Standard Electrode Potentials

*chemistry and conventions*

1. Introduction
   a. REDOX, half-equations and voltage
   b. Why do we want to measure electrode potentials?

2. Describing the Electrochemical Cell
   a. Technical terms
      i. Electrode
      ii. Half-cell
      iii. Salt bridge
      iv. Electromotive force (e.m.f.), potential difference, voltage
      v. Electrode potential

3. Chemical Causes and Conventions
   a. Cause of the electromotive force (e.m.f.)
   b. Convention of the voltmeter
   c. What does the sign of the electrochemical cell tell about the REOXD behaviour of the half-cells?

4. Standard Electrode Potentials
   a. If hydrogen is used as the reference electrode, what e.m.f. should it have?
   b. Why does it matter which side we put the reference electrode on?
   C. What things do we need to do consistently in order to build up a table of standard electrode potentials?
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REDOX, half-equations and voltage

Oxidation Is Loss Reduction Is Gain

REDOX

half-equations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Na⁺ + e⁻</td>
</tr>
<tr>
<td>½ Cl₂ + e⁻</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Na + ½ Cl₂ + e⁻</td>
<td>Na⁺ + e⁻ + Cl⁻</td>
</tr>
</tbody>
</table>

"+1.5V"

1.5V
Why do we want to measure electrode potentials?

- quantitative reactivity series
- use to predict reactions
- make batteries

Where do you think the following would be on this reactivity series?

- mild oxidising agent, such as iodine
- reactive metal, such as potassium
- transition metal, such as iron
- reactive non-metal, such as fluorine

answers (starting from top): D, A, C, B
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What technical terms do we need to know?
<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt Bridge</td>
<td>e.m.f. caused by joining two half-cells together</td>
</tr>
<tr>
<td>Electrode potential</td>
<td>prevents build up of charge in the solution</td>
</tr>
<tr>
<td>Half-cell</td>
<td>half of an electrochemical cell</td>
</tr>
<tr>
<td>Cell potential</td>
<td>potential energy due to build up of charge</td>
</tr>
<tr>
<td>Electromotive force (e.m.f.)</td>
<td>e.m.f. caused by a half-cell relative to the hydrogen half-cell</td>
</tr>
</tbody>
</table>
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1. Introduction
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3. Chemical Causes and Conventions
   a. Cause of the electromotive force (e.m.f.)
   b. Convention of the voltmeter
   c. What does the sign of the electrochemical cell tell about the REDOX behaviour of the half-cells?
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Cause of the electromotive force (e.m.f.)

Why does linking two half-cells cause a voltage?

![Diagram showing the cause of the electromotive force]
Convention of the voltmeter

Why does it matter which way around I plug in the voltmeter?

Convention of the voltmeter

Why does it matter which way around I plug in the voltmeter?
What does the sign of the electrochemical cell tell me about the REDOX behaviour of the half-cells?

What does the sign of the electrochemical cell tell me about the REDOX behaviour of the half-cells?
Would you expect a +ve or –ve voltage for the following electrochemical cells?

answers (clockwise starting from top left):
+ve, -ve, +ve
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   a. If hydrogen is used as the reference electrode, what e.m.f. should it have?
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   c. What things do we need to do consistently in order to build up a table of standard electrode potentials?

If hydrogen is used as the reference electrode, what e.m.f. should it have?
Why does it matter which side we put the reference electrode on?

CONVENTION: reference electrode on the left hand side (L.H.S.)
What things do we need to do consistently in order to build up a table of standard electrode potentials?

1. Left hand half-cell into negative terminal of voltmeter
2. Left hand half-cell to be H₂, H⁺
3. Standard conditions (1atm, 1moldm⁻³, standard states, 298K)

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3. Standard conditions (1atm, 1moldm⁻³, standard states, 298K)
tends to lose electrons

Zn\(^{2+}\), Zn \(-0.76\) V

Ni\(^{2+}\), Ni \(-0.25\) V

H\(^+\), \(\frac{1}{2}H_2\) 0 V

Cu\(^{2+}\), Cu \(+0.34\) V

Ag\(^+\), Ag \(+0.80\) V

\(\frac{1}{2}Cl_2\), Cl\(^-\) \(+1.38\) V

tends to gain electrons

Summary

We can now put these electrode potentials on the electrochemical reactivity series
More commonly written in a table of reduction half-equations

**SIGN of \( E^0 \) indicates bias of equilibrium**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( E^0 / \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(^{2+}) + 2e(^-) ⇌ Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ni(^{2+}) + 2e(^-) ⇌ Ni</td>
<td>-0.25</td>
</tr>
<tr>
<td>H(^+) + e(^-) ⇌ ( \frac{1}{2} ) H(_2)</td>
<td>0</td>
</tr>
<tr>
<td>Cu(^{2+}) + 2e(^-) ⇌ Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>Ag(^+) + e(^-) ⇌ Ag</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \frac{1}{2} ) Br(_2) + e(^-) ⇌ Br(^-)</td>
<td>+1.09</td>
</tr>
<tr>
<td>( \frac{1}{2} ) Cl(_2) + e(^-) ⇌ Cl(^-)</td>
<td>+1.38</td>
</tr>
</tbody>
</table>

-ve reverse (\( \leftrightarrow \))

+ve forward (\( \rightarrow \))

**tends to lose electrons**

**tends to gain electrons**

**Note**: the number of electrons in the half-equation does not affect \( E^0 \)

i.e. \( \frac{1}{2} \) Cl\(_2\) + e\(^-\) ⇌ Cl\(^-\) +1.38V

and Cl\(_2\) + 2e\(^-\) ⇌ 2Cl\(^-\) +1.38V
### Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical cell</td>
<td>Two half-cells connected by a salt bridge</td>
</tr>
<tr>
<td>Electrochemical series</td>
<td>Shows the redox behaviour of half-reactions relative to the hydrogen electrode</td>
</tr>
<tr>
<td>Electrode</td>
<td>The terminal through which electric current passes between metallic and nonmetallic parts of an electric circuit</td>
</tr>
<tr>
<td>Electrode potential for a cell (cell potential)</td>
<td>The e.m.f. caused by joining two half-cells together</td>
</tr>
<tr>
<td>Electrode potential for a half-cell</td>
<td>The e.m.f. caused by a half-cell relative to the hydrogen half-cell, using a right-hand electrode system.</td>
</tr>
<tr>
<td>Electromotive force (e.m.f.) potential difference, voltage</td>
<td>I do not distinguish between these three terms. They all describe the extent to which there is a build up of opposite charges on either side of the voltmeter.</td>
</tr>
<tr>
<td>Half-cell</td>
<td>Electrode dipped into a solution of ions</td>
</tr>
<tr>
<td>Half-equation</td>
<td>Ionic equation showing the gain or loss of electrons of a species. In the electrochemical series half-equations are shown as reductions, i.e. with the electrons on the left hand side of the equation.</td>
</tr>
<tr>
<td>Hydrogen electrode</td>
<td>half-cell based upon the half equation H⁺ + e⁻ ⇌ ½ H₂, and used as a reference in the electrochemical series</td>
</tr>
<tr>
<td>Salt bridge</td>
<td>Either a glass tube or filter paper saturated with K⁺ and NO₃⁻ ions. Used to link two half-cells. Ions from the salt bridge can flow into the half-cells to prevent a build up of charge within the solutions as REDOX reactions occur.</td>
</tr>
</tbody>
</table>

### References
