

# Ch 1b Lecture 19

## February 21<sup>st</sup>, 2013

Next few lectures – OK, let's do some actual chemistry!

Today: Electrochemistry

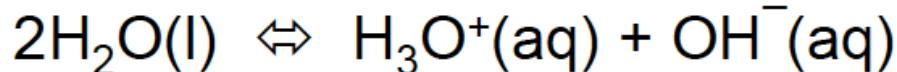
Reading: OGC Chapter 17, esp. through Section 17.5



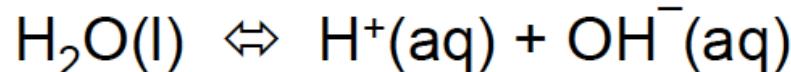
# Acids & Bases: An Extension of Chemical Equilibria

## Water Autoionization

Water = acid or base:



or, more simply,



$$K_{\text{eq}} = K_w = [\text{H}^+][\text{OH}^-]$$

25°C,  $K_w$  is  $1.0 \times 10^{-14}$ .

What drives the temperature dependence?

TABLE 15.1 Temperature Dependence of  $K_w$

$T(\text{°C})$	$K_w$	pH of Water
0	$0.114 \times 10^{-14}$	7.47
10	$0.292 \times 10^{-14}$	7.27
20	$0.681 \times 10^{-14}$	7.08
25	$1.01 \times 10^{-14}$	7.00
30	$1.47 \times 10^{-14}$	6.92
40	$2.92 \times 10^{-14}$	6.77
50	$5.47 \times 10^{-14}$	6.63
60	$9.61 \times 10^{-14}$	6.51

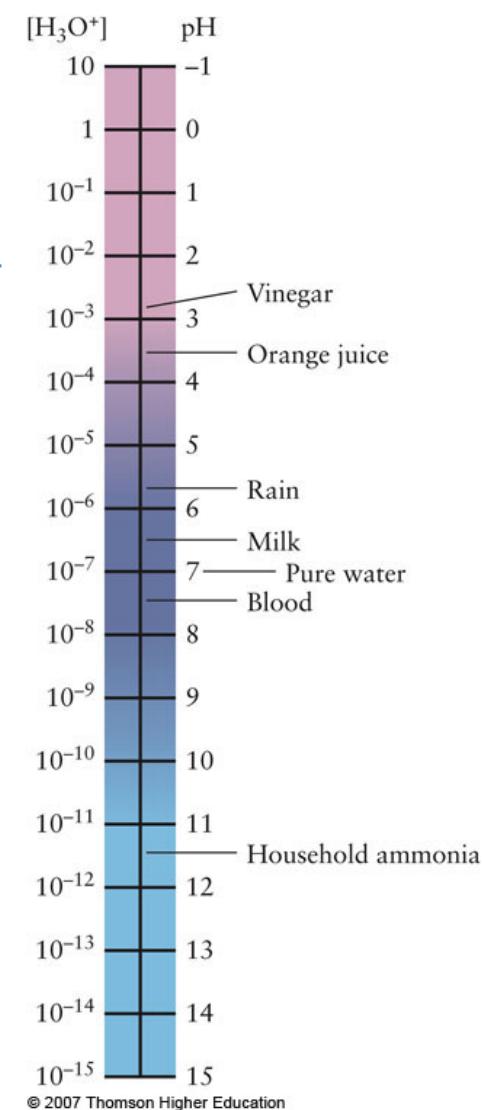
# Acids & Bases: An Extension of Chemical Equilibria

## Strong Acids and Bases

Strong acids are completely ionized in aqueous solution: HCl, HBr, HI,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HClO}_4$

Strong bases react completely to give  $\text{OH}^-$  in aqueous solution: examples -  $\text{NH}_2^-$  and  $\text{H}^-$

Water has a **leveling effect** on strong acids and bases. For example, the concentration of  $\text{H}^+$  is 0.1 molar in solutions containing any strong acid at a concentration of 0.1 molar.



# Acids & Bases: An Extension of Chemical Equilibria

## Example, Part II

Make a buffer solution that remains at approximately pH=5 from acetic acid & sodium acetate, and show that it remains close to pH=5 upon addition of 20 mM HNO<sub>3</sub>

**Assume that all HNO<sub>3</sub> ionizes (it is a strong acid)**

**[0.02M] H<sup>+</sup> is taken up by H<sub>3</sub>CO<sub>2</sub><sup>-</sup>; thereby reducing the concentration of acetate from 1.75 M to 1.73 M**

**Then set up the K<sub>a</sub> equation, allowing for the concentration of [H<sup>+</sup>] to vary**

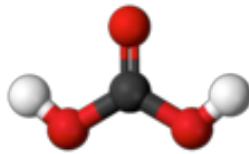
$$K_a = \frac{[A^+][B^-]}{[AB]} = 1.75 \times 10^{-5} = \frac{x[1.73 + x]}{[1.02 - x]}$$

Solve for x; **[x] = 1.032x10<sup>-5</sup>; pH = 4.98**

The pH has hardly changed, even though we added a strong acid!  
This is the point of a buffer!!

