Chapter 21 Electrochemistry

Section 21.1. Electrochemistry represents the interconversion of chemical energy and electrical energy.

Electrochemistry involves **redox** (**red**uction-**ox**idation) reactions because the electrical energy (flow of electrons) has at its origin the oxidation (loss of electrons) and reduction (gain of electrons) of species.

 Can we use the energy released when a spontaneous reaction occurs? YES (common e.g. car, fuel cells, batteries, etc)
 Can we cause a non-spontaneous reaction to occur by supplying energy? YES

In fact, you have already seen one way to accomplish 2), by supplying thermal energy (raising the temperature) if $\Delta S > 0$.

$$\Delta G = \Delta H - T \Delta S$$

If $\Delta S > 0$, then $-T\Delta S < 0$, and we can make a non-spontaneous reaction spontaneous by raising the temperature so that $-T\Delta S$ term dominates.





But is there a more convenient and <u>general</u> way of driving reactions in their non-spontaneous directions? How about supplying electrical energy? The answer is yes.

Electrochemistry brings together, as a technique, several topics we have already studied: redox reactions, equilibrium, and thermodynamics.

Electrochemistry influences many areas of our lives from batteries (car, flashlights, calculators, watches, and electric cars) to electroplating, *e.g.*, surgical instruments.





Definitions of Oxidation and Reduction

Figure 21.1 Oxidation = removal of one or more electrons Reduction = addition of one or more electrons

Oxidizing agent = substance that is doing the oxidation (taking the electrons) <u>Reducing agent</u> = substance that is doing the reduction (giving the electrons)

If something is oxidized, its oxidation state (ox. state) increases. If something is reduced, its oxidation state decreases.

e.g. add Zn metal to acid (e.g. HCl) - bubbles of H_2 gas form. The equation is $Zn(s) + 2 H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(q)$

For the reaction as written left-to-right: Zn(s) is the reducing agent, giving electrons (e⁻) to H⁺ (aq) $H^{+}(aq)$ is the oxidizing agent, taking e^{-} from Zn (s)

Zn(s) is being oxidized (it is losing e^{-}) (ox. state Zn^{0} increases to Zn^{2+}) $H^{+}(aq)$ is being reduced (it is gaining e^{-}) (ox. state H^{1+} decreases to H^{0})

For the reverse reaction right-to-left $H_2(q)$ is the reducing agent and $Zn^{2+}(aq)$ is the oxidizing agent

 $H_2(g)$ is getting oxidized, and $Zn^{2+}(aq)$ is getting reduced.

<u>Note</u>: The oxidizing agent is the substance being reduced. The reducing agent is the substance being oxidized.



Figure 21.1 A summary of redox terminology, as applied to the reaction of zinc with hydrogen ion.

$$\begin{array}{cccc} \mathbf{0} & \mathbf{+1} & \mathbf{+2} & \mathbf{0} \\ \operatorname{Zn}(s) + 2\operatorname{H}^+(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{H}_2(g) \end{array}$$

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 OXIDATION One reactant loses electrons. Reducing agent is oxidized. Oxidation number increases. 	Zinc loses electrons. Zinc is the reducing agent and becomes oxidized . The oxidation number of Zn increases from 0 to +2.	
 REDUCTION Other reactant gains electrons. Oxidizing agent is reduced. Oxidation number decreases. 	Hydrogen ion gains electrons. Hydrogen ion is the oxidizing agent and becomes reduced . The oxidation number of H decreases from +1 to 0.	

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Balancing Redox Reactions

We must keep track of the exchange of electrons among species in a redox reaction. Consider the skeleton reaction: Sample Problem 21.1

$$\mathsf{MnO}_4^{-}(\mathsf{aq}) + \mathcal{C}_2 \mathcal{O}_4^{2-}(\mathsf{aq}) \to \mathsf{MnO}_2(\mathsf{s}) + \mathcal{CO}_3^{2-}(\mathsf{aq})$$

1) Write the two (or more) half-reactions.

