Reactivity hazards and the opportunity for electrochemical reactions

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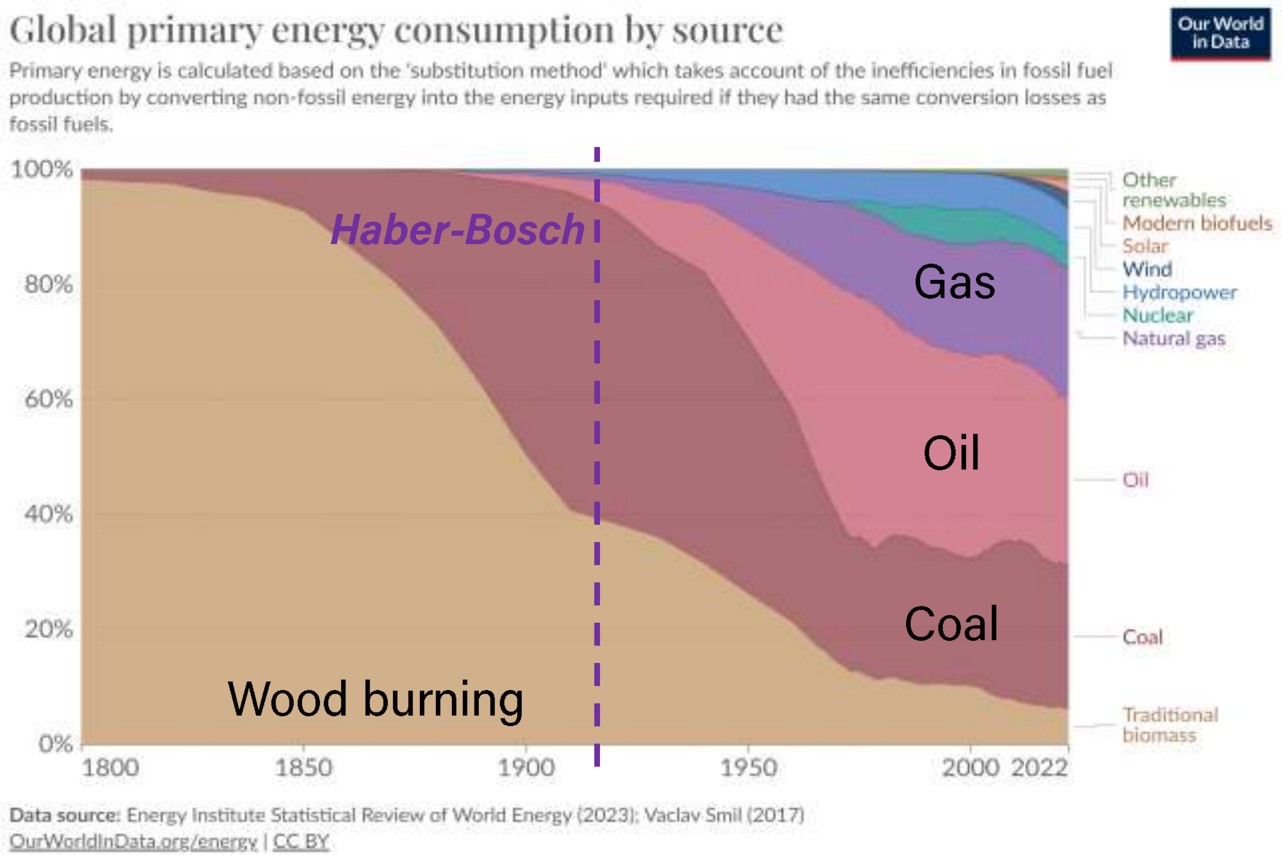
Motivation: Opportunity for Electrochemical Processes

A large majority of industrial chemical processes are heat-driven

Why do we use fossil fuel heat to produce the chemicals we need?

- Most chemical processes developed over the last ~100 years
  - **Energy only available in the form of heat** (combusting coal, oil, and gas)
- *Fuel → heat → electricity → industrial process* is inefficient, when electricity can just be cut out



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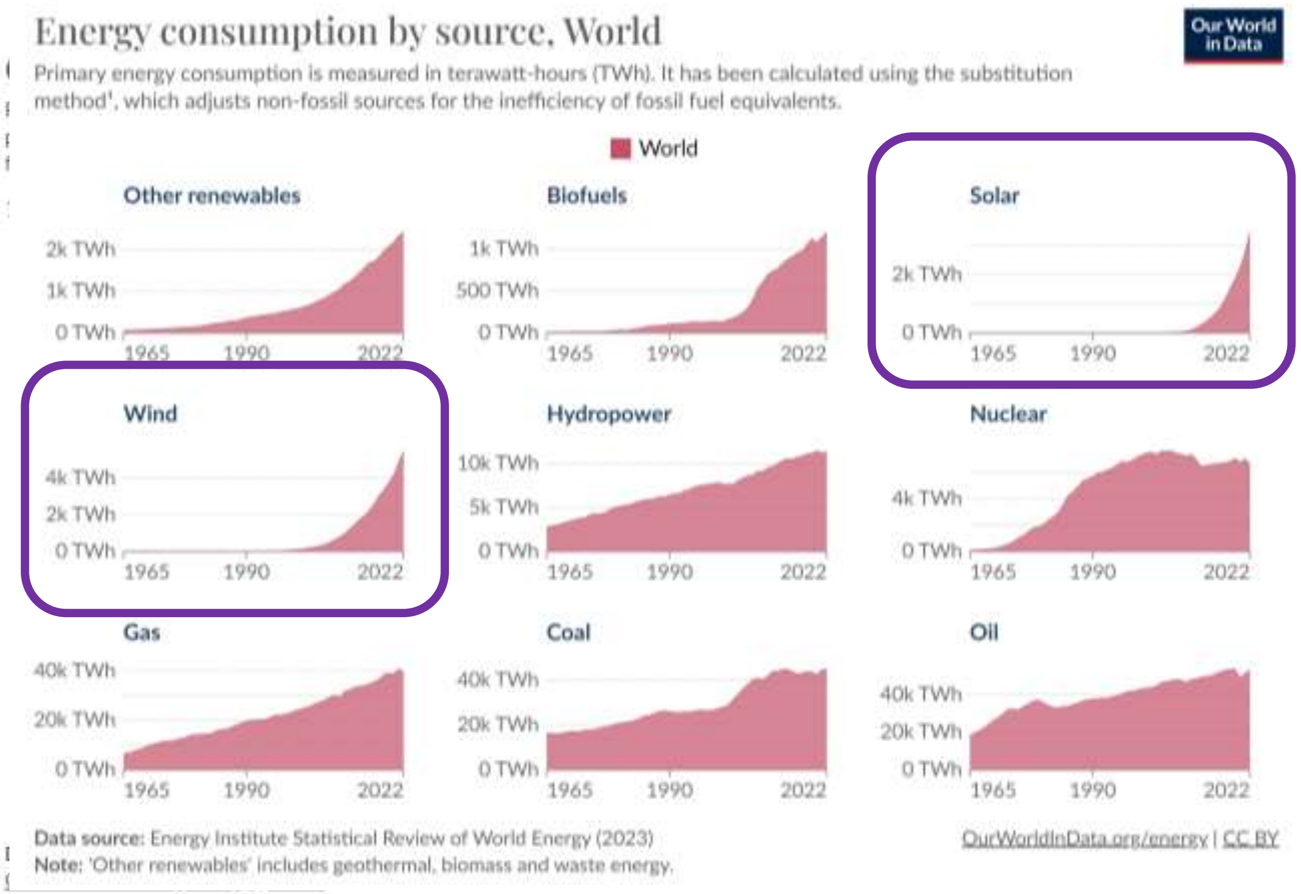
For the first time in history, we have substantial energy in the form of electricity produced via wind & solar