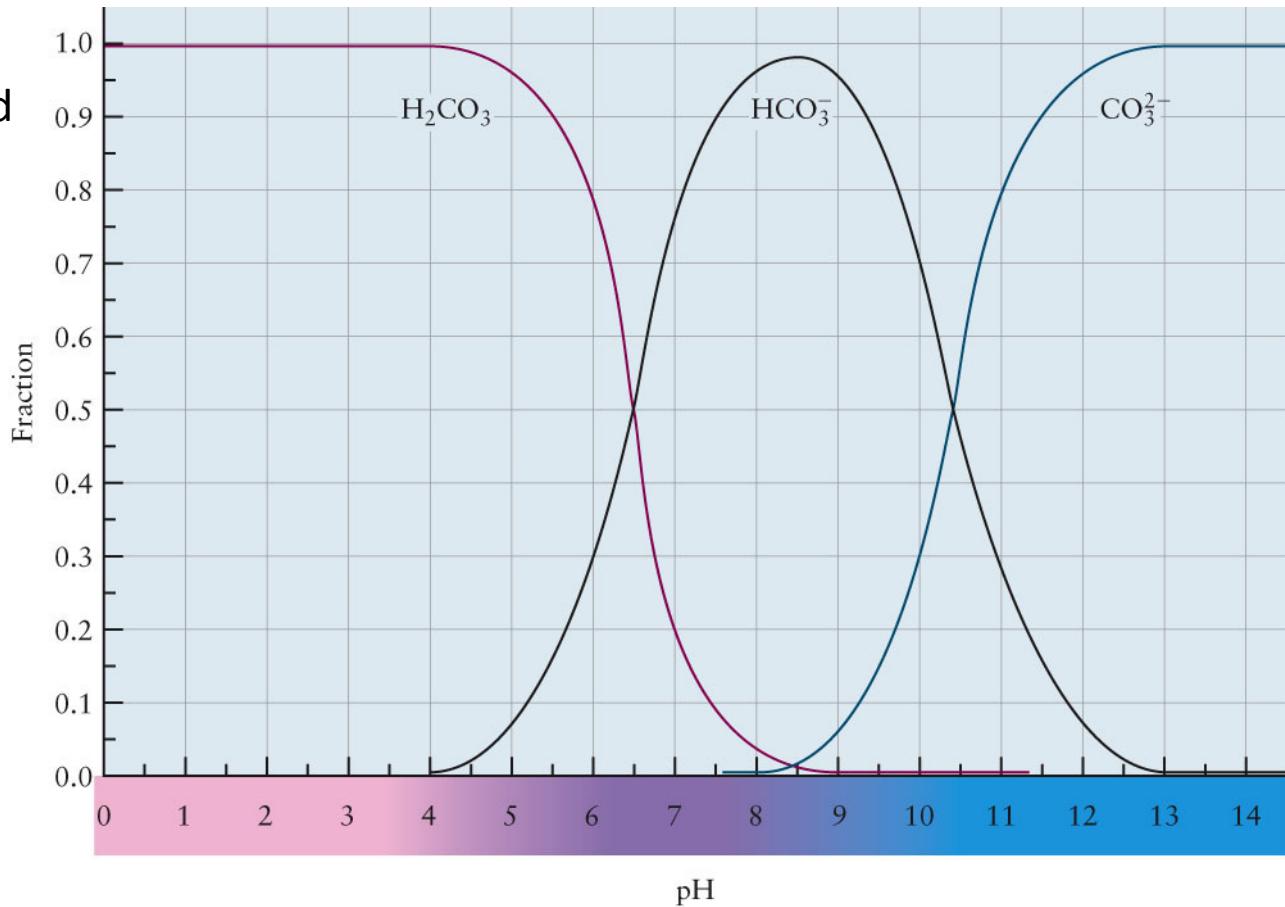
# Acids & Bases: An Extension of Chemical Equilibria

$\text{CO}_2$  is somewhat soluble in water, and the solvated  $\text{CO}_2$  can react with the water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ):

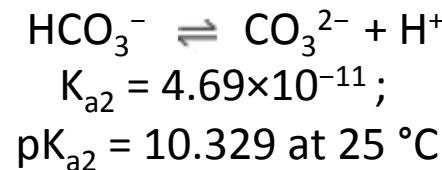
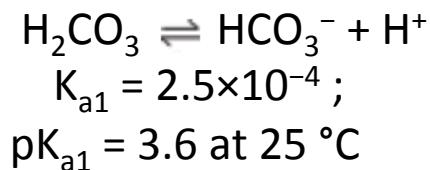


Only a small part of the gas dissolves to form  $\text{CO}_2(aq)$  and reacts to create  $\text{H}_2\text{CO}_3$ . There are two dissociation constants to consider ( $K_{a1} \gg K_{a2}$ , this is typically true).

Why?



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# Organic Acids: Recap

To estimate the acidity of



where X is a generic group

Consider the stability of



resonance stabilization (or destabilization)?  
 inductive stabilization (or destabilization)?  
 hybridization?  
 electronegativity?

Strong acids ( $\text{pK}_a < 0$ ) have very stable conjugate bases (weak bases).  
 Strong bases have very stable conjugate acids (weak acids).

Remember:

- electronegative atoms can stabilize the conjugate base inductively
- delocalization of negative charge can stabilize the conjugate base
- hybridization affects  $\text{pK}_a$ : orbitals with more s-character better stabilize negative charge

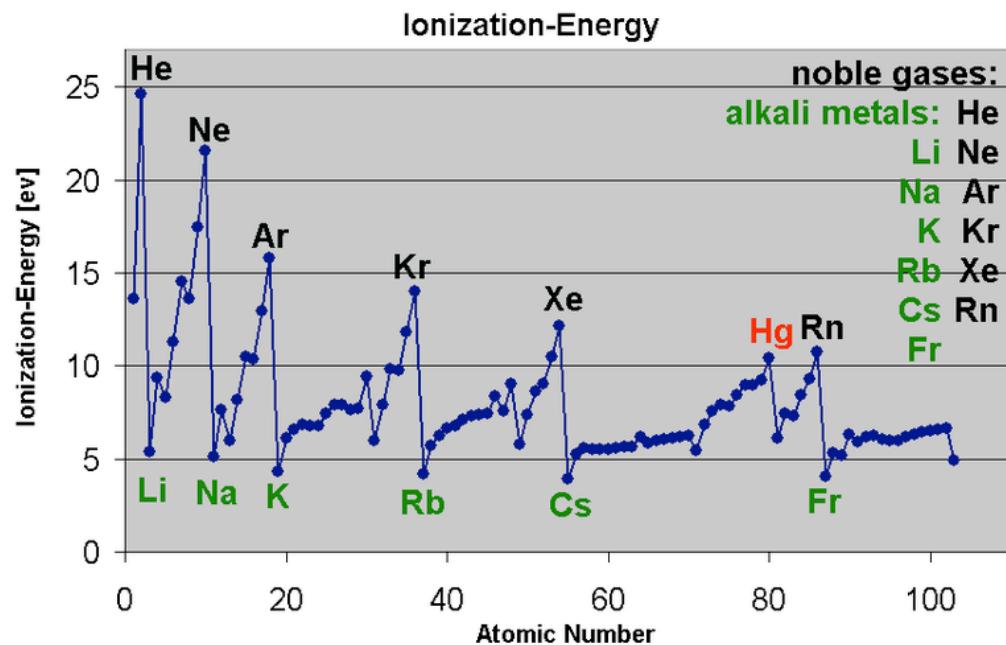


- the equilibrium will favor the more stable conjugate base

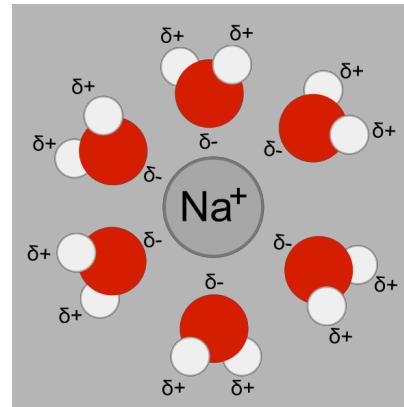
# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

Redox-, or electro-chemistry is critical to society (metal production, energy needs, etc.). What are its underpinnings?