 MnO_4^- (aq) $\rightarrow MnO_2$ (s) and $C_2O_4^{2-}$ (aq) $\rightarrow CO_3^{2-}$ (aq) (ox. state changes: Mn + 7 to + 4 and C + 3 to + 4)

2) Balance the atoms which change in oxidation state.

 $\begin{array}{l} \mathsf{MnO}_4^{-}(\mathsf{aq}) \to \mathsf{MnO}_2(\mathsf{s}) \\ \mathsf{C}_2\mathsf{O}_4^{2-}(\mathsf{aq}) \to 2 \ \mathsf{CO}_3^{2-}(\mathsf{aq}) \end{array}$

3) Add or remove electrons, as needed, to balance oxidation state changes.

 $3e^{-} + MnO_{4}^{-} (aq) \rightarrow MnO_{2} (s)$ $C_{2}O_{4}^{2-} (aq) \rightarrow 2CO_{3}^{2-} (aq) + 2e^{-}$

4) Balance the reduction and oxidation half-reactions by balancing the electrons gained and lost.

 $\begin{array}{l} 6e^{-} + 2MnO_{4}^{-} (aq) \rightarrow 2MnO_{2} (s) \\ 3 C_{2}O_{4}^{2-} (aq) \rightarrow 6CO_{3}^{2-} (aq) + 6 e^{-} \end{array}$

5) Now add the half reactions (electrons should not appear; they should cancel!)

$$2 \text{ MnO}_4^- (aq) + 3 C_2 O_4^{2-} (aq) \rightarrow 2 \text{ MnO}_2 (s) + 6 CO_3^{2-} (aq)$$





6) Balance atoms (other than O and H) that do not change in oxidation state.

7) Now balance O by adding H_2O as needed, then balance H by adding H⁺ as needed.

$$2 H_2O + 2 MnO_4^-(aq) + 3 C_2O_4^{2-}(aq) \rightarrow 2 MnO_2(s) + 6 CO_3^{2-}(aq)$$

 $2H_2O + 2 MnO_4^-$ (aq) + $3 C_2O_4^{2-}$ (aq) $\rightarrow 2MnO_2$ (s) + $6 CO_3^{2-}$ (aq) + $4H^+$ This is the FINAL BALANCED REDOX EQUATION if the reaction was done in acidic or neutral solution

8) When reaction is done in basic solution, add as many OH^- to both sides as it takes to neutralize the acid ($H^+ + OH^- \rightarrow H_2O$).

 $2H_2O + 2MnO_4^-$ (aq) + $3C_2O_4^{2-}$ (aq) $\rightarrow 2MnO_2$ (s) + $6CO_3^{2-}$ (aq) + $4H^+$

Add 4 OH- to each side, and cancel some waters, to give:

 $4OH^{-} + 2H_{2}O + 2MnO_{4}^{-}(aq) + 3C_{2}O_{4}^{2}(aq) \rightarrow 2MnO_{2}(s) + 6CO_{3}^{2}(aq) + 4H_{2}O$

This is the FINAL BALANCED REDOX EQUATION in basic solution $4OH^{-}(aq) + 2MnO_{4}^{-}(aq) + 3C_{2}O_{4}^{2-}(aq) \rightarrow 2MnO_{2}(s) + 6CO_{3}^{2-}(aq) + 2H_{2}O(l)$

See also CrO_4^{2-} reaction, page 853: $Cr_2O_7^{2-}$ (aq) + I⁻ (aq) $\rightarrow Cr^{3+}$ (aq) + I₂ (s)





An Overview of Electrochemical Cells Figure 21.2

1) A <u>voltaic</u> or <u>galvanic</u> cell uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy. Thus reactants have higher chemical potential energy (free energy) than products. All batteries contain voltaic cells. (<u>System does work on the surroundings</u>.)