- **This allows us to reimagine a sustainable and electrified chemical industry**

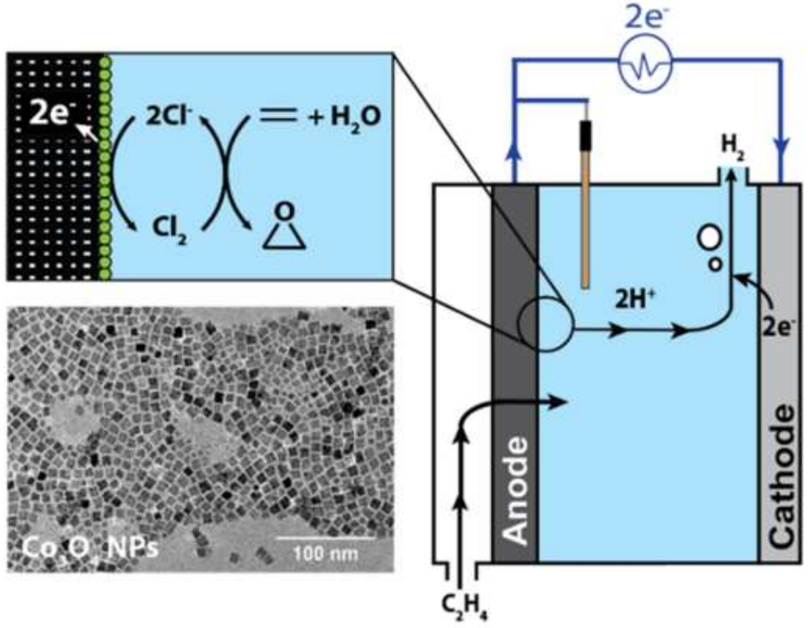


Motivation: Opportunity for Electrochemical Processes

This has sparked interest in chemical synthesis industries (commodity, specialty, fine)

→ can leverage cheap/abundant electrons to:

- Replace toxic oxidants
- Reduce operating temperatures
- Achieve selective pathways with fewer steps



Motivation: Opportunity for Electrochemical Processes

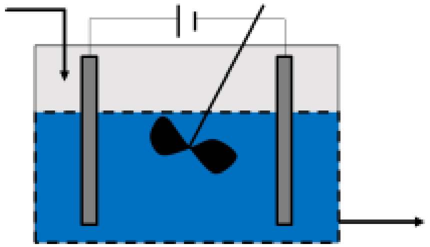
At the same time, there's a desire to move from batch to continuous processes

- ***What chemical processes could be made inherently safer if done electrochemically?***
- ***What new/different reactivity hazards should we anticipate for electrochemical systems?***

To understand, let's briefly review basic concepts of electrochemical reactions

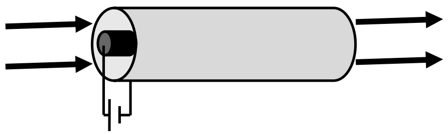
Continuous Electrochemical Reactors

Electrochemical CSTR



$$S = \frac{(F_{A0} - F_A)n\mathcal{F}}{i}$$

Electrochemical PFR



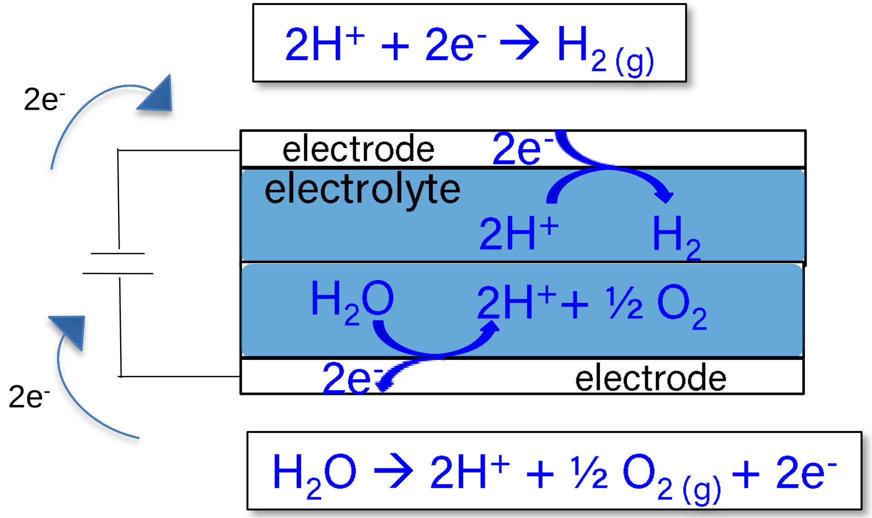
$$\frac{dC_A}{dx} = \frac{iS}{n\mathcal{F}Lv_0}$$

3 elements of an electrochemical reaction:

