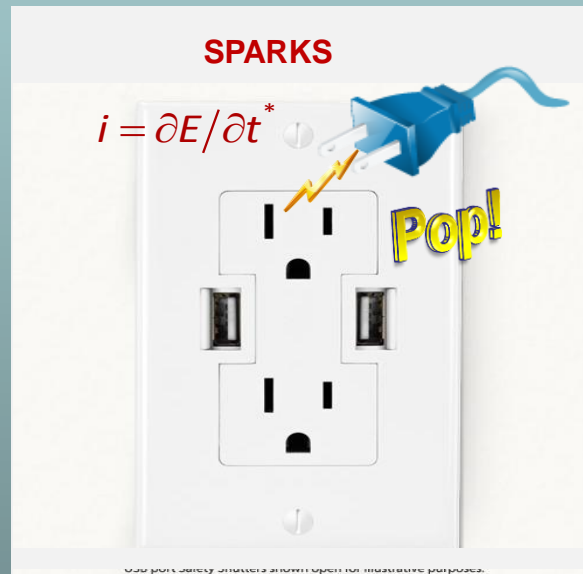*but* **Continuity of Current is Exact**

No matter what carries the current!

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**Next two slides are for fun
and GENERAL education**

**They are not part of the logical
argument**

Continuity of Current is Exact
even though
Physics of Charge Flow

Varies Profoundly

even
Creating Plasmas in air

SPARKS

$$i = \partial E / \partial t^{*}$$

Pop!

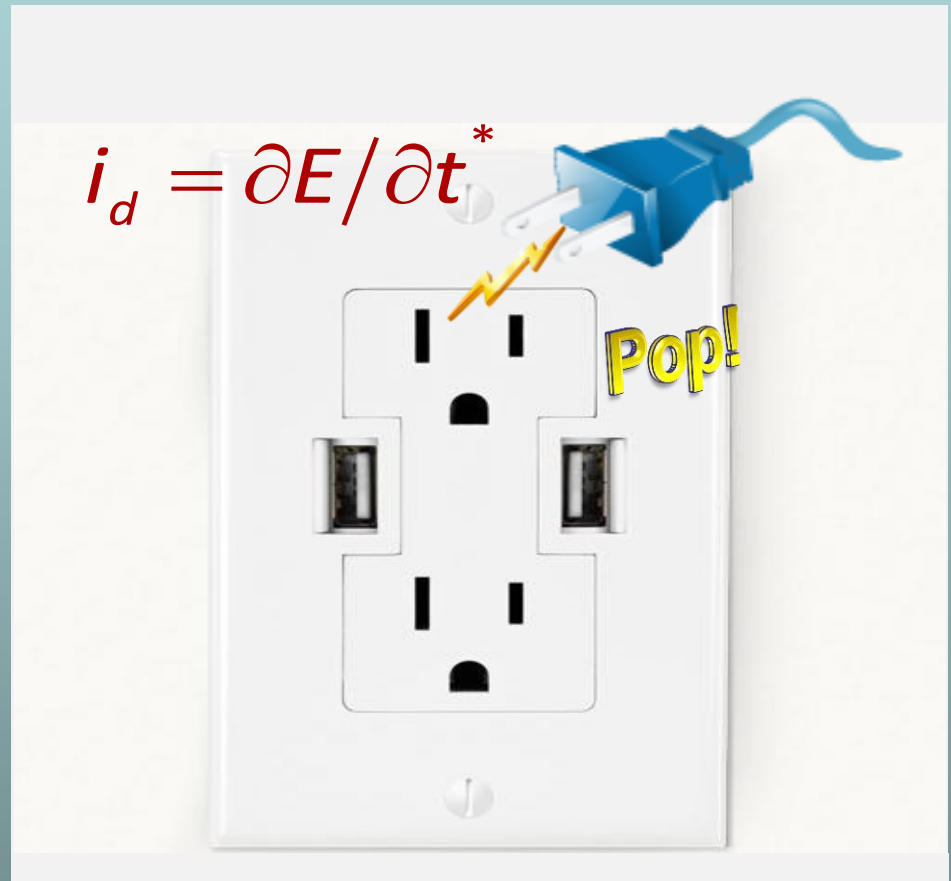USB port Safety Shutters shown open for illustrative purposes.

*speaking loosely

Mathematics of Continuity
in Maxwell equations can
Create New Kind of Physics,
New Kind of Charge

When we unplug a computer power supply,
    we often
    CREATE
     SPARKS,
*i.e., a **PLASMA,***

 *a **NEW KIND***
 of current flow

$$i_d = \partial E / \partial t^*$$

Pop!