2) An <u>electrolytic</u> cell uses electrical energy to drive a non-spontaneous reaction $(\Delta G > 0)$. Thus, products have higher free energy than reactants, e.g., metal plating. (Surroundings to work on the system.)

Section 21.2. VOLTAIC CELLS

Fig. 21.3 (Zn bar in Cu²⁺ solution) - a spontaneous reaction

Fig. 21.4A and B (the resulting Zn/Cu Voltaic cell)

• We find that the concentration of the zinc solution increases over time, concentration of copper solution decreases over time.

- We find mass of zinc rod decreases. Copper metal is deposited on the copper rod. Electrons flow through the external circuit, *e.g.*, to light a bulb, run a heater, etc.
- Left compartment: $Zn(s) \rightarrow Zn^{2+} + 2e^{-1}$
- Right compartment: $Cu^{2+} + 2e^{-} \rightarrow Cu(s)$
- Salt bridge serves to keep the solution neutral; without the salt bridge the Zn²⁺ solution would become positively charged and the Cu²⁺ solution would become negatively charged, and the reaction would stop.



Figure 21.2 General characteristics of (A) voltaic and (B) electrolytic cells.

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Figure 21.3 The spontaneous reaction between zinc and copper(II) ion.



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Figure 21.4A A voltaic cell based on the zinc-copper reaction.





Figure 21.4B A voltaic cell based on the zinc-copper reaction.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Oxidation half-reaction Zn(s) \rightarrow Zn²⁺(aq) + 2e⁻

After several hours, the Zn anode weighs less as Zn is oxidized to Zn²⁺.



Reduction half-reaction $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

The Cu cathode gains mass over time as Cu²⁺ ions are reduced to Cu.





Notation for a Voltaic Cell

 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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

1) Anode = source of electrons; Cathode = where they go to be used

2) vertical bars (|) indicate a phase boundary

3) electrodes placed at far left and right. If electrode is not involved in half-reaction, put it at end and show reagents in order they appear in half-reaction.

4) concs and pressures are shown. If not, assume 1 M and 1 atm.

5) use commas to separate components in the same phase.

e.g., $2 I^{-}(aq) \rightarrow I_{2}(s) + 2 e^{-1}$ (anode i.e. source of e^{-1})

 MnO_4^- (aq) + 8 H⁺ (aq) + 5 e⁻ \rightarrow Mn^{2+} (aq) + 4 H₂O (I)

(cathode i.e. where e⁻ go to be used in a reduction)

Electrodes are graphite, platinum, etc.: "inert" if not involved in reactions.

graphite $| I^{-}(aq) | I_{2}(s) || MnO_{4}^{-}(aq), H^{+}(aq), Mn^{2+}(aq) | graphite$

or $Pt(s) | I^{-}(aq) | I_{2}(s) | | MnO_{4}^{-}(aq), H^{+}(aq), Mn^{2+}(aq) | Pt(s)$



Figure 21.5 A voltaic cell using inactive electrodes.





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<u>Sample Problem 21.2</u> Cr bar dipping in $Cr(NO_3)_3$ solution on one side of cell, Ag bar in AgNO₃ solution on the other side, and connected by salt bridge. The Cr electrode is the negative one. Draw diagram, and give cell reaction and cell notation.

Since $Cr(s) | Cr^{3+}(aq)$ is the negative electrode, it is the anode $\therefore Ag(s) | Ag^+(aq)$ is the positive electrode \therefore it is the cathode) $\therefore Cr(s) \rightarrow Cr^{3+}(aq) + 3 e^-(anode, source of e^-, put on left of cell)$ $\therefore Ag^+(aq) + e^- \rightarrow Ag(s)$ (cathode, where e⁻ are used, put on right of cell)

∴ Cr (s) + 3 Ag⁺ (aq)
$$\rightarrow$$
 Cr³⁺ (aq) + 3 Ag (s)

cell notation is $Cr(s) | Cr^{3+}(aq) | | Ag^{+}(aq) | Ag(s)$



Why and how long does a Voltaic Cell Work?

