Looking forward… our review of Chapter “0”

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Nernst equation and Common reference electrodes
- Standard and Absolute potentials
- Latimer and Pourbaix diagrams
- Calculating $E_{\text{cell}}$ under non-standard state conditions
- Conventions

A Short History Lesson…

Electrochemistry associated with Luigi Galvani who discovered “animal electricity,” while trying to Frankenstein frogs legs (1791)

Physician, Physicist, Philosopher

Luigi Galvani (1737–1798) from Wiki
Voltaic pile

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

What are the combined half-reactions?

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

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" (2019)!

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

Electrolysis of water

Volta's results were shared with the scientific community and then, boom, many people demonstrated electrolysis the same year, and later, electroplating!
Daniell (galvanic) Cell (1836)

Half-reactions are physically separated!

\[ \begin{align*}
\text{Anode (oxidation):} & \quad \text{Zn (s)} \rightarrow \text{Zn}^{2+} (aq) + 2e^- \\
\text{Cathode (reduction):} & \quad \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s)
\end{align*} \]

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

John Frederic Daniell (1790–1845)

Voltage Produced by Galvanic Cells

The difference in electric potential between the anode and the cathode is called:

- \text{Cell potential}
- \text{Cell voltage}
- \text{emf (electromotive force)}

Cell Diagram

\[ \text{Zn (s) | Zn}^{2+} (1 M) || \text{Cu}^{2+} (1 M) | \text{Cu (s)} \]

\[ [\text{Cu}^{2+}] = 1 \text{ M and } [\text{Zn}^{2+}] = 1 \text{ M} \]

\[ \text{This should be ±0.76 V! (we will discuss this soon)} \]

**EXAMPLE:** What is the (standard) potential of a galvanic cell consisting of a Cd electrode in a 1.0 M Cd(NO_3)_2 solution and a Cr electrode in a 1.0 M Cr(NO_3)_3 solution?

Which half-reaction is reducing?

\[ \begin{align*}
\text{Anode (oxidation):} & \quad \text{Cr (s)} \rightarrow \text{Cr}^{3+} (1 M) + 3e^- \\
\text{Cathode (reduction):} & \quad 3\text{Cd}^{2+} (1 M) \rightarrow 3\text{Cd (s)} \\
\end{align*} \]

More negative of the two?

- \[ \text{Cd}^{2+} (aq) + 2e^- \rightarrow \text{Cd (s)} \quad E^0 = -0.40 \text{ V} \quad \text{Cd}^{2+} \text{ will get reduced to Cd} \]
- \[ \text{Cr}^{3+} (aq) + 3e^- \rightarrow \text{Cr (s)} \quad E^0 = -0.74 \text{ V} \quad \text{Cr will get oxidized to Cr}^{3+} \]

\[ \text{More negative of the two} \]

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\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

\[ E_{\text{cell}} = +0.34 \text{ V (positive = spontaneous, since } \Delta G = -nFE) \]

\[ \text{... if your answer is negative then you switched the anode/cathode in the galvanic cell} \]
Electrochemistry: conventions… oh, conventions!
Cathode – electrode where catholyte species are reduced
Anode – electrode where anolyte species are oxidized

Negative/Positive electrode – cathode or anode?… it depends!

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

For the charging (electrolytic) battery, label the anode and cathode.
Electrochemistry: 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 naming convention used by most is for discharge)

http://autoshop101.com

Zn(s) Zn^{2+}(aq) Cu^{2+}(aq) Cu(s)
Zn | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu

I_{cell}

The Daniell Cell (1836)

This only works for less than one second and then stops due to Kirchhoff’s current law, which states that all current at each location must sum to zero...

... capacitive charging

John Frederic Daniell (1790–1845)
from Wiki
Now it works = "electrochemistry!"
Salt bridge contains an inert, redox inactive salt solution (electrolyte)

The Daniell Cell (1836)

low impedance to measure current

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* Identify anode
* Identify cathode
* Name the electrode signs

* primary galvanic cell

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* primary galvanic cell
The Daniell cell (1836)

This will eventually fully discharge and reach equilibrium ($\Delta G = E_{cell} = 0$)

Then, either direction of polarization bias results in electrolytic function (i.e. charging)

The Daniell cell (1836)

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**PROBLEM TIME!**

You try!

