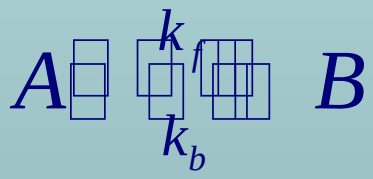
Chemistry
is about
Chemicals

not signals

Law of Mass Action

is what how chemists describe chemicals



$$-\frac{d}{dt}[A] = k_f [A]; \qquad -\frac{d}{dt}[B] = k_b [B]$$

k is constant

[A] means the activity or approximately the concentration of species A, i.e., the number density of A

Engineering

is about

Signals

not substances

Maxwell's Equations

Kirchoff's Current Law

compute

Signals

from Conservation of Charge
and
Continuity of Current,
including displacement current

Law of Mass Action

is about

Conservation of Mass and Matter

It is not about conservation of charge

$$X \underset{k_{yx}}{\overset{k_{xy}}{\rightleftharpoons}} Y \underset{k_{zy}}{\overset{k_{yz}}{\rightleftharpoons}} Z$$

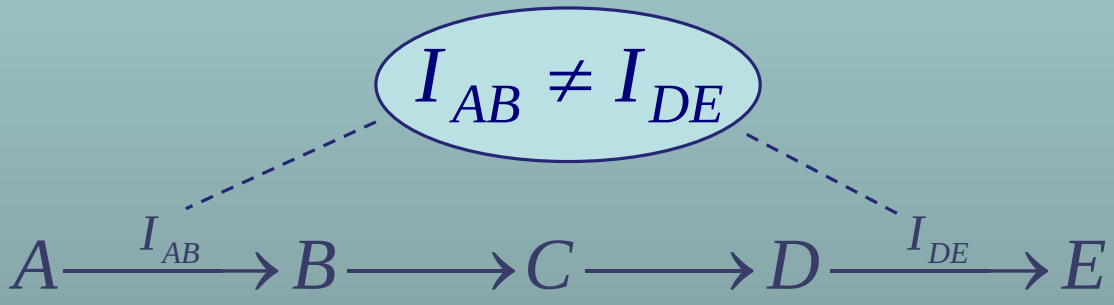
$$J_{xy}^{net} = J_{xy} - J_{yx}$$

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

$$I_{xy} = z_x F k_{xy}[X] - z_y F k_{yx}[Y]$$

[X] means the concentration, really activity of species Z, i.e., concentration is the number density

‘Current-in’
does not equal
‘Current-out’
in
Law of Mass Action



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

requires

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

More specifically

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

$$I_{AB} = \vec{k}_{AB}[A] - \overleftarrow{k}_{AB}[B]$$

$$I_{DE} = \vec{k}_{DE}[D] - \overleftarrow{k}_{DE}[E]$$

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

The discussion assumes the reactants *A, B, ….* are at different spatial locations.

The discussion assumes reactants are charged,
as they almost always are with fixed and/or permanent dipole charges

Correlation between Currents
0.999 999 999 999 999 999
because
Conservation of Charge is exact

Kirchoff Continuity of Current Law

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.

