Statistical Molecular Thermodynamics

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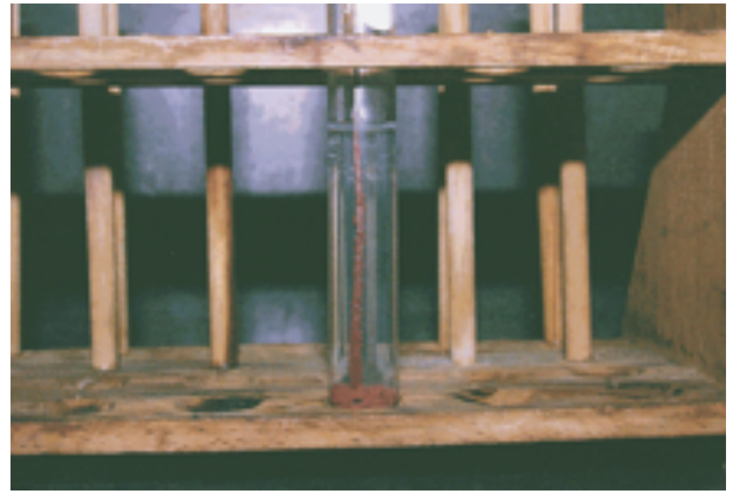
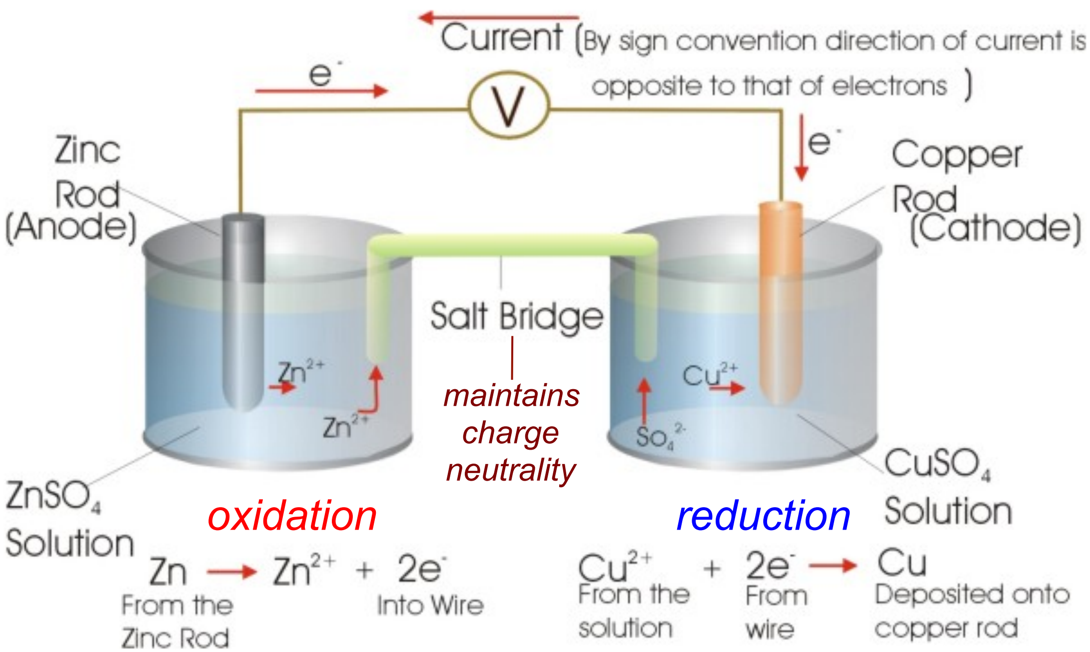
Video 13.1

Electrochemical Cells

Harnessing Electrons To Do Work

If you put a zinc rod into a deep blue copper sulfate solution, the blue disappears as copper plates onto the decomposing zinc rod →





That's a short circuit. If you don't let the solution contact the copper directly, you can still flow electrons from zinc to copper, using the spontaneity of the reaction to do work (remember free energy defines the maximum extractable non-*PV* work?)