Why? Because the reaction is spontaneous. How Long? Until the reaction is no longer spontaneous. Recall: $\Delta G = \Delta G^{\circ} + RT \ln Q$.

At the start, $\Delta G < 0$. As concs in the anode and cathode cells change, Q increases. *i.e.*, ΔG becomes less negative. When $\Delta G = 0$, reaction is at equil, the cell is fully discharged, and no more electrons flow.

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Section 21.3. Cell Potential

Reaction is spontaneous if $\Delta G < 0$.

The reaction drives the current from anode to cathode. In electrochemistry language, we talk about the cell potential (E_{cell}) or electromotive force (emf), *i.e.*, the electrical potential difference (or "voltage" in everyday English) between the anode and cathode (units volts)

 $\mathsf{E}_{\mathsf{cell}}$ results from the spontaneous reaction \therefore related to $\Delta G.$

$$\Delta G = - nFE_{cell}$$

n = Number of electrons exchanged in balanced chemical reaction. F = Faraday Constant = 9.65 x 10⁴ J/V.mol e⁻

$$\begin{array}{ll} \therefore \text{ if } & \Delta G < 0, & \mathbb{E}_{cell} > 0 \text{ (spontaneous = Voltaic cell)} \\ & \Delta G > 0, & \mathbb{E}_{cell} < 0 \text{ (non-spontaneous = Electrolytic cell)} \\ & \Delta G = 0, & \mathbb{E}_{cell} = 0 \text{ (equilibrium)} \end{array}$$

Remember: $\Delta G = w_{max}$

 \therefore ΔG and E_{cell} tell us maximum work the cell can do.



Standard Cell Potentials

Measured cell potential (E_{cell}) depends on concs and pressures. At standard conditions (1 atm gas, 1 M solutions):

> E_{cell} = E°_{cell} E°_{cell} = standard cell potential E°_{cell} for Zn/Cu cell = 1.10 V.

 $Zn(s) | Zn^{2+} (aq, 1 M) || Cu^{2+} (aq, 1 M) | Cu (s)$

How can we <u>measure</u> E°_{cell} ? Experimentally, we can use a voltmeter



Fig 21.6

The **standard cell potential** is designated **E°_{cell}** and is measured at a specified T with no current flowing and **all components in their standard states**.

How do we calculate E°_{cell} ? We use $E^{\circ}_{half-cell}$ for the two half-reactions





Table 21.1 Voltages of Some Voltaic Cells

Voltaic Cell	Voltage (V)
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells ≈ 12 V)	2.1
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070



<u>Half-Cell Electrode Potentials (E° half-cell</u>)

Each half of cell has a half-cell potential that together give total E_{cell} or E°_{cell} . By convention, half-cell potentials refer to half-reactions written as reductions i.e. $ox + e^- \rightarrow red$ (ox = oxidized form; red = reduced form) and this is the way they are listed in Tables such as Appendix D

Reversing direction changes sign of half-cell potential. So, for

$$\begin{aligned} & Zn(s) + Cu^{2+}(aq) \to Zn^{2+}(aq) + Cu(s) \\ & Zn^{2+}(aq) + 2 e^{-} \to Zn(s) \\ & Cu^{2+}(aq) + 2 e^{-} \to Cu(s) \end{aligned} \qquad \begin{array}{l} & E^{\circ}_{\ \ Cathode} & = E^{\circ}_{\ \ Cu} (\text{listed like this}) \\ & E^{\circ}_{\ \ cathode} & = E^{\circ}_{\ \ Cu} (\text{listed like this}) \end{aligned}$$

In the cell, the Zn half-reaction happens in the opposite direction (oxidation), so we change the sign:

