Lecture #7 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: TW)

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Chemical Properties *(let's review* TThFMTW*)*

- T: Molecular nomenclature, Solutions, Balanced chemical reactions, State functions, Standard states, Thermochemistry
- **Th: Non-ideal gases, Intermolecular forces, Physical properties, Phase changes**
- F: Colligative properties, Water activity, Free energy, (X)Chemical potential, Entropic "force", Activity coefficients, Chemical equilibrium
- **M: van't Hoff equation, Le Chatelier's principle**
- T: Schrödinger equation, Internal energy, Atomic orbitals, Hybridization, Valence bond theory, Molecular orbital theory, Band diagrams
- **W: Crystal field theory, Ligand field theory**

Charged Interfaces

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Quiz Time!

Charged Interfaces

126

- **Vacuum level, Redox half-reactions**
- **Nernst equation**
- **History, Conventions**
- **Electrodes, Potentiostat**
- Electric double layer
- Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential
- pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation
- Latimer diagram, Pourbaix diagram

Who's best equipped to succeed in EChem?

127

(A) Chemists?
(B) Physicists?
(C) Chemical Engineers?
(D) Electrical Engineers?
(E) Materials Scientists?

Answer: Everyone!… having each of these people in a room is best… **or just one of you all!**

Vacuum Level and Other Reference States

128

Hess's law allows one to accurately determine the overall change in a state function ($\Delta G^{o,\alpha}$, $\Delta H^{o,\alpha}$, $\Delta S^{o,\alpha}$, etc.) via knowledge of the change in the state function for intermediate steps…

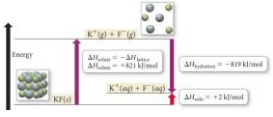
$$A \rightleftharpoons B + 2C \rightleftharpoons D$$

Just add'em up!… is this concept easy, medium, or hard for you?

… Good!… and we learned that sometimes it helps to think of a reaction moving species to the local vacuum level to form intermediates… *a reference state loved by physicists*… and then putting the species back into the system… even though that does not happen in practice…

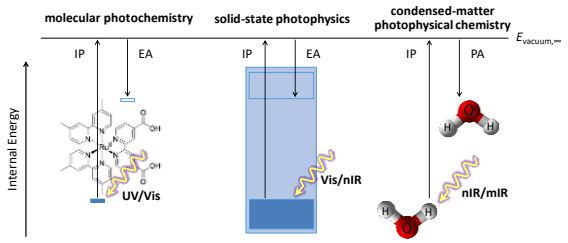
… is this concept easy, medium, or hard for you?

… Good, again!… given that, **reduction potentials** and **acidity** should be easy for you to grasp, since they follow directly from these ways of thinking…



Gas-Phase Chemistry Terminology

129



… is this most relevant to **internal energy (Schrodinger equation)** or **free energy (reactivity)**?

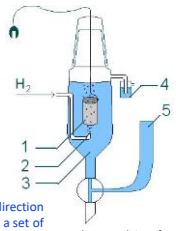
Red–Ox (Redox) Half-Reactions

130

Each reduction half-reaction is referenced to something…

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = -\Delta G/nF$$

Since the method of half-reactions ultimately results in us taking their difference, we can add an arbitrary constant to all half-reactions… by one (somewhat arbitrary) convention, many standard tables assume that E° for the standard hydrogen electrode **(SHE)** is equal to zero, and that a hypothetical SHE has 1 atm H_2 (standard state) and $a_{H^+} = 1$.



* one rendition of an experimental SHE

Half-Reaction for evolution of hydrogen gas (H_2) (SHE):

$$\text{Pt}(e^-) + H^+(aq) \rightarrow \tfrac{1}{2}H_2(g)$$

… every time you see a single direction arrow, it should really be a set of stacked reversible arrows

$$E_{H_2} = E^{\circ}_{H_2} + \tfrac{RT}{F}\ln\frac{\sqrt{P_{H_2}}}{[H^+]} \qquad E^{\circ}_{H_2} = 0$$

… anyway, potentials for half-cell reactions **are** actually full-cell potential (difference(s)) *versus* SHE…
… or other another electrode… like AgCl(s)/Ag(s),Cl^-(aq)… or the local vacuum level!)

