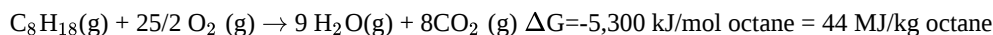


## 9.3: Electrochemistry and the Nernst Equation

Batteries are an integral part of renewables.

Burning gas:



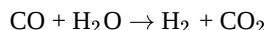
Problems: security, sustainability, climate, environment.

Alternative:

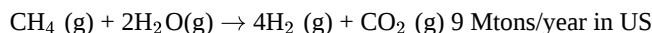


Two problems: storage at STP 1L H<sub>2</sub> contains 10 kJ of energy

Production: steam reforming



H<sub>2</sub> is produced industrially from steam reformation & WG shift reaction:



A viable economy requires an energy consumption rate of ~30 TW in 2050

~1800 Mtons H<sub>2</sub>/year

Sun delivers energy at 120,000 TW

**9.3.1 Battery Design: The Galvanic Cell.** A battery is a type of galvanic cell, which produces electricity based on a spontaneous reaction. The cell is composed of electrodes, which are metallic conductors inserted into a phase boundary across which a potential difference occurs.

Consider the device shown in Figure 9.6, which is a bucket of acid with two metal rods sticking out of it. One is made of zinc and the other copper, and ...

**9.3.2 The standard electromotive force.** These are based on Faraday's Laws:

[\[GrindEQ\\_\\_1\\_\] The mass of a given substance that is produced or consumed at an electrode is proportional to the quantity of electrical charge passed through the cell.](#)

[\[GrindEQ\\_\\_2\\_\] Equivalent masses of different substances are produced or consumed at an electrode with the passage of a given quantity of electrical charge through the cell.](#)

Gibbs Free Energy:  $G = H - TS = U + PV - TS$

Electrochemical cells operate at constant T and P

$$\Delta G = \Delta H + P\Delta V - T\Delta S$$

First law of Thermo: Heat (q) and work (w) are the two forms in which internal energy (U) is transferred to and from a system

$$\Delta U = q + w$$

And work could be mechanical (pressure-volume, PV) work or electrical work (w<sub>el</sub>)

$$\Delta U = q + w_{PV} - w_{el} \quad \Delta G = \Delta H - T\Delta S - w_{el}$$

If the cell is reversible, then q<sub>rev</sub> = TΔS (2nd law of thermo), and putting it all together:

$$\Delta G = \Delta H + T\Delta S - (T\Delta S) - w_{el} = \Delta H - w_{el} \quad \Delta G = \Delta H - w_{el}$$

$$\Delta G = -w_{el} \quad \Delta G = -nFE$$

Cell potentials can be determined away from standard conditions using the Nernst equation:

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

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$\ln \frac{Q}{K}$

For any conditions,  $\Delta G = RT$

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$\ln \left( \frac{Q}{K} \right) = -\frac{\Delta G}{RT}$

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$\ln \frac{K}{RT}$

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$\ln \frac{Q}{K} = \frac{\Delta G}{RT}$

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$\ln \frac{Q}{K}$

And, we've established that  $\Delta G^\circ = -nFE^\circ$ . It follows that away from standard conditions,  $\Delta G = -nFE$ .

So,  $\Delta G = -nFE = -nFE^\circ + RT \ln \frac{Q}{K}$

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$\ln \frac{Q}{K}$  and dividing each term by  $-nF$ ,

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

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$\ln \frac{Q}{K}$

### Reference electrodes:

Electrical potential (like any potential energy) requires a reference.

Any electrode in which all components of the reaction are present at unit activity has a fixed potential at constant temperature and pressure, and can be used as a reference electrode.

The international standard is the Normal Hydrogen Electrode

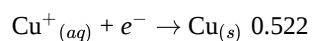
$2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2 (\text{g}), E^\circ = 0 \text{ V}$

Note, this electrode requires working in strong acid (1 M H<sup>+</sup>) and bubbling in 1 atm explosive H<sub>2</sub> gas. Not practical for battery work. But, we use this reference to measure...

$\text{Li} (\text{aq}) + \text{e}^- \rightleftharpoons \text{Li} (\text{s}), E^\circ = -3.04 \text{ V vs NHE} (0 \text{ V vs. Li}^+/\text{Li})$

he overall reaction and potential for a  $\text{Cu}^{2+} / \text{Cu}^+$  cell given the following:

$\text{Cu}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu} (\text{s}) \quad 0.340$



Make sure you show how to determine the potential by adding  $\Delta G$ 's.

### References

Mohammed J. Meziani, Christopher E. Bunker, Fushen Lu, Heting Li, Wei Wang, Elena A. Gulians, Robert A. Quinn, Ya-Ping Sun. "Formation and Properties of Stabilized Aluminum Nanoparticles" *ACS Appl. Mater. Interfaces* 2009, 13, 703-709.

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