9.3: Electrochemistry and the Nernst Equation

Batteries are an integral part of renewables.

Burning gas:

$C_8H_{18}(g) + 25/2\ O_2\ (g) \rightarrow 9\ H_2O(g) + 8CO_2\ (g)$ ΔG=-5,300 kJ/mol octane = 44 MJ/kg octane

Problems: security, sustainability, climate, environment.

Alternative:

$H_2\ (g) + 1/2\ O_2\ (g) \rightarrow H_2O\ (g)$ ΔG= -237 kJ/mol H_2 = 120 MJ/kg H2

Two problems: storage at STP 1L H2 contains 10 kJ of energy

Production: steam reforming

$CH_4\ (g) + H_2O\ (g) \rightarrow CO + H_2\ (g)$ ΔG= -237 kJ/mol H_2 = 120 MJ/kg H2

$CO + H_2O \rightarrow H_2 + CO_2$

H_2 is produced industrially from steam reformation & WG shift reaction:

$CH_4\ (g) + 2H_2O(g) \rightarrow 4H_2\ (g) + CO_2\ (g)$ 9 Mtons/year in US

A viable economy requires an energy consumption rate of $\sim$30 TW in 2050

$\sim$1800 Mtons H2/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

Δ��= Δ��+��Δ�� −��Δ��

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

Δ��=��+��

And work could be mechanical (pressure-volume, PV) work or electrical work (wel)

Δ��=��+��_����−��Δ��

If the cell is reversible, then qrev = TΔS (2nd law of thermo), and putting it all together:

Δ��=��Δ��+��_(����,������)−��Δ��+��Δ�� −��Δ��=��_(����,������)

Δ��= ��_(����,������)=−����=−������

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

\[E=E{}^\circ ~-~\frac{RT}{nF}

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\ln \ Q\ \nonumber \]

For any conditions, \(\Delta G=RT

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\ln left(\frac{Q}{K}\right)=~\ -RT

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\ln \ K+RT

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\ln \ Q=~\Delta G{}^\circ +RT

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\ln \ Q)

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

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\ln \ Q) and dividing each term by –*nF*,

\[E=E{}^\circ ~-~\frac{RT}{nF}

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\ln \ Θ\ \nonumber \]

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

$2H^+$ (aq) + $2e^{--}$ $\rightleftharpoons$ H_2 (g), E° = 0 V

Note, this electrode requires working in strong acid (1 M H+) and bubbling in 1 atm explosive H2 gas. Not practical for battery work. But, we use this reference to measure…

Li+(aq) + e– $\rightleftharpoons$ Li(s), E° = –3.04 V vs NHE (0 V vs. Li+/0)

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

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

$Cu^{+}{}_{(aq)} + e^{-} \rightarrow Cu_{(s)}$ 0.522

Make sure you show how to determine the potential by adding ΔG's.

References

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