 $\label{eq:Zn} \begin{array}{ll} \text{Zn}(s) \to \text{Zn}^{2+} \mbox{(aq)} + 2 \ e^- & \mbox{E}^\circ_{anode} = - \mbox{E}^\circ_{\text{Zn}} \\ \text{Now, E}^\circ_{cell} \ \mbox{is the sum of the two half-cell reactions} \end{array}$

$$\therefore E^{\circ}_{cell} = E^{\circ}_{cathode} + (-E^{\circ}_{anode}) = E^{\circ}_{Cu} + (-E^{\circ}_{Zn})$$

Since the anode is always an oxidⁿ, $E^{\circ}_{anode} = -E^{\circ}_{half-rxn}$ always



 $\therefore \mathbf{E^{o}_{cell}} = \mathbf{E^{o}_{cat}} - \mathbf{E_{anode}}$ ** Note: the minus sign already takes into account

the fact that the anode reaction occurs in the opposite direction from that listed in Appendix D, so do NOT change the sign of numbers you take from Appendix D and plug into this equation! ** 21-18



Standard Electrode (Half-Cell) Potentials

All values at 298K. Written as reductions; E^o value refers to all components in their standard states: 1 M for dissolved species, 1 atm pressure for a gas, the pure substance for solids and liquids.

Half-Reaction $E^{\circ}(V)$ $F_2(g) + 2e^- \Longrightarrow 2F^-(aq)$ +2.87 $O_3(g) + 2H^+(aq) + 2e^- \implies O_2(g) + H_2O(l)$ +2.07 $\operatorname{Co}^{3^+}(aq) + e^- \longrightarrow \operatorname{Co}^{2^+}(aq)$ +1.82 $H_2O_2(aq) + 2H^+(aq) + 2e^- = 2H_2O(l)$ +1.77 $PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$ +1.70 $\operatorname{Ce}^{4+}(aq) + e^{-} \rightleftharpoons \operatorname{Ce}^{3+}(aq)$ ± 1.61 $MnO_4^{-}(aq) + 8H^+(aq) + 5e^- \implies Mn^{2+}(aq) + 4H_2O(l)$ +1.51 $\operatorname{Au}^{3+}(aq) + 3e^{-} \Longrightarrow \operatorname{Au}(s)$ ± 1.50 $Cl_2(g) + 2e^- \Longrightarrow 2Cl^-(aq)$ +1.36 $Cr_2O_7^2(aq) + 14H^+(aq) + 6e \implies 2Cr^{3+}(aq) + 7H_2O(l)$ +1.33 $MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$ +1.23 $O_2(g) + 4H^+(aq) + 4e^- \implies 2H_2O(l)$ +1.23 $Br_2(l) + 2e \implies 2Br(aq)$ +1.07 $NO_3^-(aq) + 4H^+(aq) + 3e^- \implies NO(g) + 2H_2O(l)$ +0.96 $2 Hg^{2+}(aq) + 2e^{-} = Hg_{2}^{2+}(aq)$ +0.92 $Hg_2^{2+}(aq) + 2e^- \Longrightarrow 2Hg(l)$ +0.85 $Ag^+(aq) + e^- \longrightarrow Ag(s)$ +0.80 $Fe^{3+}(aq) + e^{-} \Longrightarrow Fe^{2+}(aq)$ +0.77 $O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ +0.68 $MnO_4(aq) + 2H_2O(l) + 3e \implies MnO_2(s) + 4OH(aq)$ +0.59 $I_2(s) + 2e^- \Longrightarrow 2I^-(aq)$ +0.53 $O_2(g) + 2H_2O(l) + 4e^- \implies 4OH^-(aq)$ +0.40 $Cu^{2+}(aq) + 2e^{-} \Longrightarrow Cu(s)$ +0.34 $AgCl(s) + e^{-} \Longrightarrow Ag(s) + Cl^{-}(aq)$ +0.22 $SO_4^{2^-}(aq) + 4H^+(aq) + 2e^- \implies SO_2(g) + 2H_2O(l)$ +0.20 $\operatorname{Cu}^{2^+}(aq) + e^- \Longrightarrow \operatorname{Cu}^+(aq)$ +0.15 $\operatorname{Sn}^{4+}(aq) + 2e^{-} \Longrightarrow \operatorname{Sn}^{2+}(aq)$ +0.13 $2H^+(aq) + 2e^- \Longrightarrow H_2(g)$ 0.00 $Pb^{2+}(aq) + 2e^- \Longrightarrow Pb(s)$ -0.13 $\operatorname{Sn}^{2+}(aq) + 2e^{-} \Longrightarrow \operatorname{Sn}(s)$ -0.14 $N_2(g) + 5H^+(aq) + 4e^- \implies N_2H_5^+(aq)$ -0.23 $Ni^{2+}(aq) + 2e^{-} \Longrightarrow Ni(s)$ -0.25 $\operatorname{Co}^{2^+}(aq) + 2e^- \rightleftharpoons \operatorname{Co}(s)$ -0.28 $PbSO_4(s) + H^+(aq) + 2e^- \implies Pb(s) + HSO_4^-(aq)$ -0.31 $Cd^{2+}(aq) + 2e^{-} \rightleftharpoons Cd(s)$ -0.40 $Fe^{2+}(aq) + 2e^- \Longrightarrow Fe(s)$ -0.44 $Cr^{3+}(aq) + 3e^- \Longrightarrow Cr(s)$ -0.74 $\operatorname{Zn}^{2+}(aq) + 2e^{-} = \operatorname{Zn}(s)$ -0.76 $2H_2O(l) + 2e^- \implies H_2(g) + 2OH^-(aq)$ -0.83 $Mn^{2+}(aq) + 2e^{-} \Longrightarrow Mn(s)$ -1.18 $Al^{3+}(aq) + 3e^{-} \Longrightarrow Al(s)$ -1.66 $Mg^{2+}(aq) + 2e^{-} \Longrightarrow Mg(s)$ -2.37 $Na^+(aq) + e^- \Longrightarrow Na(s)$ -2.71 $Ca^{2+}(aq) + 2e^{-} \Longrightarrow Ca(s)$ -2.87 $\operatorname{Sr}^{2+}(aq) + 2e^{-} \Longrightarrow \operatorname{Sr}(s)$ -2.89 $Ba^{2+}(aq) + 2e^{-} \Longrightarrow Ba(s)$ -2.90 $K^+(aq) + e^- \Longrightarrow K(s)$ -2.93 $Li^+(aq) + e^- \Longrightarrow Li(s)$ -3.05