1. Molecular transformation where an electron (e^-) is a reactant or a product

2. Inherently heterogeneous process with at least 2 phases
   - Electron conducting phase (electrode)
   - Ion conducting phase (electrolyte)

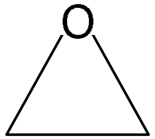
3. Contains 2 electrodes to maintain electroneutrality



- ***Current = reaction rate*** *(rate of flow of electrons)*
- ***Potential = driving force*** *(impetus for electron flow)*

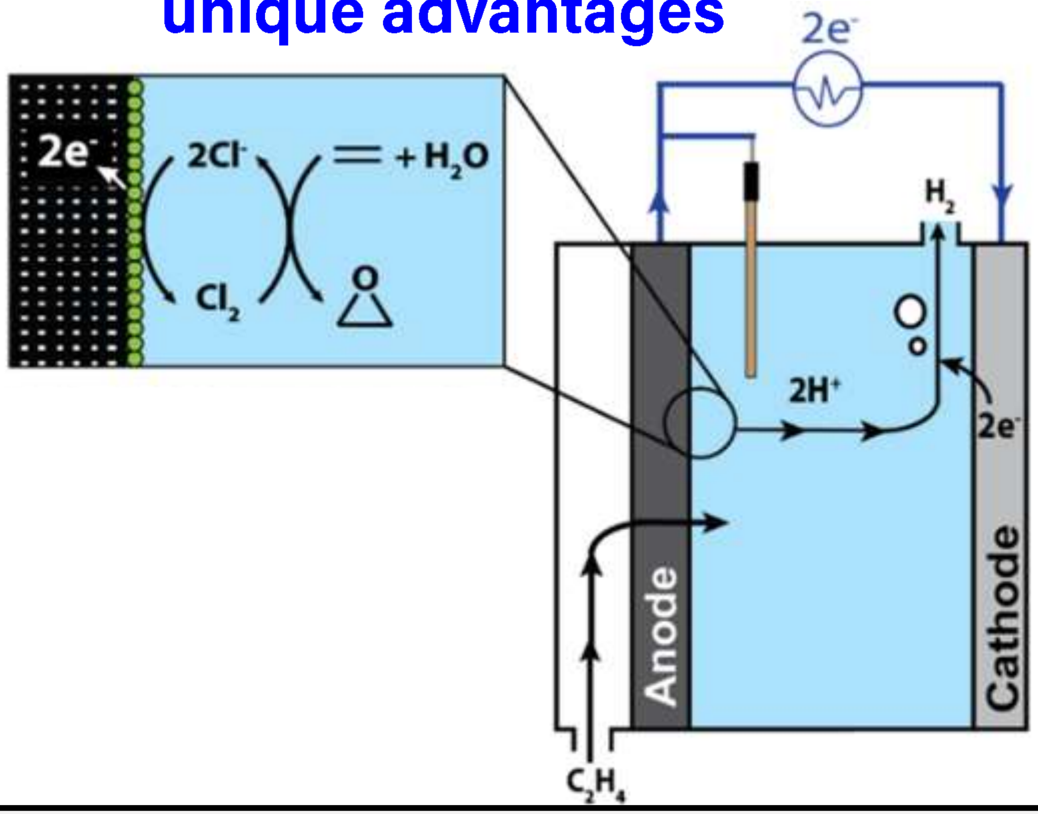
Reducing Hazards via Electrochemistry

Case Study: Ethylene Oxide Synthesis



- Cl_2 mediator is generated electrochemically at an electrode by electron transfer from aqueous Cl^- salt
  - ***No bulk Cl_2 handling or processing (replace/eliminate hazardous chemicals)***
- Cl_2 and H_2O transform ethylene to EO in the same manner as chlorohydrin process
- Resulting Cl^- ions are recycled and reinitiated as mediators
  - ***No stoichiometric waste (reduce processing steps)***
- Occurs @ 90 C
  - ***No explosion hazard (Operate at low temperature)***

→ **E-chem synthesis provides unique advantages**



What are the most compelling opportunities for electrochemistry to improve safety?

Scoping Reactivity Hazards & Electrochemical Replacements

- 100 serious accidents reported in the US over the past 25 years
- Could accident have been avoided with substitute electrochemical process? (***replace hazardous chemical, reduce processing step, operate at low T***)
  - "Maybe" = 24
  - "Yes" = 6 (often thermal runaway rxns)

Name of Incident	Year	Country	Economic Impact	Accident type	Desired Chemical Reaction (R1)	Secondary Chemical Reaction (R2)	Type of Reaction	Incident Error	Extra Notes	Valuable?	Electrochemical Intervention?
Sierra Chemical Co. High Explosives Incident	1998	US			N/A, just mixing			50-100lbs of high explosives solidified overnight and were set off by an agitator blade. This explosion detonated several thousand pounds of explosives nearby	Booster explosives would not be needed if there were simpler and safer ways to detonate the larger explosions	maybe	
Union Carbide Nitrogen Asphyxiation Incident	1998	US						Workers blocked a pipe exit to reduce the light entering the pipe while they worked, but they trapped accumulating nitrogen and this led to asphyxiation		no	no
Barton Solvents IKS Explosion and Fire	2007	US		Static Charge				Static spark ignited naphtha vapors		no	
Macondo Blowout and Explosion	2010	US	$65B	oil spill						no	
Sonat Exploration Co. Catastrophic Vessel Over pressurization	1998	US	$200,000				Combustion	In the process of purging a new well with hydrocarbons, flammable gases were released after vessel failure and the gases ignited. Outlet and block valves that could have been used to vent the purge gases were closed.		no	
Tosco Avon Refinery Petroleum Naphtha Fire	1999	US	$41M				Naphtha ignition	Workers were fixing a leak while the unit remained active and without being able to successfully drain the 90 gallons of naphtha. Naphtha escaped from the open end of pipe and ignited from the hot fractioner surface		no	
Concept Sciences Decomposition Explosion	1999	US			Hydroxylamine Sulfate (NH2OH * H2SO4) + 2 Potassium Hydroxide = Hydroxylamine + Potassium Salt + Water	Hydroxylamine's explosive decomposition (fueled by high Temp and Concentration, ~equivalent to TNT by weight)		Hydroxylamine (HA) was left in a shut down tank and piping and subsequently explosively decomposed (crystals of HA are explosively unstable)	Electrochemical method must control concentration more effectively. There may be electrochemical methods of producing the goods that need HA	yes	yes

Case Study: Hydroxylamine Synthesis

The incident

- Feb 19, 1999, Allentown, PA
  Concept Sciences Inc.
  Produce 50 wt% hydroxylamine – used in semiconductor industry and in fine/specialty chem.