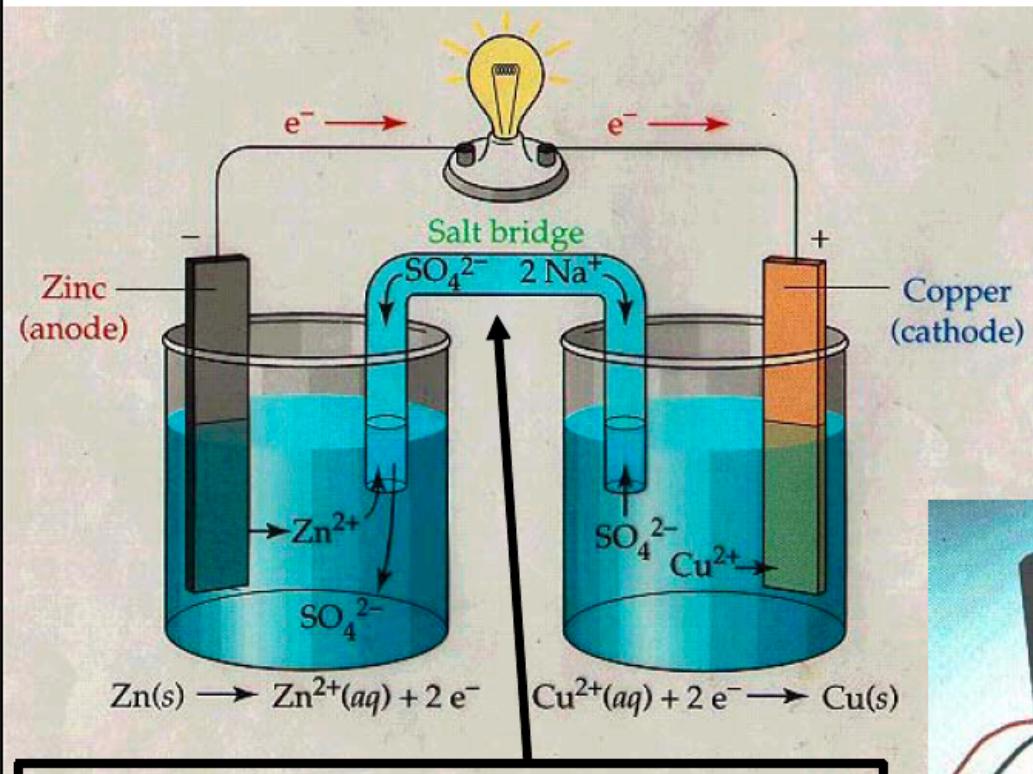
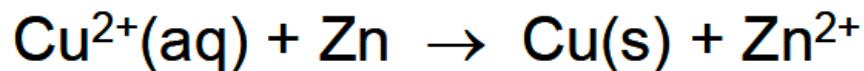
You learned about periodic trends in atomic ionization potentials in Ch 1a...



From this, and the nature of bonding in metals (think about the mechanical properties of Pb versus Ti, for example) & solvation, we expect solutions with different elements to have  $\Delta G$  values that vary significantly!



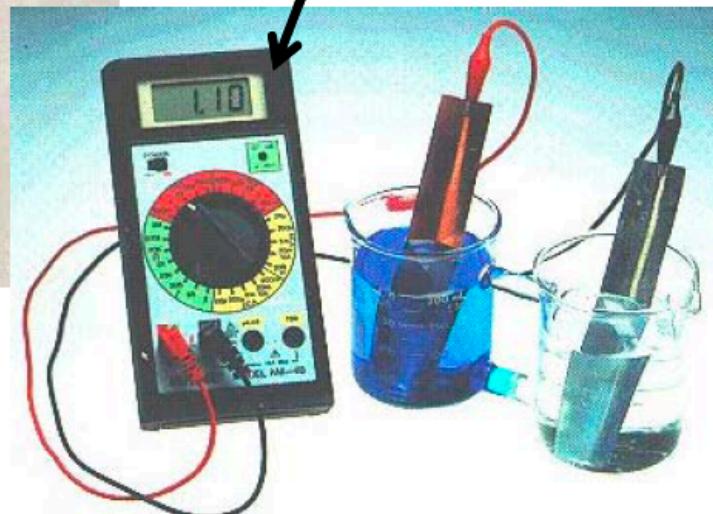
# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:



The salt bridge conducts ions between both chambers to maintain electrical neutrality.

A laboratory version of a Daniell Cell

Note reading of voltmeter: 1.10 V



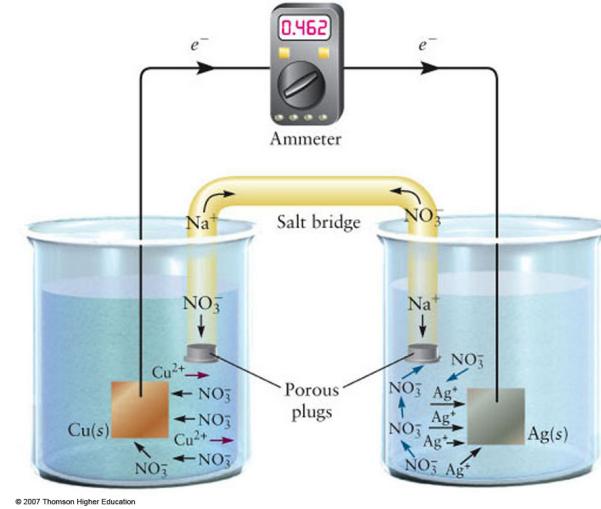
Would be tedious to measure all possible pairs...

# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

- Electrolytic cells are those in which electrical energy from an external source causes non-spontaneous chemical reactions to occur.
- Voltaic cells are those in which spontaneous chemical reactions produce electricity and supply it to an external circuit (load).

## Electrodes

- Electrodes are surfaces on which the oxidation and reduction half-reactions occur.
- The cathode is the electrode at which the reduction reaction occurs (Ag in figure).
- The anode is the electrode at which the oxidation reaction occurs (Cu in figure).