Back to the logical argument

Maxwell's Equations

are about

Conservation of Charge

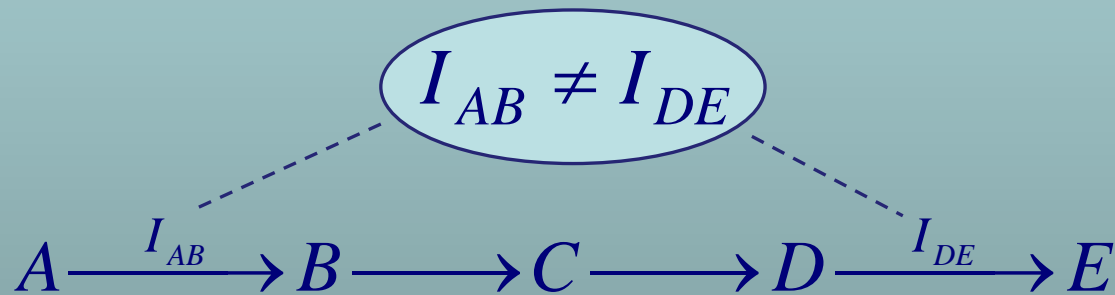**and continuity of current, including displacement current**

Rate Models Fail

because

'Current-in'

does not equal

'Current-out'

if rate constants are independent of potential

$$I_{AB} \neq I_{DE}$$

$$A \xrightarrow{I_{AB}} B \longrightarrow C \longrightarrow D \xrightarrow{I_{DE}} E$$

but **Kirchoff Current Law** *(i.e., Maxwell Eqns)*

requires

$$I_{AB} = I_{DE}$$

Kirchoff Current Law
requires

$$I_{AB} = I_{DE}$$

under all conditions

ALWAYS $\pm\, 6 \times 10^{-17}$, *or so*

Kirchoff Current Law
and
Maxwell Equations
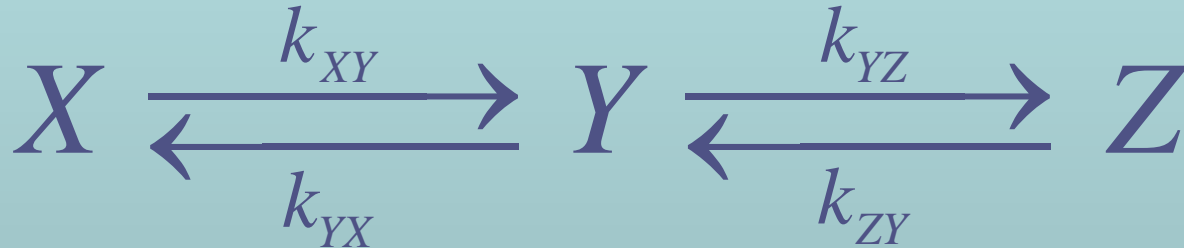## are nearly the same thing

Bhat & Osting (2011). IEEE Trans Antennas and Propagation 59: 3772-3778
Heras (2007) American Journal of Physics 75: 652-657
Heras (2011) American Journal of Physics 79: 409
Itzykson & Zuber Quantum Field Theory (1990) p. 10

Rate Models Fail
because
Current-in does not equal Current-out!!
(if rate constants are independent of potential)

$$X \; \underset{k_{YX}}{\overset{k_{XY}}{\rightleftharpoons}} \; Y \; \underset{k_{ZY}}{\overset{k_{YZ}}{\rightleftharpoons}} \; Z$$

$$J_{XY} = k_{XY}[X] - k_{YX}[Y]; \quad J_{YZ} = k_{YZ}[Y] - k_{ZY}[Z]$$

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

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

Kirchoff's Current Law = Maxwell's Equations

Correlation coefficient 0.999 999 999 999 999 999

**EVERYTHING
INTERACTS
WITH
EVERYTHING ELSE**
including the boundaries 'at infinity'

Artifactual Charge is Produced by $I_{XY} - I_{YZ}$

$$I_{XY} = Fz_X \cdot k_{XY}\left[X\right] - Fz_Y \cdot k_{YX}\left[Y\right]$$

$$I_{YZ} = Fz_Y \cdot k_{YZ}\left[Y\right] - Fz_Z \cdot k_{ZY}\left[Z\right]$$

The Electric Field is Strong

If you were standing at arm's length from someone and each of you had

***One percent* more electrons than protons,**

**the force
would lift the
Entire Earth!**

Violation of Continuity of Current

Set all concentrations and rate constants to one

$$\frac{I_{YZ}}{I_{XY}} = \frac{z_Y - z_Z}{z_X - z_Y}$$

Set all concentrations and valences to one

$$\frac{\hat{I}_{YZ}}{\hat{I}_{XY}} = \frac{k_{YZ} - k_{ZY}}{k_{XY} - k_{YX}}$$

Effects are Huge
much more than 1%

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

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

The Electric Field is Strong

Artifactual Charge can create Artifactual Results

Artifactual Charge
can
inactivate channels
denature enzymes
breakdown membranes
protonate weak bases
even strip electrons off atoms, destroying compounds

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How improve law of mass action?