(a) What is the standard $E_{cell}$ for a galvanic cell based on zinc and silver?

(b) If we wanted to electrolytically charge the cell from part a (before any reactions took place), what potential would we have to apply?

(a) $E_{cell} = +0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$

(b) $E_{bias} < -1.56 \text{ V}$

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Coulomb (in units of C = A·s) is the unit of charge (96,485 C are in a mole of singly charged species). Electricity is the flow of current (A = C/s) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g., e⁻, H⁺).

Electrolytic cells require a power input to drive redox reactions; thus, the reactions are thermodynamically unfavorable. Batteries have a potential (E) of \( \approx 96,500 \text{ C/mol} \) and are preferred over electrolytic cells.

Electricity is the flow of current (A = C/s) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g., e⁻, H⁺). Galvanic cells produce power (in units of W = A x V = C/s x J/C = J/s) by spontaneous redox reactions depending on the direction and sign of the current.

For a redox reaction, the electrode (electric) potential (\( \phi \)) is defined as the Gibbs free energy change when resistance is constant, \( \mu_nF \), with respect to time. You can subtract redox potentials but do not change the sign of the potential and then call it an oxidation potential!

\[ E^0(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V vs. SHE} \]

This relates to Gibbs free energy as \( \Delta G = -nFE \) potential (in units of J/mol), where \( n \) is the number of electrons transferred, \( F \) is the Faraday constant, and \( E \) is the electrode potential (in units of V). Also, standard state is a solvent, a solid, and a species at ~1 bar. Sources: IUPAC, Chemistry (IUPAC), goldbook.iupac.org/
Coulomb (in units of C = A·s) is the unit of charge (96,485 C are in a mole of singly charged species = Faraday constant, F = 96,500 C/mol = 10^7 C/mol).

Electricity is the flow of current (A = C/s) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g. e, H^+).

(Electrode) (electric) potential (V or E) in units of V = J/C is written as a reduction

\[
E^0(\text{Cu}^{2+}) = +0.34 \text{ V vs. SHE} \\
E^0(\text{Cu}^{2+}) = -0.34 \text{ V vs. SHE}
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(Source: B&F, M3LC course textbook, and http://goldbook.iupac.org/)

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Based on our current sign convention, it is best to only write reduction potentials; however, if we lived in an oxidation-potential-centric world, we could write them all (i.e. everything) as oxidation potentials; simply put, it is best to not mix the conventions and so stick with reduction potentials.

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International Union of Pure and Applied Chemistry (IUPAC)

(Accepted) Nomenclature and Terminology that you know, but may have forgotten

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Coulomb (in units of C = A·s) is the unit of charge (96,485 C are in a mole of singly charged species = Faraday constant, F = 96,500 C/mol = 10^4 C/mole)

Electricity is the flow of current (A = C/s) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g. H^+, e^-)

(Electrode) (electric) potential (V or E) in units of V = J/C is written as a reduction
This relates to Gibbs free energy as ΔG = -RT ln(α) - mFϕ (chemical work per mole), and... partial mol Gibbs free energy is the electrochemical potential (ϕ, in units of J/mol)

Chemical potential (μ, in units of J/mol)
Electrochemical potential (ϕ, in units of V)

and in summary, μ = ϕ

Also, standard state is a solvent, a solid, and a species at unit activity (1 M solutes, 1 bar gases)
Also, E, R, T (Ohm’s law) when resistance is constant

Sources: B&F, M3LC course textbook, and http://goldbook.iupac.org/
**International Union of Pure and Applied Chemistry (IUPAC)**