- Process:
  - **Reaction**:
    $(NH_2OH)_2{*}H_2SO_4 + 2KOH \rightarrow 2NH_2OH + K_2SO_4 + 2H_2O$
  - **Filtration**: remove K_2SO_4 precipitates
  - **Vacuum Distillation**: concentrate 30% HA to 50% HA
  - **Final Purification**: via ion exchange cylinders

- **Hazard**: Hydroxylamine (NH_2OH) solid crystals/solutions decompose explosively at high concentration, especially when heated

Case Study

U.S. Chemical Safety and Hazard Investigation Board

The Explosion at Concept Sciences: Hazards of Hydroxylamine

No. 1999-13-C-PA
March 2002


Tom Volk, The Morning Call

CONCEPT SCIENCES, INC.
Hanover Township, Pennsylvania
February 19, 1999

Introduction

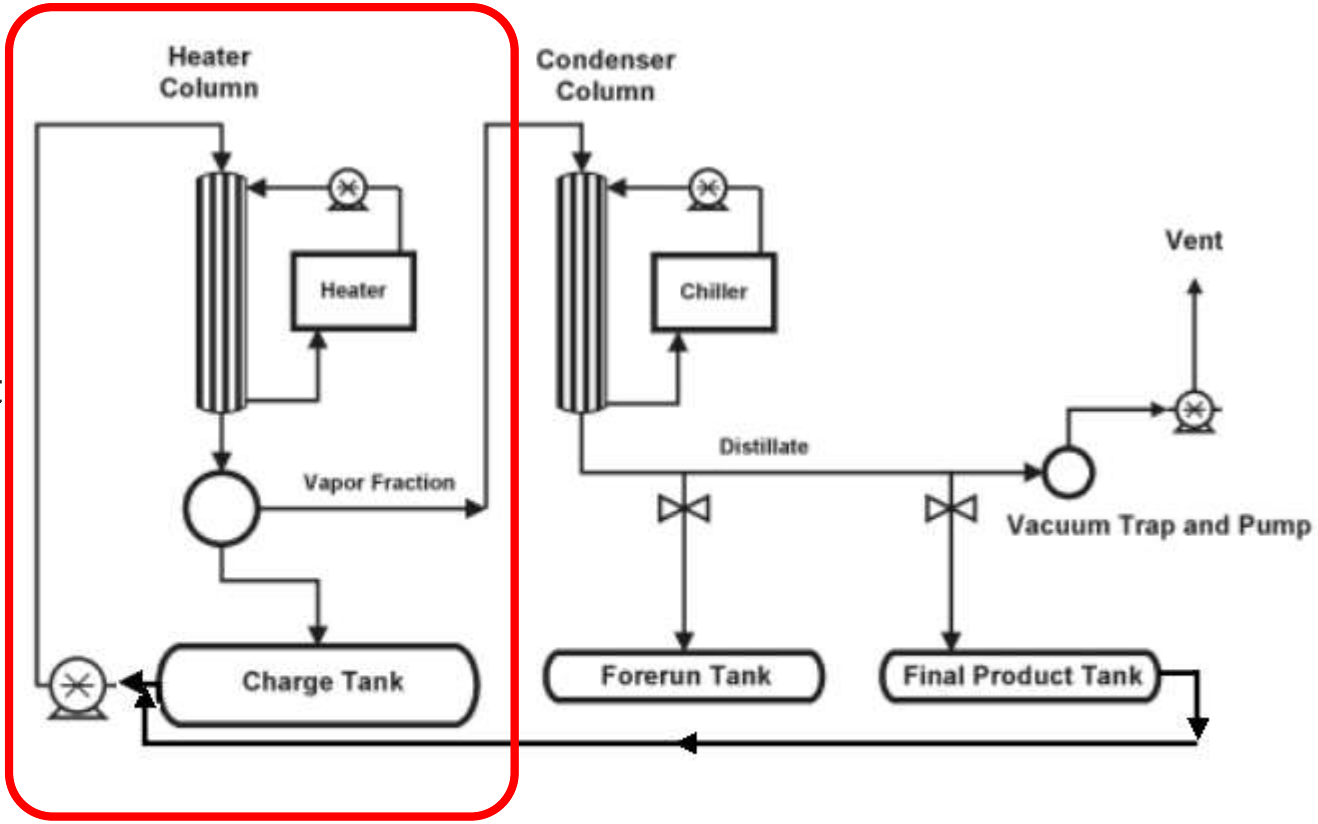
This Case Study describes a catastrophic hydroxylamine (HA) explosion that occurred on February 19, 1999, at the Concept Sciences, Inc. (CSI), facility in Hanover Township, Lehigh County, Pennsylvania. Four CSI employees and one employee of an adjacent business were killed; 14 people were injured.

The incident

- Vacuum Distillation
  - Distill charge (reactor effluent) and condense into forerun tank until 10 wt% HA
  - Divert distillate to final product tank until 45 wt%
  - Shut of charge tank, re-distill 45 wt% from final product tank until 50 wt%

On the day of the incident, some feed lines were repaired, and HA concentration in the charge tank increased to 85 wt%. There was concern over crystal formation (likely at HA > 80%) in the heater column, so second distillation was not performed.