Types of Electrodes — Half Cells

Solid metal with aq. ions

$Zn^{2+}(aq) + 2e^- \leftrightarrows Zn(s)$

$Cu^{2+}(aq) + 2e^- \leftrightarrows Cu(s)$

Pure metal with aq. ions and insoluble salt

$AgCl(s) + e^- \leftrightarrows Ag(s) + Cl^-(aq)$

$Hg_2SO_4(s) + 2e^- \leftrightarrows Hg(l) + SO_4^{2-}(aq)$

Gas electrode with catalyst

$H^+(aq) + e^- \leftrightarrows (1/2)H_2(g)$

$(1/2)Cl_2(g) + e^- \leftrightarrows Cl^-(aq)$

Aqueous metal ions with catalyst

$Tl^{3+}(aq) + 2e^- \leftrightarrows Tl^+(aq)$

$Fe^{3+}(aq) + e^- \leftrightarrows Fe^{2+}(aq)$

Convention is to write a half-cell reaction as reduction, although in a full circuit it may operate in oxidation mode

Full Electrochemical Cells

Written as anode (oxidation) to left, cathode (reduction) to right, single bars between half-reaction couples, and a double bar for a salt bridge (if present)

$$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$$

metal oxidized → metal ion in solution *metal ion reduced → metal in solid state*

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a wire connecting the two half-cells permits electrons to flow from anode to cathode, the salt bridge permits charge neutrality to be maintained by a corresponding flow of positive and negative ions

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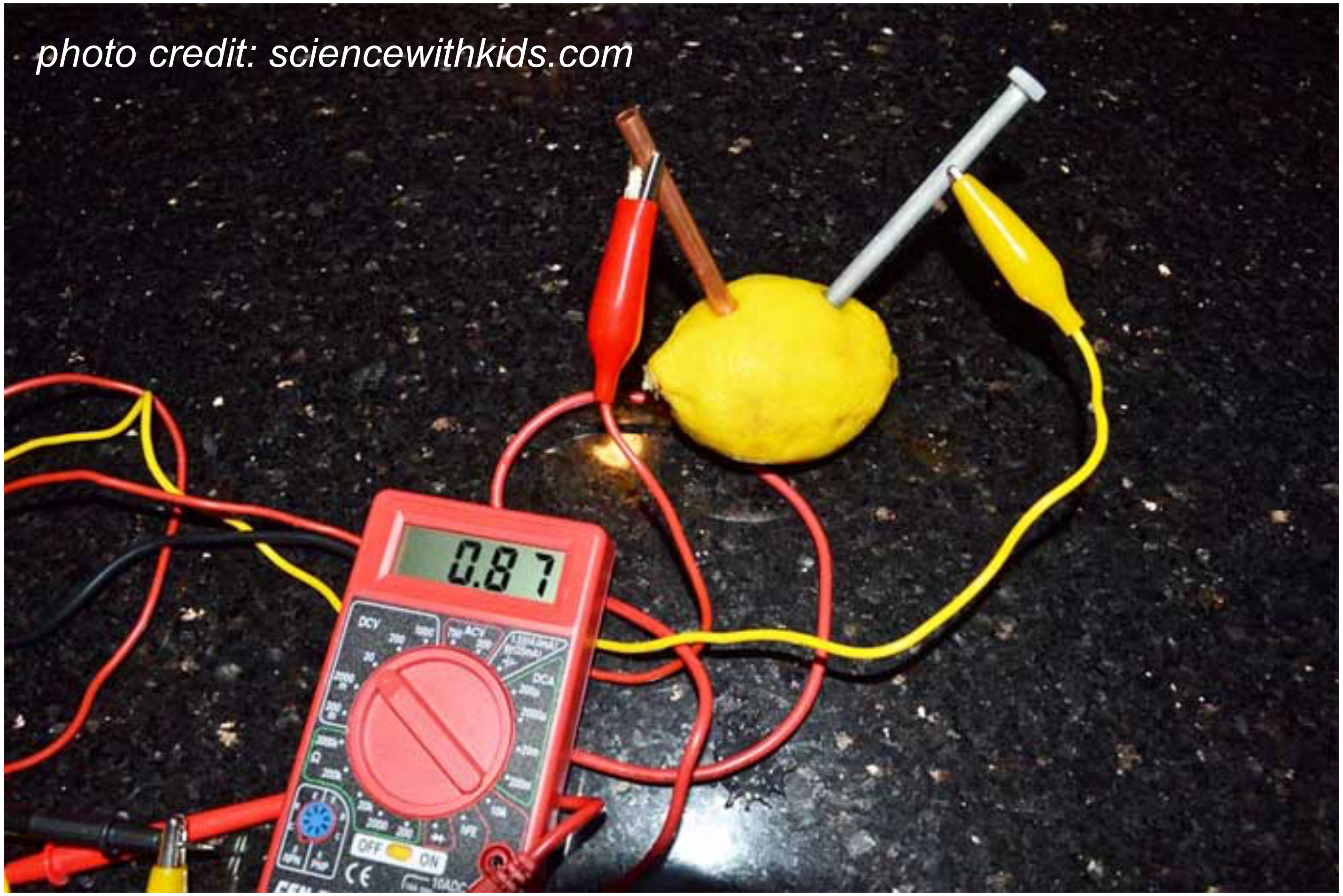
$$Cd(s) \mid CdSO_4(aq) \mid Hg_2SO_4(s) \mid Hg(l)$$