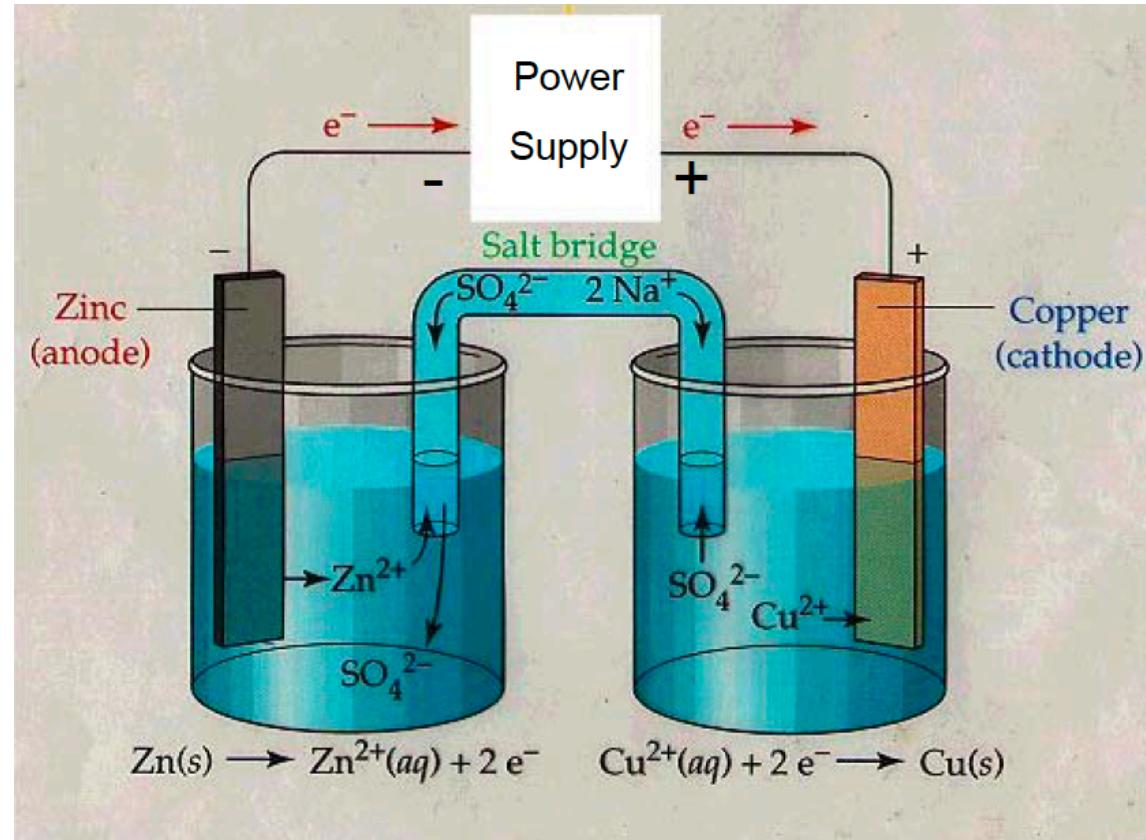


# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

Daniell Galvanic Cell – Lab Version:  $\text{Cu}^{2+}(\text{aq}) + \text{Zn} \longrightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}$

Suppose we attach a power supply that opposes the current flow. What happens as the potential (voltage) is increased?

At sufficiently high voltage the reaction reverses and the galvanic cell becomes an electrolysis cell:



- < 1.10 V, nothing happens
- = 1.10 V, no current flows
- > 1.10, current and reaction reverse

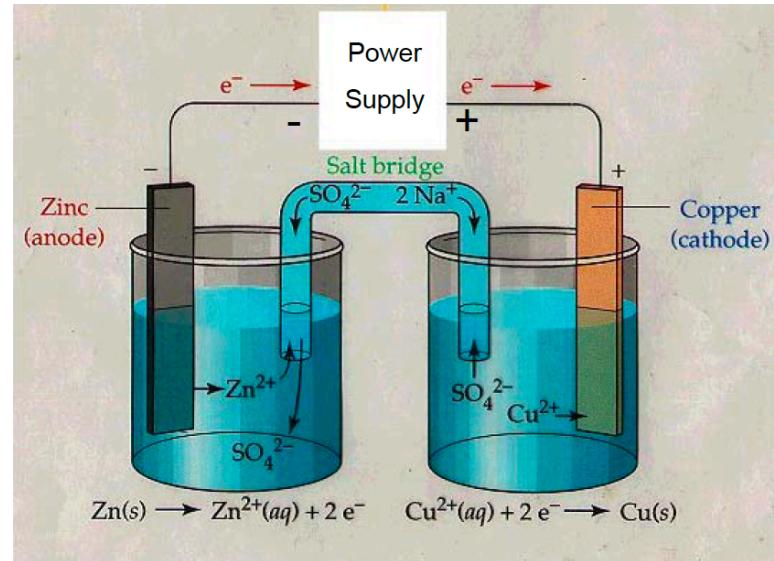
# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

Daniell Galvanic Cell – Lab Version:  $\text{Cu}^{2+}(\text{aq}) + \text{Zn} \longrightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}$

How do we establish the basic thermodynamics at play?

$$\text{Electrical Work} = -q \int E \, dr$$

$$G = H - TS = U + PV - TS$$



$$\Delta U = q + w_{elec} - P\Delta V \quad (\text{Heat} + \text{work})$$

If we are at constant P,T and operate the cell reversibly:

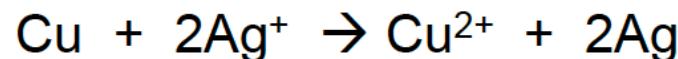
$$q = q_{rev} = T\Delta S \quad \text{and} \quad \Delta G = w_{elec} = -n\mathcal{F}\Delta\epsilon$$

Where  $\mathcal{F}$ = Faraday's constant =  $N_A * 1.602 \times 10^{-19} \text{ C} = 96,485.34 \text{ C mol}^{-1}$

# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

As with chemical equilibrium, we need to establish *standard states* under which the cell voltages are measured. We denote the conditions with a  $^\circ$  superscript as before:

A galvanic cell based on the combined reduction of copper and oxidation of silver,



has half cell reactions (both written as reductions) :



$$\Delta G^\circ \propto \Delta \varepsilon^\circ$$



$\varepsilon^\circ$  is a measure of  $\Delta G$  of this reaction

It is also a measurement of how much work can be extracted from this reaction

# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

A numerical example...