Explosion occurred ~30 minutes after still was shut down



High temp likely initiated explosive decomposition (similar incident occurred in Japan ~1 year later)

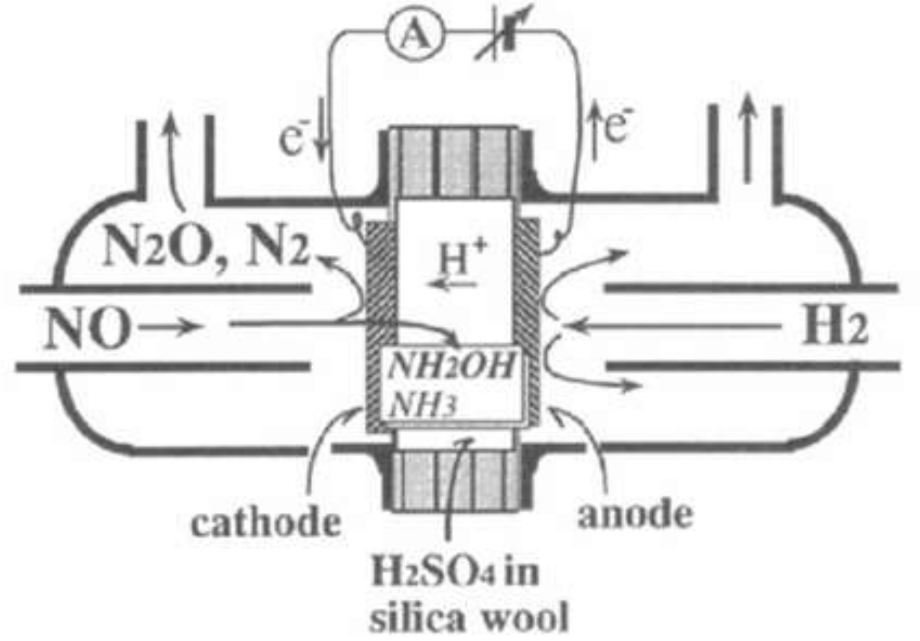
Case Study: Hydroxylamine Synthesis

Electrochemical Alternative

- Electrocatalytic hydrogenation of NO to hydroxylamine

$$NO + 3H^+ + 3e^- \rightarrow NH_2OH$$
$$E^0 = 0.34\ V$$
$$T = 25\ °C$$

Selectivity to NH_2OH(%)	Conversion of NO (%)
90	6.4
99	15.2
93	17.6
72	2.8



Galenko, et al. *Journal of the Electrochemical Society* **1996**, 143 (11), 3491

Next Steps

- Complete case studies from other "yes" scenarios and explore relevant electrochemical literature

- Prescribe needed electrochemical improvements (and pursue them experimentally)

Long term: create a generalized framework to map the impact and feasibility of hazard reduction via electrochemistry

3 | CASE STUDY 1: HYDROXYLAMINE

a) Material Properties and Uses
b) Incident Details
c) Traditional Synthesis Method
d) Electrochemical Synthesis Method
e) Additional Notes

4 | CASE STUDY 2: MONONITROTOLUENE

a) Material Properties and Uses
b) Incident Details
c) Traditional Synthesis Method
d) Electrochemical Synthesis Method
e) Additional Notes

5 | CASE STUDY 3: ACRYLIC POLYERMIZATION

a) Material Properties and Uses
b) Incident Details
c) Traditional Synthesis Method
d) Electrochemical Synthesis Method
e) Additional Notes

6 | CASE STUDY 4: ACETYLENE

a) Material Properties and Uses
b) Incident Details
c) Traditional Synthesis Method
d) Electrochemical Synthesis Method
e) Additional Notes

7 | CASE STUDY 5: REFRIGERATION

a) Material Properties and Uses
b) Incident Details
c) Traditional Synthesis Method
d) Electrochemical Synthesis Method
e) Additional Notes

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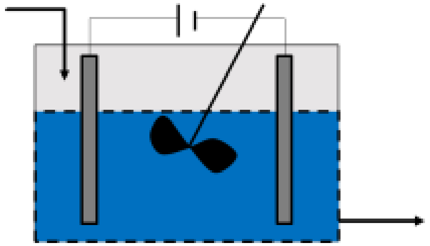

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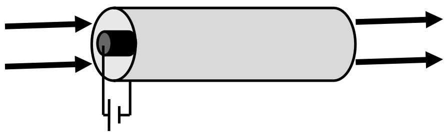
Electrochemical PFR

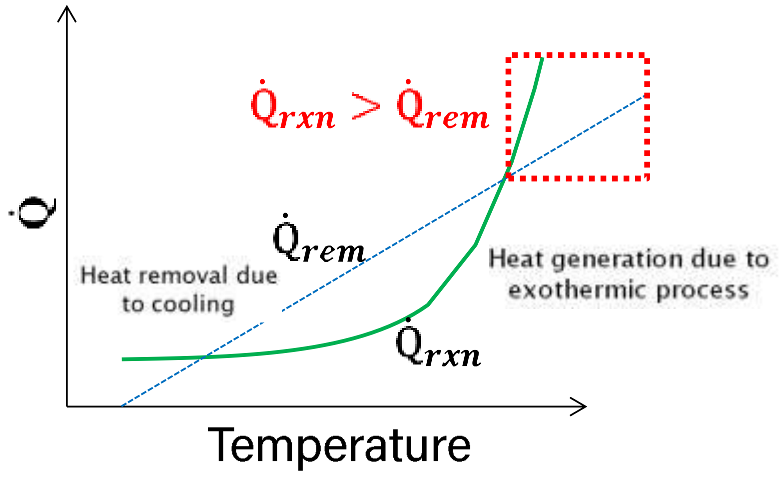


$$\frac{dC_A}{dx} = \frac{iS}{n\mathcal{F}Lv_0}$$

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Runaway Reactions



- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

Electrochemical Reactors

Runaway Reactions?

- Echem rxns don't experience substantial T effects as result of reaction
- Energy of reaction manifests as electron potential, rather than heat

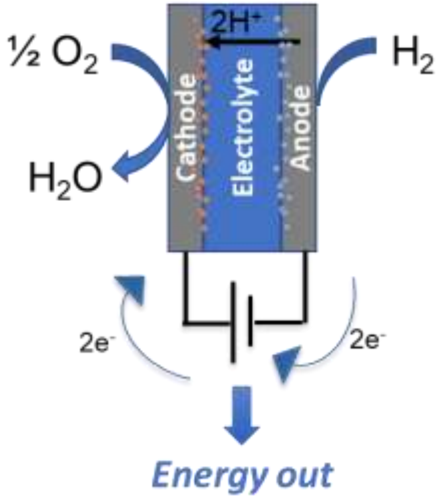
Ex)