Currents in Rate Models

are

Independent of Charge and Potential

but

in the real world

Currents depend on Charge and Potential

Continuity of Current is Exact

even though

Physics of Charge Flow

Varies Profoundly

Maxwell Equations are Special

‘Charge’ is an Abstraction with VERY different Physics in different systems

Kirchoff Current Law

requires

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

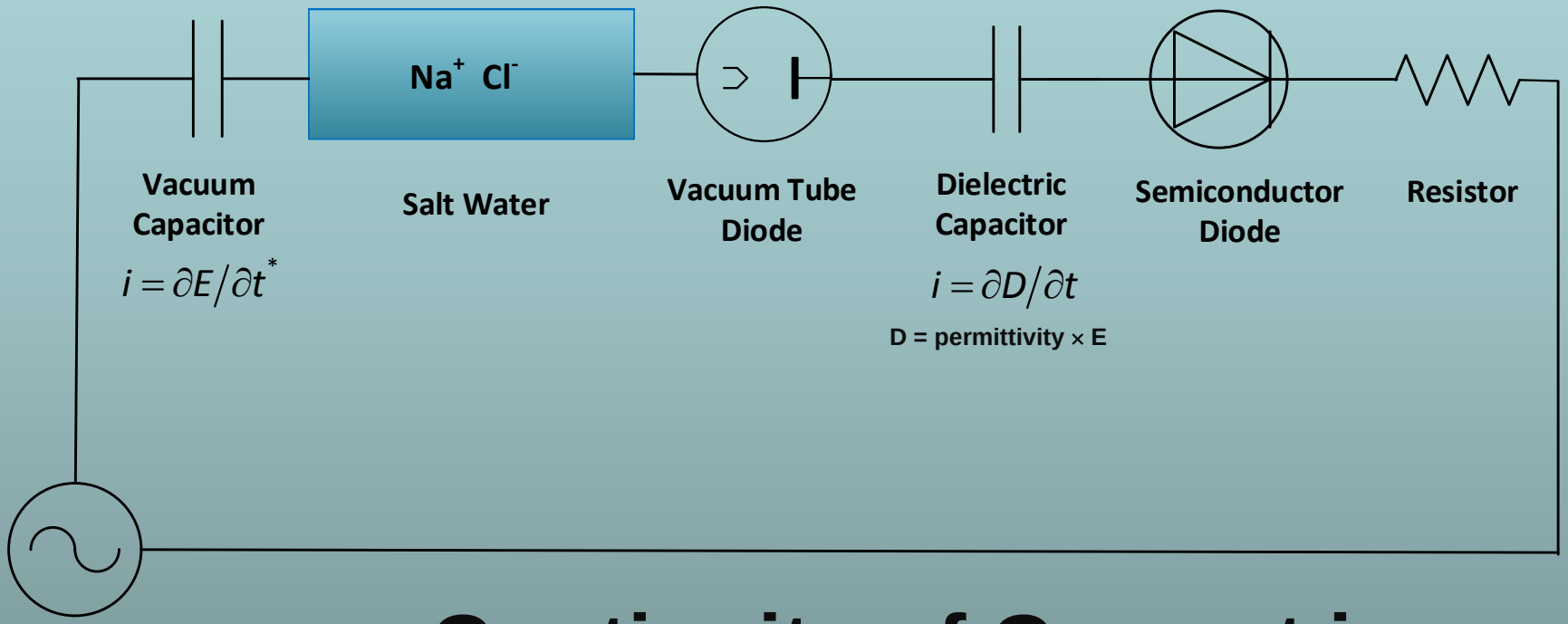
under all conditions

ALWAYS $\pm 10^{-17}$, *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

‘Charge’ is an Abstraction with different Physics in different systems



but **Continuity of Current is Exact**

No matter what carries the current!