To oxidize copper and reduce 2 moles of silver:



$$\Delta G^\circ = -nF\Delta\varepsilon^\circ$$

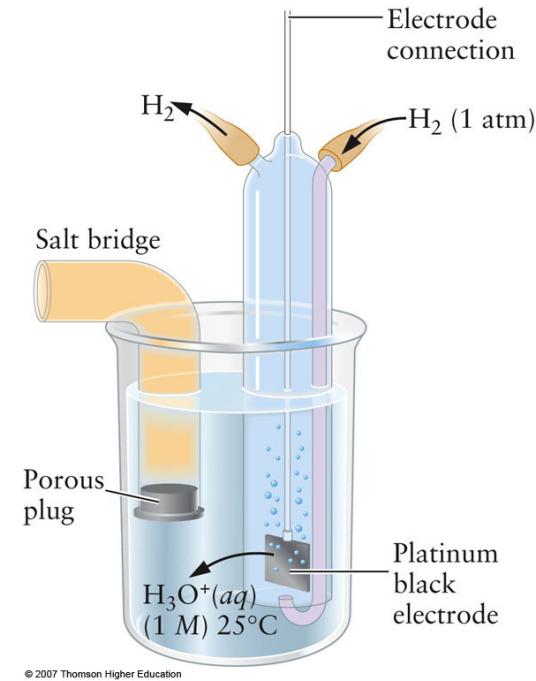
$$-(2 \text{ mol e-})(9.65 \times 10^4 \text{ C/mol})(0.46 \text{ J/C})(1 \text{ kJ}/10^3 \text{ J}) = -88.8 \text{ kJ}$$

Note:  $\Delta G$  depends upon the number of charges (requires balancing eqtn)  
 $\Delta\varepsilon$  only depends upon the summation of the  $\frac{1}{2}$  cell voltages

# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

## Conventions for $\varepsilon^\circ$ (Half-cell Potentials)

1. Assign the standard hydrogen electrode a potential of 0.0 V.
2. When half-reactions are written as reductions, reactions that proceed as reductions more readily than  $\text{H}^+/\text{H}_2$  are assigned positive V, those that proceed less readily are assigned negative voltages.
3. If the direction of the half-reaction is reversed, the sign of the standard half-cell potential is also reversed. **But, if the reaction is multiplied by some factor, the standard cell half-potential remains unchanged.**
4. The value of the half-cell potential is a measure of the tendency of the reaction to proceed from left-to-right (as written).



# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

## Reduction ½ Cells

### A Sampling of Half Cell Potentials

<u>Half Reaction</u>	<u><math>\varepsilon^\circ(V)</math></u>	
$F_2 + 2e \rightarrow 2F^-$	2.89	Oxidizing agents
$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.51	
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.23	
$Ag^+ + e \rightarrow Ag$	0.80	
$Cu^{2+} + 2e \rightarrow Cu$	0.34	
$2H^+ + 2e \rightarrow H_2$	0.00	
$Fe^{2+} + 2e \rightarrow Fe$	-0.44	
$Zn^{2+} + 2e \rightarrow Zn$	-0.76	
$Mn^{2+} + 2e \rightarrow Mn$	-1.18	Reducing agents
$Na^+ + e \rightarrow Na$	-2.70	

Not favorable in this direction

See Appendix E, OGC, for a more complete list.

# Electrochemical Cells, $\Delta G^\circ$ , and Equilibrium:

What do we do under non-standard state conditions?

Recall from the previous lectures that:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where  $Q$  is the reaction quotient (equal to  $K$  at equilibrium).

$$\text{Since } \Delta G = w_{elec} = -n \mathcal{F} \Delta \varepsilon$$

$$\Delta \varepsilon = \Delta \varepsilon^\circ - (RT/n \mathcal{F}) \ln Q$$

***The Nernst Equation***

Numerically, remember that 1 Joule/Coulomb = 1 V, so:

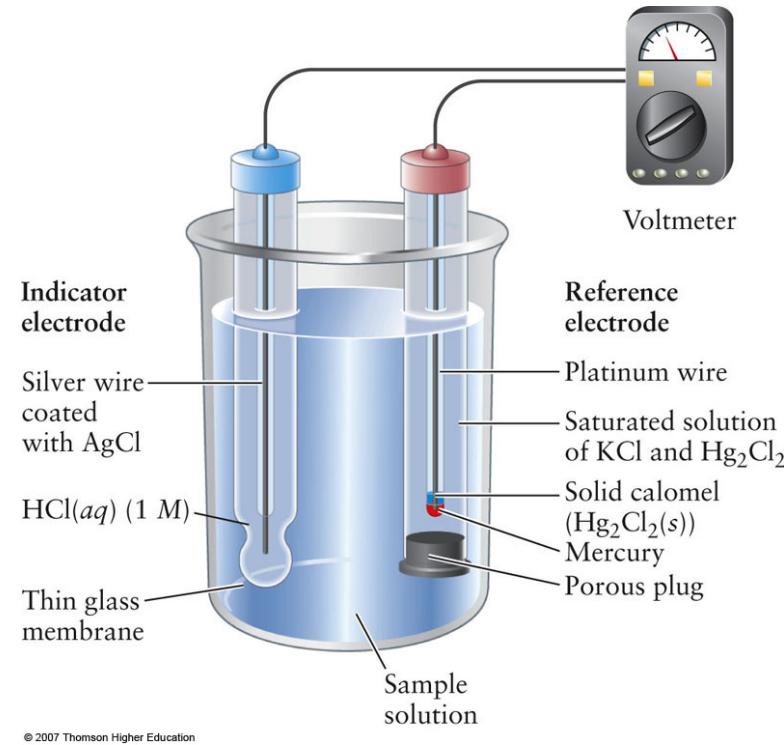
$$\Delta \varepsilon = \Delta \varepsilon^\circ - (0.0592 \text{ V}/n) \ln Q \quad \text{and}$$

$$\log_{10} K = (n/0.0592 \text{ V}) \Delta \varepsilon^\circ \quad \text{at } 25^\circ \text{ C.}$$

# Applications of Electrochemical Cells: pH Meters

The American Chemical Society designated the development of the Beckman pH meter a National Historic Chemical Landmark on March 24, 2004. The plaque commemorating the event reads (now in the Beckman Institute courtyard):

*Arnold O. Beckman developed the first commercially successful electronic pH meter while a member of the faculty of the California Institute of Technology. This rugged and portable "acidimeter," which had all necessary components housed in a single unit, allowed scientists to measure acidity accurately and rapidly. It immediately met an important need of the California citrus industry: how to measure the pH of lemon juice. The innovative features of the pH meter, including an early use of integrated electronic technology, were the basis for subsequent modern instrumentation developed by Beckman & Beckman Instruments.*

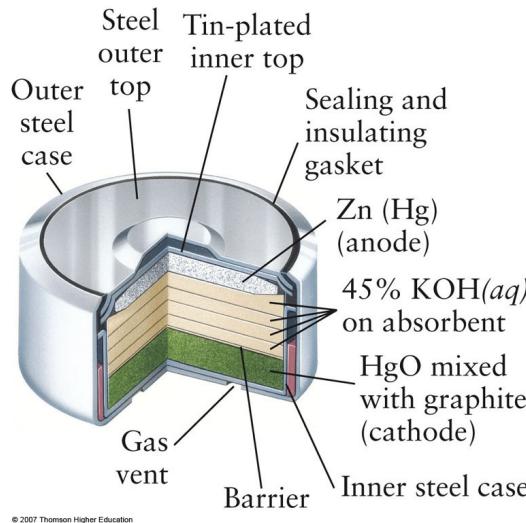


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$$\text{pH} = (\Delta \varepsilon - \Delta \varepsilon^{\text{ref}}) / 0.0592 \text{ V}$$