(Accepted) Nomenclature and Terminology that you know, but may have forgotten

- Coulomb (in units of $C = A \cdot s$) is the unit of charge ($96,485 \, C$ are in a mole of singly charged species = Faraday constant, $F = 96,500 \, C/mol = 10^5 \, C/mol$)
- Electricity is the flow of current ($A = C/s$) and is negative (cathodic) or positive (anodic) depending on the direction and sign of the current-carrying species (e.g. $e^-$, $H^+$)
- (Electrode) (electric) potential ($V$ or $E$; in units of $V = J/C$) is written as a reduction. This relates to Gibbs free energy as $\Delta G = -RT \ln K = -nFE_{cell}$ (electrical work per mole), and partial molar Gibbs free energy is the electrochemical potential ($\mu$, in units of $J/mol$)
  - Chemical potential ($\mu$, in units of $J/mol$)
  - Galvani/Inner (electric) potential ($\phi$, in units of $V$)
- Also, standard state is a solvent, a solid, and a species at unit activity ($\sim 1 \, M$ solutes, $\sim 1 \, bar$ gases).
- A battery has an anode/anolyte and a cathode/catholyte, but these descriptors change depending on whether the battery is being discharged (galvanic) or charged (electrolytic); negative electrode/negolyte and positive electrode/posolyte are better.

For “clarity,” a brief (more rigorous) “review” of thermodynamics…

**Electrochemical potential** of species $i$ in phase $\beta$ is an energy ($J/mol$),

$$\bar{\mu}_i^\beta = \left( \frac{\Delta G}{n_i} \right)_{T,\beta, n_{j\neq i}} = \mu_i^\beta + z_i F \phi^\beta,$$

where

- $\Delta G$ (Gibbs free energy ($J$))
- $n_i$ (amount of species $i$ (mol))
- $\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential ($J/mol$))
- $z_i$ (valency of species $i$)
- $F = 10^5$ (Faraday constant ($C/mol$))
- $\phi^\beta$ (Galvani/inner electric potential ($V$))
- $a_i$ (activity of species $i$)

For an uncharged species $\bar{\mu}_i^\beta = \mu_i^\beta$.

Parsons, Pure & Appl. Chem., 1973, 37, 504
IUPAC Gold (http://goldbook.iupac.org)

Half reactions, at non-unity activity, obey the Nernst equation…

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$, 

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Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

But first... what is $Q$, again? ... the reaction quotient!

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

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$$Q = \frac{\prod_v a_v^{n_v}}{\prod_v a_0^{n_v}} = \frac{\left( \frac{c_i}{c_i^0} \right)^{v_i}}{\left( \frac{c_i}{c_i^0} \right)^{v_i}}$$, because fundamentally $\mu_i = \mu_i^0 + RT \ln a_i$

$$Q = \frac{\prod_v a_v^{n_v}}{\prod_v c_v^{n_v}}$$, for dilute solutions... which we never have!

$a_p$ is the activity of product $p$

$a_r$ is the activity of reactant $r$

$v_i$ is the stoichiometric number of $i$

$\gamma_i$ is the activity coefficient of $i$

$c_i$ is the concentration of $i$

$c_i^0$ is the standard state concentration of $i$
Half reactions, at non-unity activity, obey the Nernst equation…

Take $\Delta G = \Delta G^0 + RT \ln Q$ and use the relation $\Delta G = -nFE$.

$$-nFE = -nFE^0 + RT \ln Q$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = E^0 - \frac{RT \log Q}{nF \log e}$$

$$E = E^0 - \frac{RT}{0.4343nF} \log Q$$

$$E = E^0 - \frac{2.3026RT}{nF} \log Q$$

**... and at 298.15 K, $E = E^0 - \frac{0.05916 V}{n} \log Q$**

**Memorize $\sim 60 \text{ mV per order in log}_10$, but do not forget $n$ and that this is at 25°C!**

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**Physicist Walther Hermann Nernst (1864–1941)
Nobel Prize (Chemistry, 1920)**

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\[
E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}
\]

Since we always use half cell differences, we can add an arbitrary constant to all half cells. By convention, we assume that the \( E^0 \) for the standard hydrogen electrode (SHE) is equal to zero:

**Half Cell Reaction for Hydrogen:**

\[
H^+ + e^- \rightarrow \frac{1}{2} H_2(g) \]

\[
E_H = E_H^0 + \frac{RT}{F} \ln \frac{P_{H_2}}{[H^+]} \quad E_H^0 = 0
\]

Thus, the potentials for half-cell reactions are actually full-cell potential (difference(s)) versus SHE, or other!

