### Rate Models Fail because

# Current-in does not equal Current-out!!

(if rate constants are independent of potential)

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

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

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

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

#### More specifically

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

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

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

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

### Parameterization is not Possible

under more than one condition

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

## Different charges or potentials will change the currents in the real world

but

Currents in the Rate Models are Independent of Charge and Potential

## Kirchoff Current Law requires

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

### **ALWAYS**

$$\pm 10^{-17}$$
 , or so

and
Maxwell Equations
are nearly the same thing

Bhat & Osting (2011). IEEE Trans Antennas and Propagation 59: 3772-3778.

Heras (1991) American Journal of Physics 59: 111-117

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

### Continuity of Current is Exact

even though

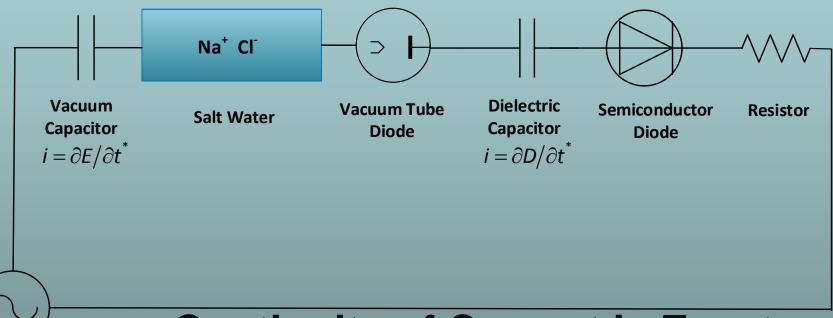
Physics of Charge Flow

Varies Profoundly

Maxwell Equations are Special

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

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



### but Continuity of Current is Exact

No matter what carries the current!

\* motaphorical aquations: displacement field D = permittivity × E

#### **Continuity of Current is Exact**

# Physics of Charge Flow Varies Profoundly

even Creating Plasmas

in air Sparks

### **Mathematics of Continuity**

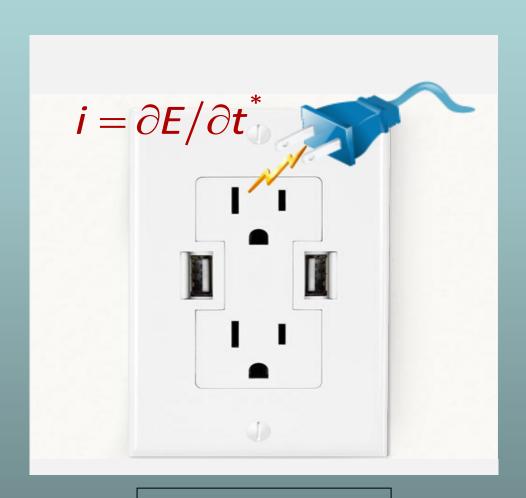
in Maxwell equations can

### 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



\*speaking loosely

### 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