Nernst Equation

131

"Half-reactions", at non-unity activity, obey the Nernst equation…
… take $\Delta G = \Delta G^0 + RT\ln Q$ and use the relation $\Delta G = w' = zq\phi = -nFE$,

$$-nFE = -nFE^{\circ} + RT\ln Q$$

← Reaction quotient… … product and quotient of species activities

$$E = E^{\circ} - \frac{RT}{nF}\ln Q$$

$$E = E^{\circ} - \frac{RT}{nF}\frac{\log Q}{\log e}$$

$$E = E^{\circ} - \frac{RT}{0.4343nF}\log Q$$

$$E = E^{\circ} - \frac{2.3026RT}{nF}\log Q$$

… and at 298.15 K, $E = E^{\circ} - \frac{0.05916\ \text{V}}{n}\log Q$

Physicist

Walther Hermann Nernst (1864–1941)
Nobel Prize (Chemistry, 1920)
from Wiki

$$\text{a A} + \text{b B} \rightleftharpoons \text{c C} + \text{d D}$$

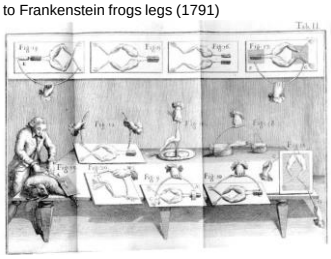
$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

… look what I found… this is incorrect… but why?… what can we do to fix this?

… memorize ~60 mV per order in $\log_{10}$, but do not forget *n* and that this is at 25 °C!

A Brief History Lesson on Electrochemistry

Electrochemistry is associated with Luigi Galvani who discovered "animal electricity" … while trying to Frankenstein frogs legs (1791)



Physician, Physicist, Philosopher

Luigi Galvani
(1737–1798)
from Wiki

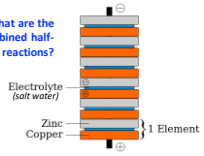
(Almost) The First Battery: the Voltaic Pile

Invented by Alessandro Volta (1800), but…
… the elements of the pile (galvanic cells) were named after Galvani

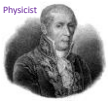
At the Tempio Voltiano (the Volta Temple) near Volta's home in Como, Italy.

http://en.wikipedia.org/wiki/Voltaic_pile

What are the combined half-reactions?



Physicist



Alessandro Volta
(1745–1827)
from Wiki

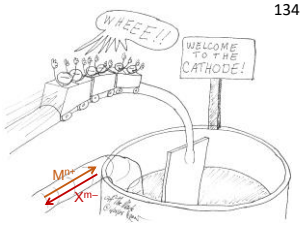
Volta presenting his "Voltaic Pile" to Napoleon and his court… and now he is a Count!

http://en.wikipedia.org/wiki/Alessandro_Volta

Galvanic Cells

Every non-equilibrium cell is a galvanic cell (in one direction, i.e. the spontaneous direction)

Physically separating the half-reactions allows the electrons to go over a long distance, from the anode to the cathode via a (solid) conductor: basis for conversion of chemical energy into electricity = "Electrochemistry"!



Salt bridge is an ionic conduit to prevent capacitive buildup of charge in both compartments and also to prevent bulk mixing of the two solutions

Electrolysis of Water

135

Chemist

William Nicholson
(1753–1815)

Surgeon

Sir Anthony Carlisle
(1768–1840)

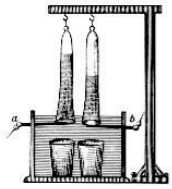
Chemist

Johann Wilhelm Ritter
(1776–1810)

Chemist

William Cruickshank
(177?–1810(1))

Volta's results were shared with the scientific community and then, *boom*, many people demonstrated electrolysis the same year, and later electroplating!