$H_2 + ½\ O_2 \rightarrow H_2O$

$\Delta H_{rx} = -242$ kJ/mol

↓

1.23 V @ 298K
in electrochemical reactor



Reactivity Hazards for Continuous Reactors

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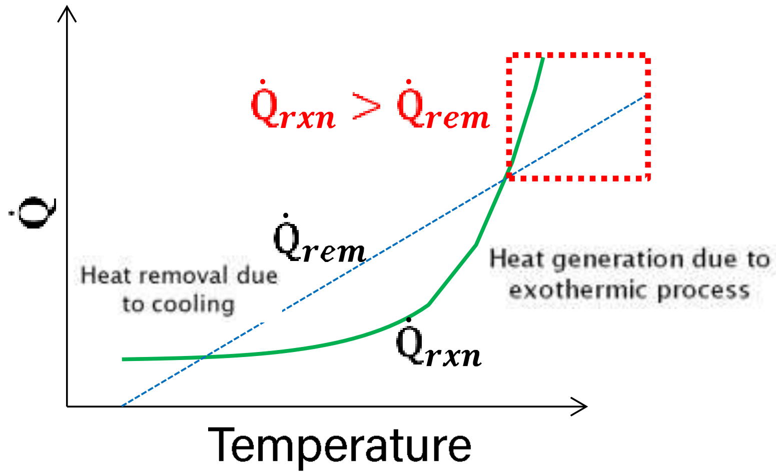


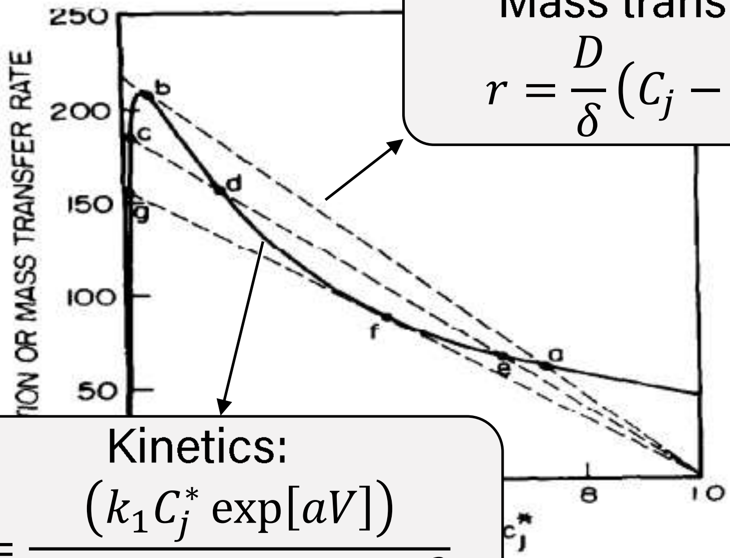
- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

What are the hazards?

Electrochemical Reactors

Runaway Reactions?

- **But** echem reactors can still experience ***multiple steady states***, creating potentially hazardous operating conditions



Mass transfer:

$$r = \frac{D}{\delta}\left(C_j - C_j^*\right)$$

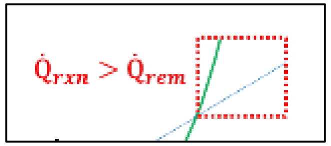
Kinetics:

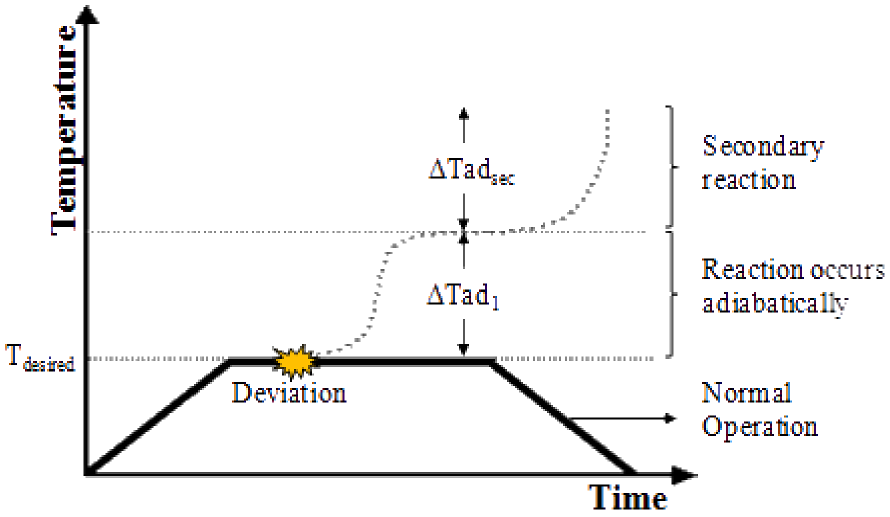
$$r = \frac{\left(k_1 C_j^* \exp[aV]\right)}{\left(1 + k_2 C_j^* \exp[aV]\right)^2}$$

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Hazards during runaway conditions



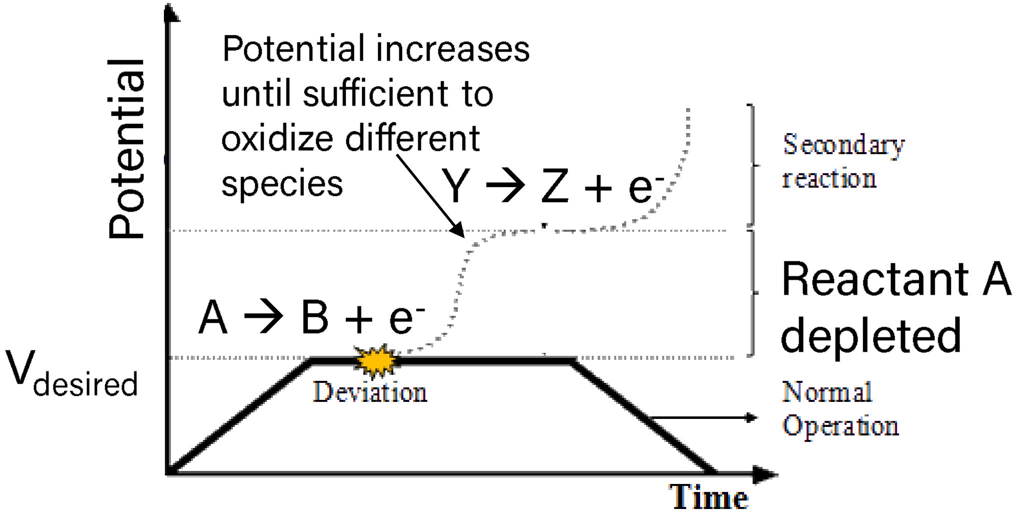


- High T exceeds reactor specs
- **High T initiates secondary rxn**
  - Gas generation/pressure increase
  - Hazardous/undesired chemicals