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**Outmoded Terminology: The Normal Hydrogen Electrode**

* Normal hydrogen electrode (NHE) is an empirical SHE ([H^+] = 1; not standard state)
* Standard hydrogen electrode (SHE) is a hypothetical, perfect NHE (a = 1; not empirical)
* Reversible hydrogen electrode (RHE) is the SHE but the same regardless of pH
* And generally, formal potentials (\( E^0 \)) take into consideration non-idealities and changes in ionic strengths so that the reaction quotient only has concentrations, and not activities

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Given this value, what is this experimental redox potential versus?

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\[ E_H^0 = 0 \text{ vs. SHE} \]
EXAMPLE: Write a balanced chemical equation and calculate the standard cell potential for the galvanic cell:
\[
\text{Zn}(s) \mid \text{Zn}^{2+} \text{(1 M)} \parallel \text{MnO}_4^- \text{(1 M)}, \text{Mn}^{2+} \text{(1 M)}, \text{H}^+ \text{(1 M)} \mid \text{Pt}(s)
\]

Look up half-reactions and standard reduction potentials in an Electrochemical Series table (CRC, B&F Appendix C, WWW):

Anode: \[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E_{\text{anode}} = -0.76 \text{ V}
\]

Note: Although strictly correct, do not use \(\overline{\overline{E}}\) as the \(E\) for oxidation

Cathode: \[
\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E_{\text{cathode}} = +1.51 \text{ V}
\]

Note: Be careful to choose the correct half-reaction with \(\text{MnO}_4^-\)

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To get the balanced overall reaction... ?
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Note: Be careful to choose the correct half-reaction with \(\text{MnO}_4^-\).

To get the balanced overall reaction, multiply the anode reaction by 5 and add to 2 times the cathode reaction, giving:

\[ 2\text{MnO}_4^- (aq) + 16\text{H}^+ (aq) + 5\text{Zn} (s) \rightarrow 5\text{Zn}^{2+} (aq) + 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O} (l) \]

\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 1.51 \text{ V} + 0.76 \text{ V} = +2.27 \text{ V} \]

Q: What processes occur in electrochemistry? … one more …

CRC Handbook of Chemistry and Physics, 92nd Edition

* All values versus SHE

http://folk.ntnu.no/andersty/2.%20Klasse/KJ1042%20Termodynamikk%20med%20Lab/Lab/Oppgave%205%20Standard%20reduksjonspotensial/RapportfilenE0.pdf

Q: What processes occur in electrochemistry? … one more …

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than unsolvated electrons and holes – through phase(s), or the transfer of charge across interface(s).

Example: solvated electrons

Prof. Robert Hamers (Univ. of Wisconsin)

Zhu, …, Hamers, Nature Materials, 2013, 12, 836
First description of conductivity using solvated electrons

During the first part of the twentieth century, E. C. Franklin and C. A. Kraus probably did more to elucidate the chemistry of liquid ammonia solutions than everybody else combined. It is perhaps little known that their work was prompted by the research and insight of H. P. Cady, carried out while he was an undergraduate! While working on cobalt ammine complexes, Cady proposed that ammonia in these (and other “double salts”) must function in a manner akin to water in sols with water of crystallization. He suggested further that liquid ammonia would probably be found in reasonable water in its physical and chemical properties—thus adding a second to our list of ionizing solvents. Cady’s undergraduate work, carried out without supervision, published in 1897, was perhaps the first physical-chemistry study of liquid ammonia solutions.


<table>
<thead>
<tr>
<th>Salt used</th>
<th>Dissolved in ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matsubara</td>
<td>707</td>
</tr>
<tr>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>4.4</td>
<td>4.5</td>
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</table>

Cady, J. Phys. Chem., 1897, 1, 707

Q: What is electrochemistry? … one more …

A: Any process involving the motion/transport of charge—carried by entities other than unsolvated electrons and holes—through phase(s), or the transfer of charge across interface(s).