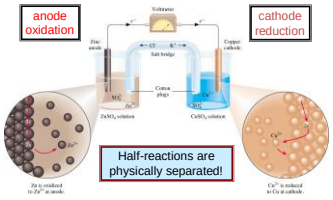
http://en.wikipedia.org/wiki/Johann_Wilhelm_Ritter

The First Battery: the Daniell Cell (1836)

136

anode
oxidation

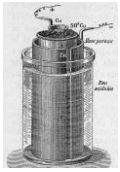
cathode
reduction



$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$ $\qquad$ $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

NET REACTION: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

No more H_2 from a (primary) galvanic cell… meaning non-rechargeable battery!



Chemist, Meteorologist

John Frederic Daniell
(1790–1845)
from Wiki

… the net reaction occurs when Zn(s) is immersed into $CuSO_4$(aq)… **spectator ions**, e.g. SO_4^{2-}, are omitted
… EChem gives you a way to drive the reaction backward… using electricity to perform chemical work

Acronym's Anyone?

137

OIL RIG

- Oxidation
- Is
- Loss. (of electrons)

- Reduction
- Is
- Gain. (of electrons)

… Ugh!… you didn't hear this from me!

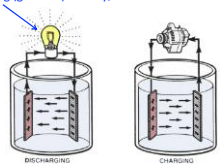
138

Conventions… Oh, Conventions!

Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized

Does a Negative/Positive Electrode = Cathode or Anode?… It depends!

For the discharging (galvanic) battery, label the anode and the cathode.



http://autoshop101.com/

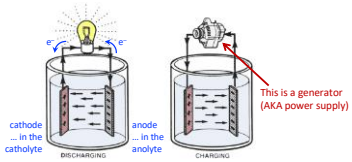
139

Conventions… Oh, Conventions!

Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized

Does a Negative/Positive Electrode = Cathode or Anode?… It depends!

For the charging (electrolytic) battery, label the anode and the cathode.



http://autoshop101.com/

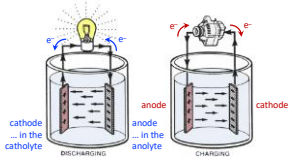
140

Conventions… Oh, Conventions!

Positive electrode – positively charged; immersed in the **posolyte**
Negative electrode – negatively charged; immersed in the **negolyte**

… **I'm not kidding!**

… **Sheesh!**…
… **Take-home message: For batteries, don't call electrodes anodes and cathodes** *(but the naming convention used by most is for discharge)*



http://autoshop101.com/

Conventions… Oh, Conventions!

141

http://upload.wikimedia.org/wikipedia/commons/thumb/c/cc/Map_of_USA_TX.svg/2000px-Map_of_USA_TX.svg.png

Conventions… Oh, Conventions!

142

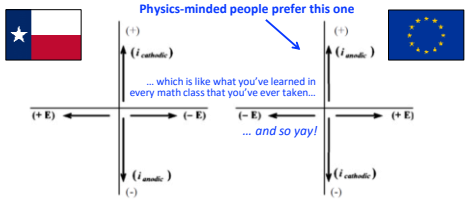


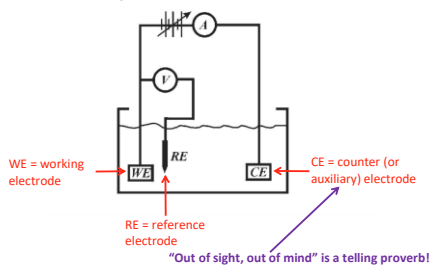
Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.

… Sadly, one if the top Electrochemistry textbooks by Bard & Faulkner uses the convention on the left…
… which makes learning electrochemistry harder than it needs to be… Ugh!

Handbook of Electrochemistry, Zoski (ed.), Elsevier, 2007

… Electrochemists resort to a *3-electrode potentiostat*…

143



http://www.porous-35.com/electrochemistry-semiconductors-10.html

Charged Interfaces *(summary for today)*

- **Vacuum level, Redox half-reactions**
- **Nernst equation**
- **History, Conventions**
- **Electrodes, Potentiostat**
- Electric double layer
- Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential
- pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation
- Latimer diagram, Pourbaix diagram

Paper Time!