Continuity of Current is Exact

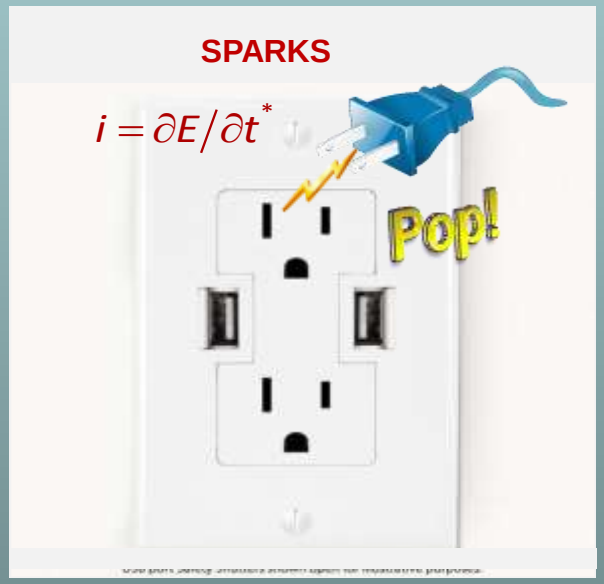
even though

Physics of Charge Flow

Varies Profoundly

even

Creating Plasmas in air



***speaking loosely**

Mathematics of Continuity

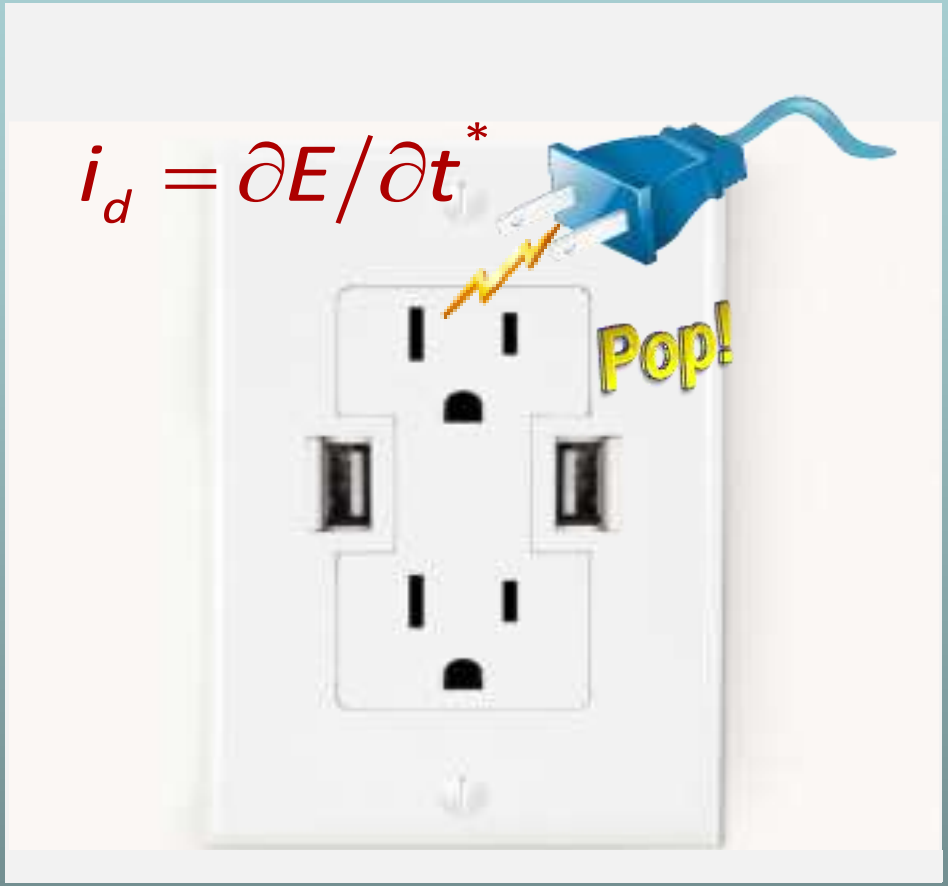
in Maxwell equations can

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



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

Replacement of "Law of Mass Action" is Feasible for Ionic Solutions

using the

All Spheres

(primitive = implicit solvent model of ionic solutions)

and

Theory of Complex Fluids

It is not surprising that

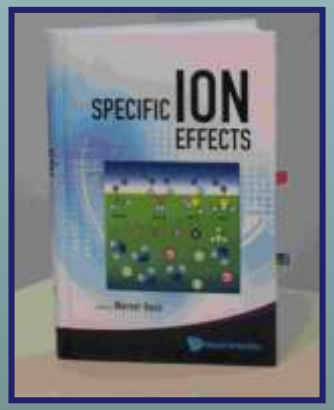
Inconsistent Treatments

of ionic solutions

have been so

Unsuccessful

despite more than a century of work by fine scientists and mathematicians



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."

Kunz, W. "**Specific Ion Effects**"
World Scientific Singapore, 2009; p 11.

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.