Example: solvated electrons

Prof. Robert Hamers (Univ. of Wisconsin)

http://hamers.chem.wisc.edu/people

Zhu, …, Hamers, Nature Materials, 2013, 12, 836

Absolute potentials can be measured / approximated very carefully…

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

THE ABSOLUTE ELECTRODE POTENTIAL: AN EXPLANATORY NOTE

On the basis of the values in Table 1, the recommended absolute potential of the standard hydrogen electrodes nor deviate from both eqn. (12) and (14) with the same accuracy, i.e.

\[ E^{\text{H}^+} + 0.059(\text{pH}) = 0.0005 \times \text{Temp.} \text{ K} \]

Prof. Sergio Trasatti

(Università de Milano, Italy)

\[ E^{\text{H}^+} + 0.059(\text{pH}) = 0.0005 \times \text{Temp.} \text{ K} \]

Note: See the recommendations for the standard hydrogen electrode for details on the calculation. Yes, it is very accurate and easy to use, but remember that the validity of the data is important. As for the calculation of the absolute potential, see Trasatti, Pure & Appl. Chem., 1986, 58, 955.
Absolute potentials can be measured/approximated... very carefully...

FOR YOUR REFERENCE

\[ E^\circ (\text{H}_2/O_2) = \left( \frac{\Delta G^\circ}{nF} \right) + \frac{1}{2} \left( \frac{\Delta G^\circ}{nF} \right) \]

(12)

### Table

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<th>Value</th>
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<tbody>
<tr>
<td>( E^\circ (\text{H}_2/O_2) )</td>
<td>( -0.82 \text{ V} )</td>
<td>(15)</td>
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</tbody>
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\[ \text{Born–Haber cycle:} \]

\[ \text{(gas)} \quad \xrightarrow{\Delta G} \quad \text{H}^+ (\text{aq}) + e^{-} (\text{vacuum}) \]

Trasatti, Pure & Appl. Chem., 1986, 58, 955

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… but we need an electrode!
Absolute potentials can be measured / approximated... very carefully...

Born–Haber cycle:

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\text{H}^+ (\text{aq}) & \xrightleftharpoons{\text{H}^+ (\text{aq})} \text{H} (\text{gas}) + e^+ (\text{vacuum}) \\
\text{H}_2 (\text{gas}) & \xrightarrow{\text{Mg}} \text{H}_2 (\text{aq}) + e^- (\text{H}g)
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Absolute potentials can be measured / approximated... very carefully...

\[
\begin{align*}
E^0 (\text{H}_2/\text{H}) (\text{abs}) & = (\Delta_{\text{H}_2} G^0 + 2 \Delta_{\text{H}_2} G^0) / 2 \\
\text{H}_2 (\text{g}) & \xrightarrow{\text{Mg}} \text{H}_2 (\text{aq}) + e^- (\text{H}g)
\end{align*}
\]

... but we need an electrode!
Absolute potentials can be measured / approximated very carefully...

**FOR YOUR REFERENCE**

\[
\begin{align*}
\Phi^0(E^0/\text{Hg}(\text{ab})/\text{Hg}) & = (E^0_{\text{Hg}(\text{ab})}^0 + n_e \mu_e^0) + \mu_{\text{Hg}}^0/\Gamma \\
\Phi^0_E & = \Phi^0(E^0/\text{Hg}(\text{ab})/\text{Hg}) - \Phi^0_E^0 \\
\eta_e & = \Phi^0 - \Phi_E^0 - \Phi_E^0 \text{ (OHP)}
\end{align*}
\]

Born–Haber cycle:

\[
\text{H}_2(\text{gas}) \rightarrow \text{H}_2(\text{gas}) + e^0(\text{vacuum})
\]

Trasatti, Pure & Appl. Chem., 1986, 58, 955

… but we need an electrode!