Rate Constants
must depend on
Electrical Potential
EVERYWHERE

Everything is hidden

in K_{eq}, k_f and k_b

Interactions exist:
*k's and K **are function(al)s***
not constants

Parameterization is not Possible

under more than one condition

**Rate constants chosen at one boundary charge or one potential
cannot work for different charges or potentials.**

Different Boundary Charges or Potentials
<u>Change Currents</u>

in the real world

but

Currents in Rate Models

are

Independent of Charge and Potential

How improve law of mass action?

Rate Constants
**must be determined
from Differential Equations or
a Variational Principle**

Physical Chemists are Frustrated by Real Solutions

It is not surprising that
Inconsistent Treatments
of ionic solutions
have been so
Unsuccessful
despite more than a century of work by fine scientists and mathematicians

There are no successful theories of ionic conductance, and no successful theories of properties of ionic mixtures even at equilibrium.

No simulations even address the properties of ionic mixtures or ionic conductance.

Good Data

Good Data
Compilations of Specific Ion Effect

1.   **>152,076 Data Points** [Oct 2014] *on-line*
        IVC-SEP Tech Univ of Denmark
        http://www.cere.dtu.dk/Expertise/Data_Bank.aspx

2.   Kontogeorgis, G. and G. Folas, *2009:*
                Models for Electrolyte Systems. Thermodynamic
                        John Wiley & Sons, Ltd. 461-523.

3.   Zemaitis, J.F., Jr., D.M. Clark, M. Rafal, and N.C. Scrivner, *1986,*
                Handbook of Aqueous   Electrolyte Thermodynamics.
                        American Institute of Chemical Engineers

4.   Pytkowicz, R.M., *1979,*
                Activity Coefficients in Electrolyte Solutions. Vol. 1.
                        Boca Raton FL USA: CRC. 288.

The classical text of Robinson and Stokes
(not otherwise noted for its emotional content)
gives a glimpse of these feelings when it says

"In regard to concentrated solutions, many workers adopt a counsel of despair, confining their interest to concentrations below about 0.02 M, ... "

p. 302 *Electrolyte Solutions* (1959) Butterworths , also Dover (2002)
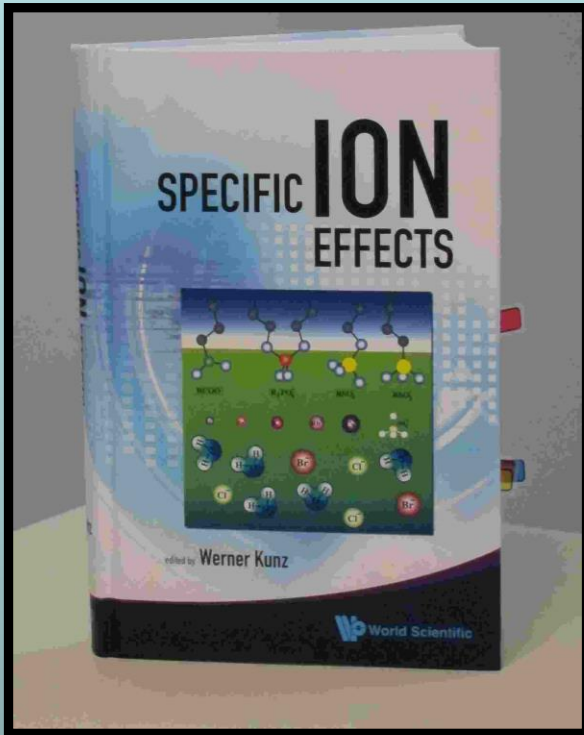
Kunz, W. "**Specific Ion Effects**"
World Scientific Singapore, 2009; p 11

Werner Kunz
"It is still a fact that over the last decades,

it was easier to fly to the moon

than to describe the

free energy
of even the simplest salt solutions

beyond a concentration of 0.1M or so."

Physical Chemists will be Frustrated by Real Solutions

until

Everything Interacts with Everything Else

in their theories and simulations
including the

Special Role of the Electric Field
Strong, Global, true on all scales

A poet hopes we will never learn the difference between dreams and realities

"Ah, but a man's reach should exceed his grasp,

Or what's a heaven for?"

Robert Browning
"Andrea del Sarto", line 98.

Scientists must Grasp

and not just reach

That is why calibrations are necessary

Otherwise,
progress is slow and machines and devices do not work

Reconciling

Mass Action

and

Maxwell-Kirchoff

will no doubt be a

Long Journey

"Journey of a thousand miles starts with a single step"

in the right direction,
I beg to add to this Chinese saying

That direction needs to include the electric field,
calculated and calibrated,
global and local,

if the journey is ever to end, in my view

Only Variational Methods Guarantee Consistency among all fields
including electric field

although, apparently,
Poisson is enough to ensure
Conservation of charge
and
Continuity of current

When the journey is done consistently, with honest calibrated simulations and theory,

it can end in

Moore's Law

Semiconductor Technology

BILLIONS* of times more powerful than 50 years ago

Nothing remotely like it in all of human history

$$^*\text{Moore's law} \Rightarrow 2^{50/2.0} = 10,822,639,409$$