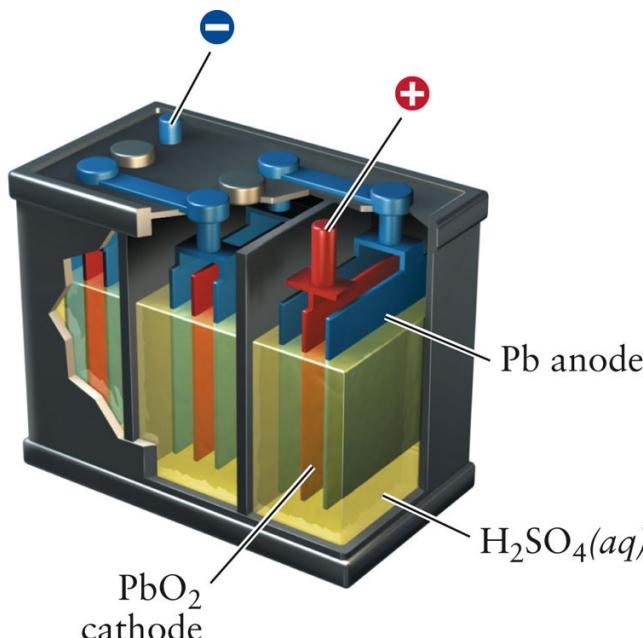
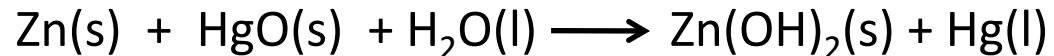


# Applications of Electrochemical Cells: Batteries

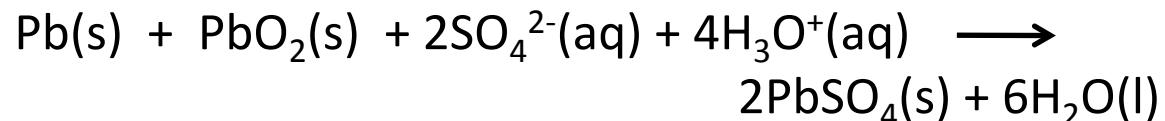


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The Zn-mercury oxide cell produces 1.34 V:



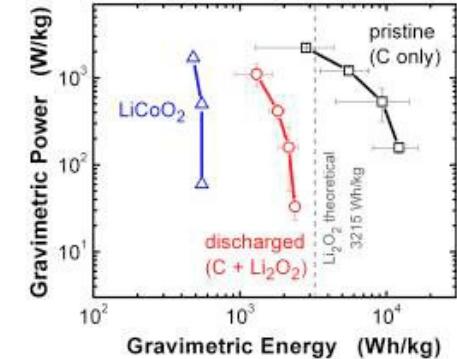
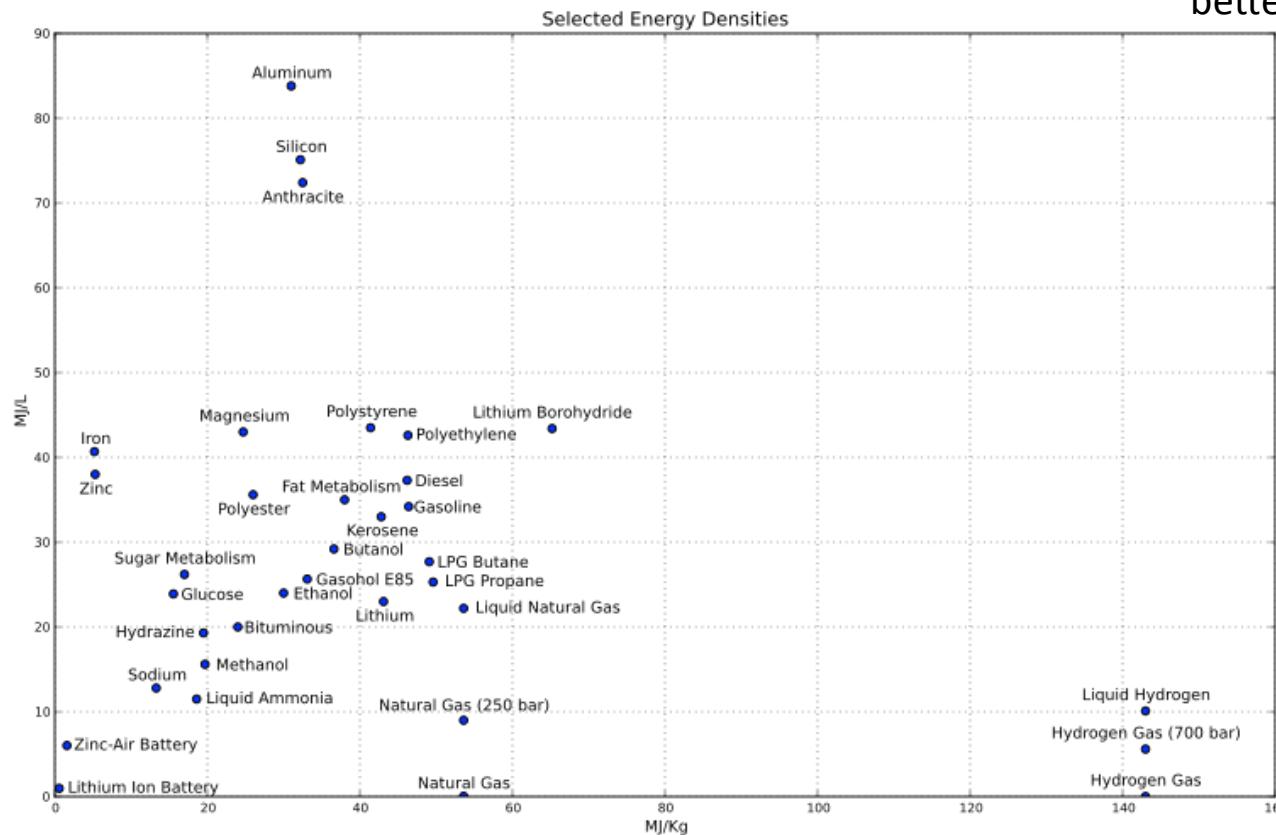
The Pb-acid battery 2.0 V:



Societal issues associated with heavy metals (both production & recycling).

# Applications of Electrochemical Cells: Batteries

<http://web.mit.edu/newsoffice/2011/better-battery-storage-0725.html>



Lithium-air battery designs are getting close to gasoline in energy density (~40 MJ/kg).