Electrochemical Reactors

Hazards during "runaway" conditions

Constant current operation

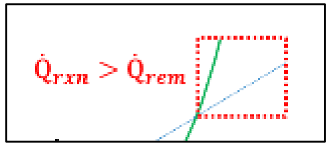


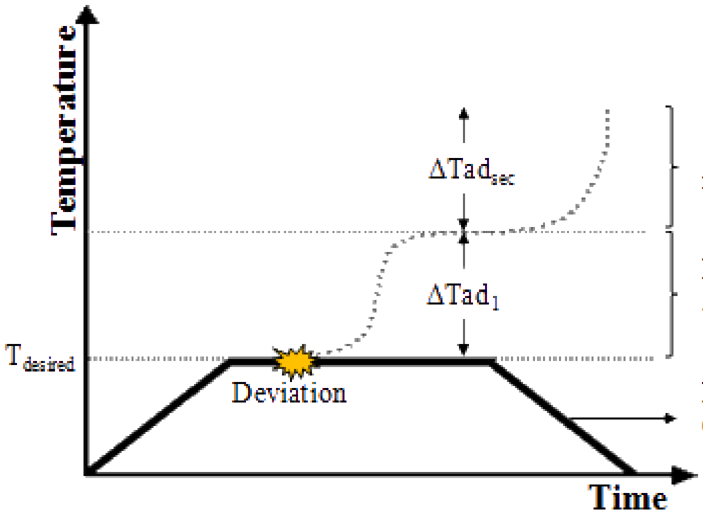
- Depletion of reactant initiates secondary rxn
  - Solvent/electrode decomposition
  - H_2/O_2 generation
  - Polymerization
  - ***Higher T due to increased Joule heating***

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Hazards during runaway conditions





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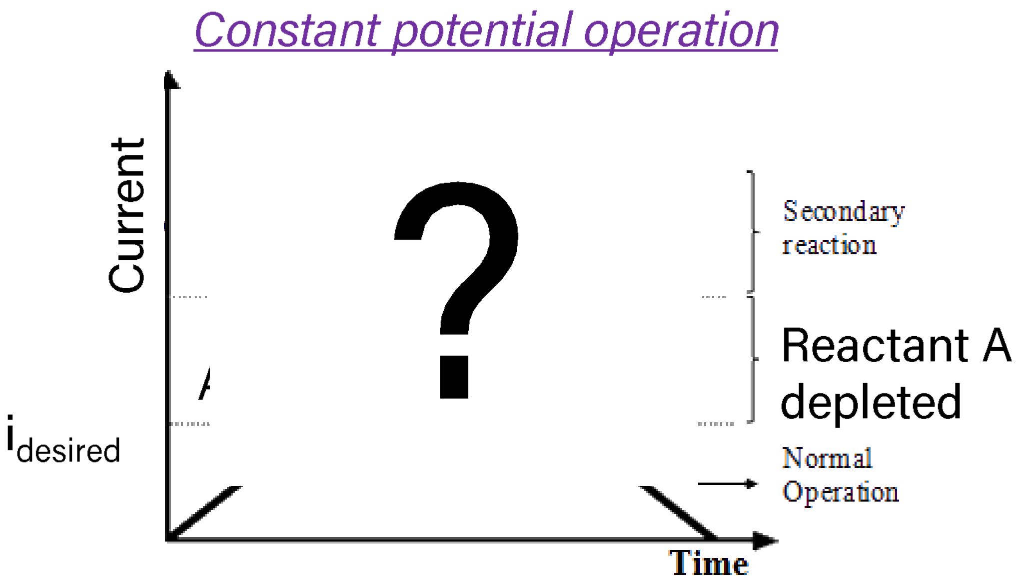


- Unpredictably high/low current (reaction rate)
  - Could lead to oscillation/control issues

Oscillation in Electrochemical Systems

How can we identify and characterize dynamic reaction behavior in electrochemical systems?

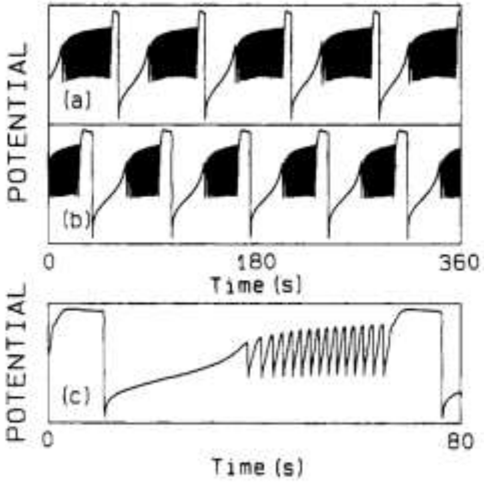
Bifurcations → Oscillations → Multiplicity of Steady States

Bifurcations

- Reaction conditions at which there is a significant change in system stability
  - Can occur with or without perturbation
- Common types:
  - Oscillatory behavior
  - Multiplicity of steady states (MSS)
  - Chaos

Oscillations

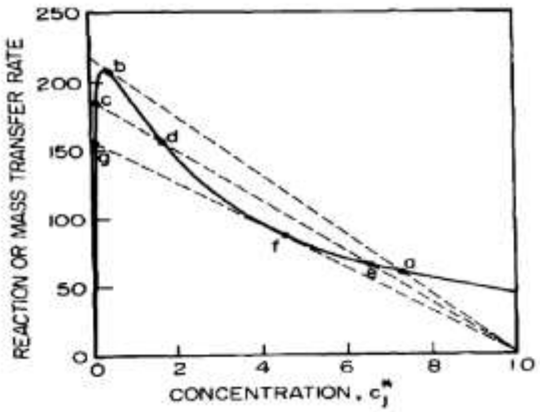
- Can form as a response to a reaction instability or a perturbation
- With sustained period and amplitude, can form a "pseudo-steady state"



Oscillations present in CP scans of an electrochemical reaction.