metal oxidized → metal ion in solution *metal ion reduced → metal in liquid state*

note lack of salt bridge because only a single electrolyte solution is present

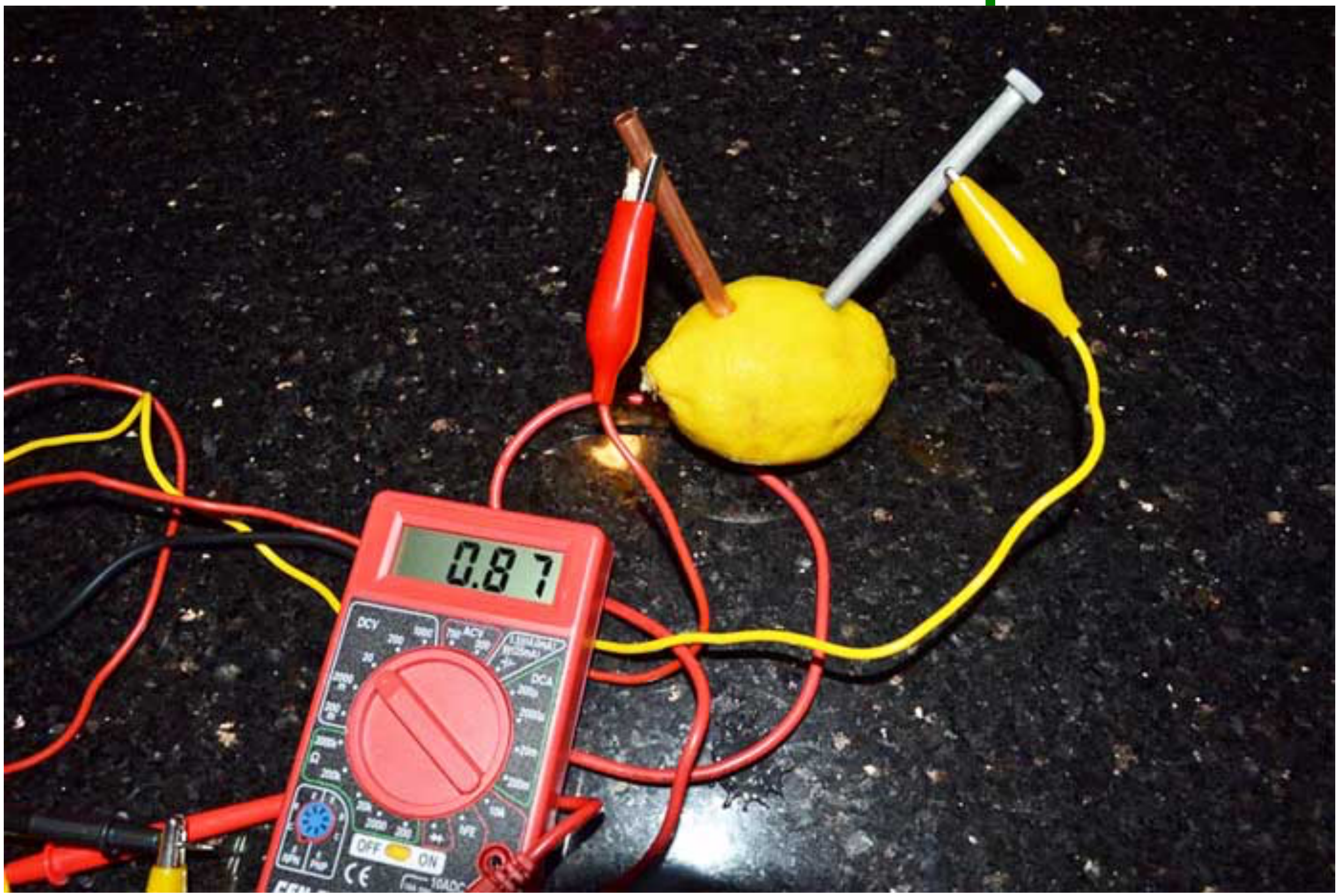
Again, current flows as "holes" (blame physicists)—that is, current flows in the direction opposite to that of the electrons, i.e., cathode to anode

Self-assessment



A galvanized (zinc-coated) nail and a copper tube are shown here inserted (not touching) into a lemon, and connected via alligator clips through a multimeter reading 0.87 V. Identify the key components of this electrochemical cell by name.

Self-assessment Explained



Galvanized (zinc-coated) nail: <u>anode</u>
Copper tube: <u>cathode</u> (which is catalyzing reduction of H^+ in the lemon)
Lemon: <u>salt bridge</u>

Next: Potential and Electromotive Force