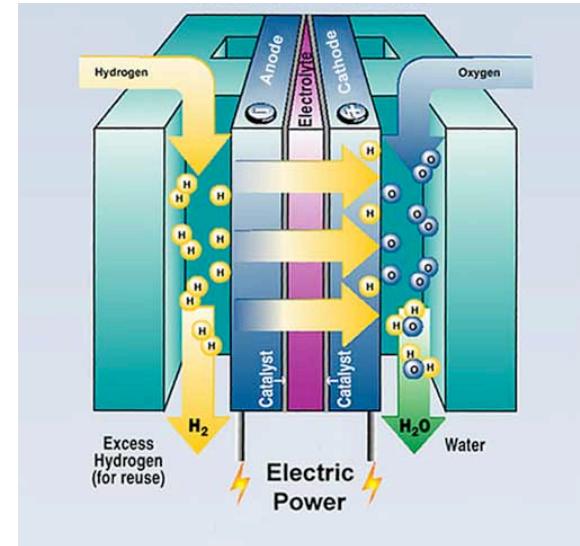
Plot of the energy density of batteries versus chemical shows a dramatic difference:

Biology has figured this out – Metabolism runs on chemical fuels, connectivity/information with electrochemistry.

# Applications of Electrochemical Cells: Fuel Cells

Which leads us to **fuel cells**.

Fuel cells are continuously operated systems that extract electric power from chemical fuels via electrochemistry.

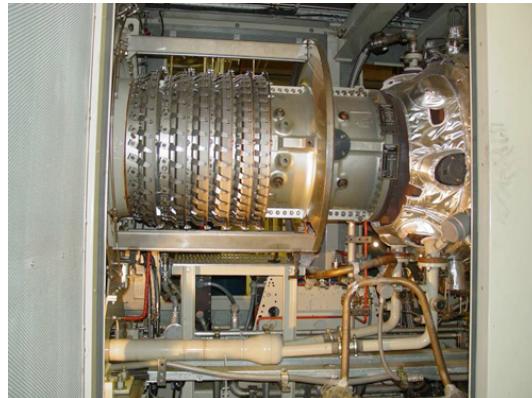


One advantage is the continuous operation (if fuel is supplied) and the high energy density of materials.

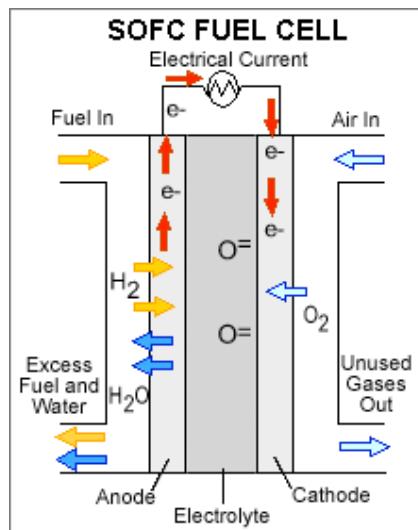
For the second, recall  $|\Delta G| = w_{elec}$  for a fuel cell, and  
*efficiency*\* $|q_p| = w = |\Delta H|(T_h - T_l)/T_h$  for a Carnot cycle.

For highly exothermic processes,  $\Delta G \sim \Delta H$ ; and so fuel cells can be more efficient than combustion engines.

# Applications of Electrochemical Cells: Fuel Cells



<http://sustainability.caltech.edu/energy/CaltechFuelCells>

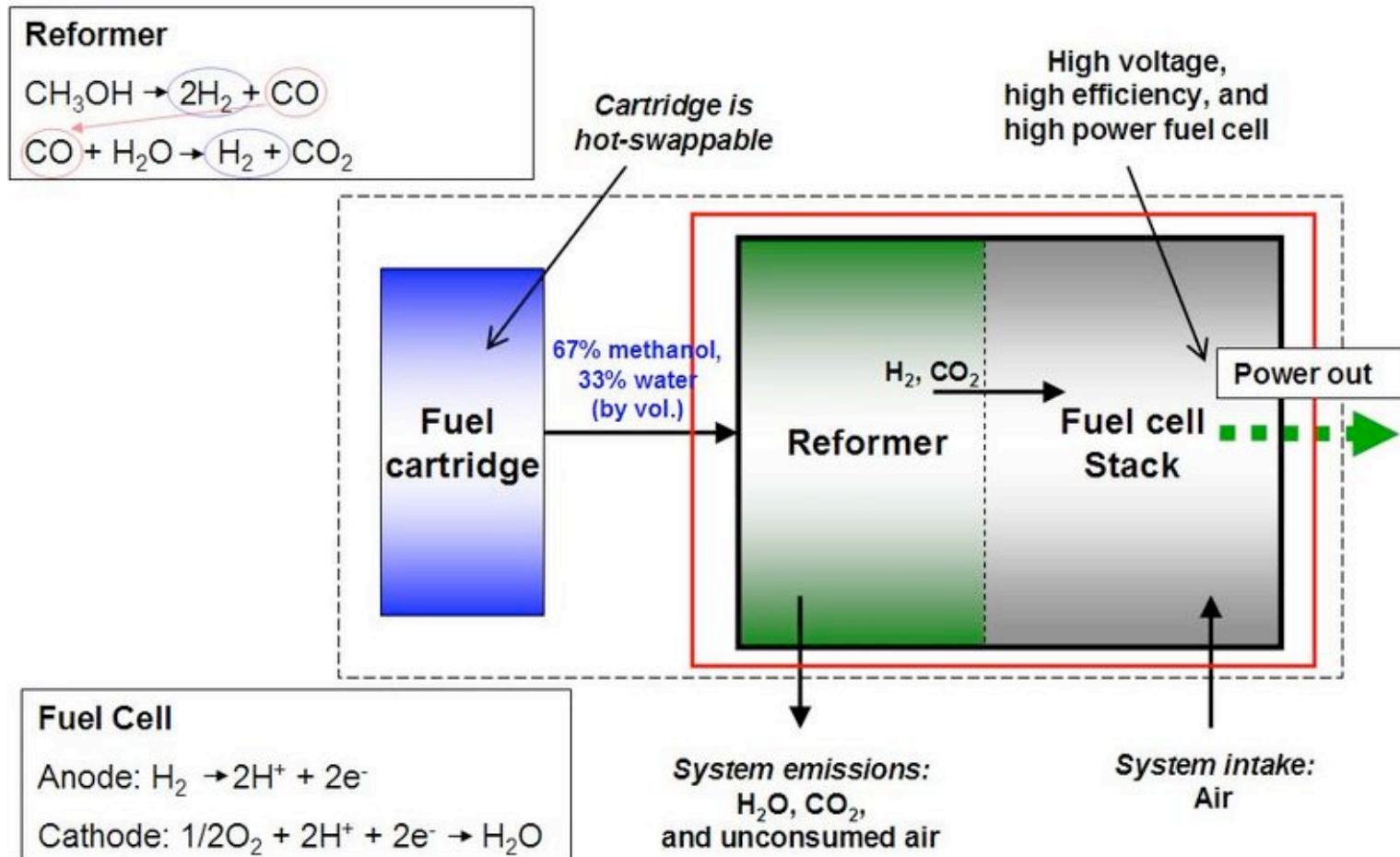


Here at Caltech we use a large turbine-based cogeneration plant for the bulk of our energy needs (that is, we capture the waste heat from a Carnot cycle to heat water for the campus), which are supplemented by (high temperature) solid oxide fuel cells from Bloom Energy.