Multiplicity of Steady States

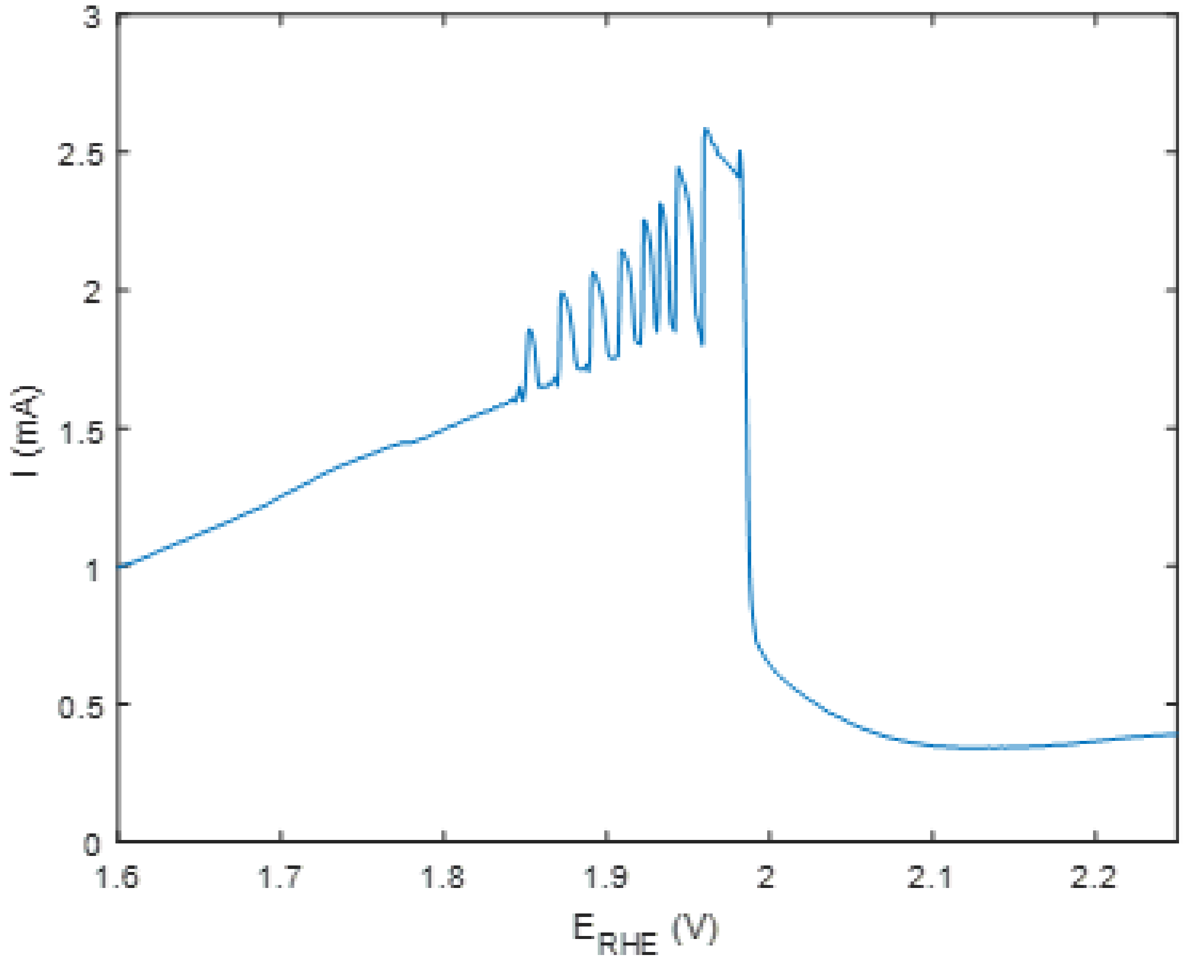
- The existence of more than one steady state for **one set of rate constants, concentrations, and applied conditions**
- Transition between states



Mathematical analysis of multiplicity in an electrochemical reaction.

Experimental Observations of Oscillatory Electrochemical Reactions

Oscillations during electrochemical formate oxidation



.476M Sulfuric acid, .5M sodium formate (solution pH: 3.72) |
1:1 150mL mixture
Pt disk, Hg/HgSO4 ref
RPM: 1000
Bandwidth: 5
Scan rate: 20 mV/s
Ar flowed through for 30 mins, continuously through scan
E1: 2.5, E2: -03

Summary and outlook

Electrochemical processes can inherently mitigate reactivity hazards:

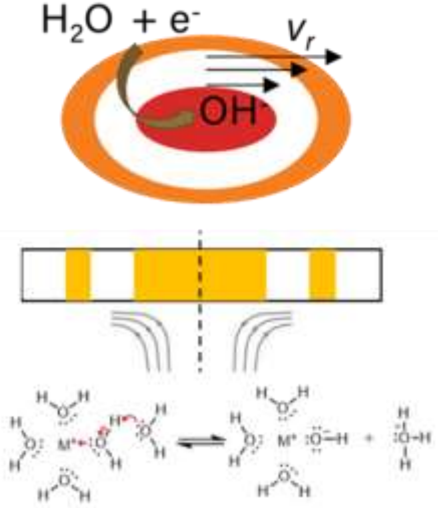
- Ambient T operation
- Substitution of toxic oxidants
- Simplified reaction schemes

But continuous electrochemical reactors can experience analogous reactivity hazards due to *multiple steady states*

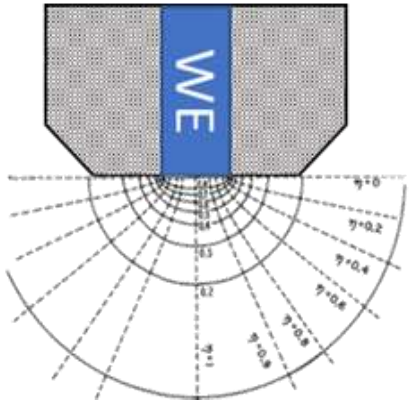
- Secondary reactions
- Unpredictable oscillations

The first step to addressing such hazards is experimental exploration of multiple steady state behavior

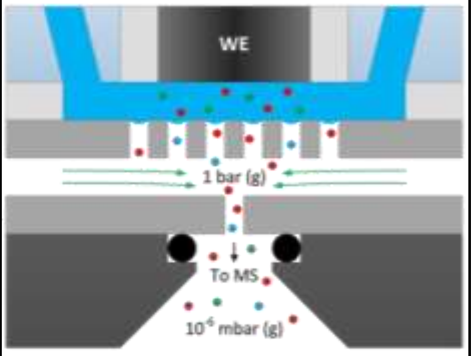
Rotating Ring-Disk Electrode



Micro Electrode



Electrochemical Mass Spec



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