The Chemistry of the Solid Oxide Fuel Cell  
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{e}^- + \text{Heat}$

<http://www.bloomenergy.com/fuel-cell/solid-oxide-fuel-cell-animation//>

# Applications of Electrochemical Cells: Fuel Cells



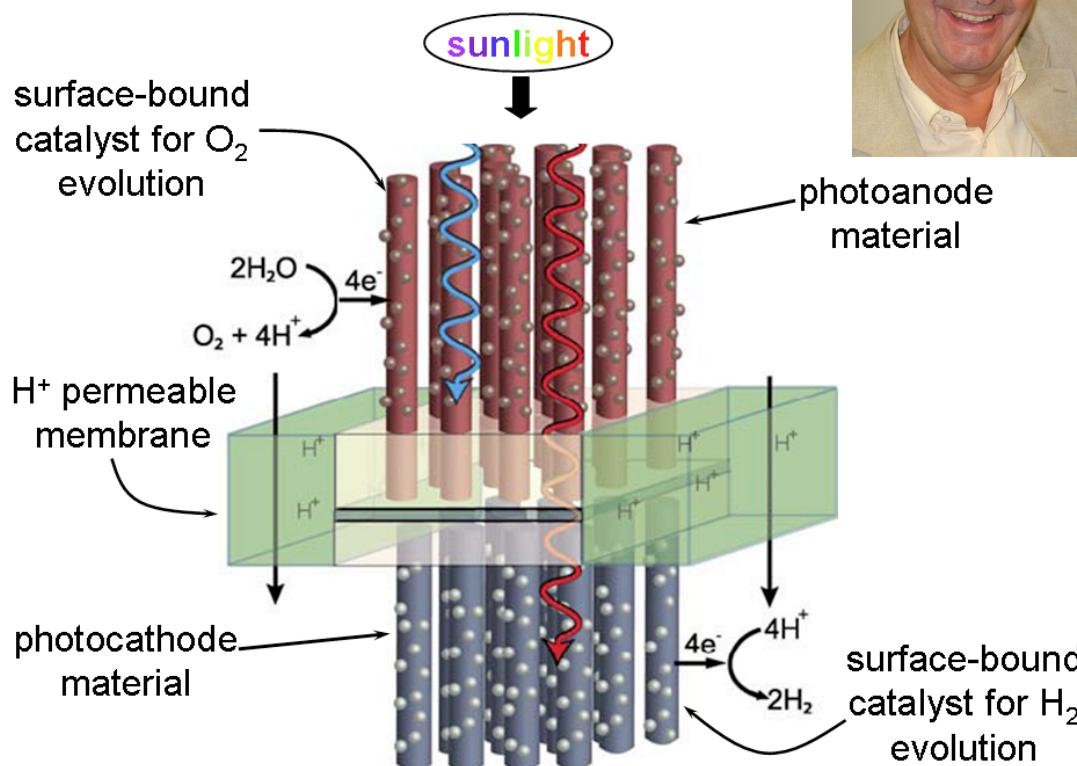
Another approach is to use methanol as the fuel, as outlined above.

In these so-called **reforming fuel cells** the  $\text{H}_2$  is generated from fuels containing carbon, and so  $\text{CO}_2$  is released (Haber process also).

# Applications of Electrochemical Cells: Fuel Cells



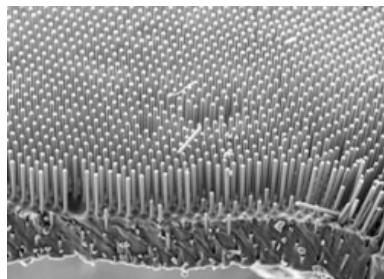
<http://ccisolar.caltech.edu/webpage/95>



Wouldn't it be nice to be able to drive a system that is carbon free? There's plenty of  $H_2$  and  $O_2$  on the Earth, in water, the challenge is to split the water efficiently.

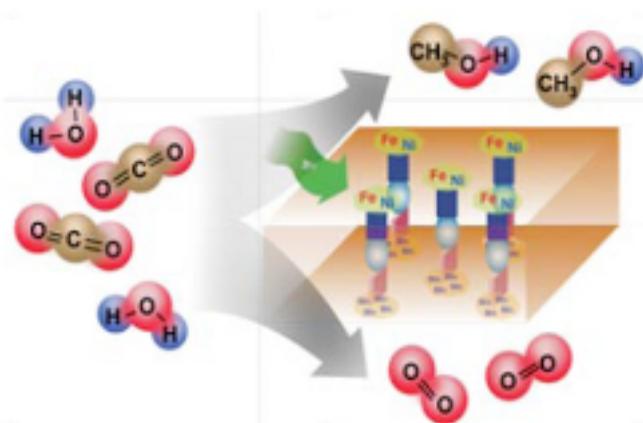
There are several significant efforts on campus, two that involve chemistry as a driver. The first is headed by His Imperial Eminence Lord Harry Gray:

# Applications of Electrochemical Cells: Fuel Cells



The second is lead by Prof. Nate Lewis, whom you know (JCAP has now moved into the renovated Jorgensen lab).

<http://solarfuelshub.org/about-jcap>



## Mission:

JCAP will develop and demonstrate a manufacturable solar-fuels generator, made of Earth-abundant elements, that will take sunlight, water and carbon dioxide as inputs, and robustly produce fuel from the sun 10 times more efficiently than typical current crops (as Nate says, “Think potato chip, not silicon chip!”).

# Just for fun: Thermite



Highly exothermic (851.5 kJ/m)



Tying it all together, thermodynamics, kinetics, phase changes, you name it:



Steam explosion, or  
 $3\text{Fe(s)}+4\text{H}_2\text{O(g)}\rightarrow\text{Fe}_3\text{O}_4\text{(s)}+4\text{H}_2\text{(g)}$   
followed by reaction with  $\text{O}_2$ ?