<u>Determining $E^{\circ}_{half-cell}$ with the Standard H₂ Electrode</u>

 E°_{cell} is related to ΔG . G not known absolutely, only differences (ΔG). Similarly, we measure differences in half-cell E° values, by always measuring them vs. a reference electrode.

Reference electrode = standard hydrogen electrode (SHE)

SHE = Pt solid dipping in 1 \underline{M} aq strong acid through which 1 atm H₂ gas is bubbled. This is, by convention, given a value of 0.00 V

2 H⁺ (aq, 1<u>M</u>) + 2 e⁻ \rightarrow H₂ (g, 1 atm) E°_{ref} = 0.00 V

So, construct voltaic cell with SHE on one side and unknown on other; we can get unknown E° , since E°_{cell} is known (measured with a voltmeter)

If SHE is cathode: $E^{\circ}_{cell} = 0.00 - E_{unk}$ \therefore $E^{\circ}_{cell} = -E_{unk}$ If SHE is anode: $E^{\circ}_{cell} = E^{\circ}_{unk} - 0.00$ \therefore $E^{\circ}_{cell} = E^{\circ}_{unk}$ Fig 21.7 \therefore $E^{\circ}_{cell} = E^{\circ}_{unk}$ This way, $E^{\circ}_{half-cell}$ for any half-cell can be obtained. Appendix D



Figure 21.7 Determining an unknown $E^{\circ}_{half-cell}$ with the standard reference (hydrogen) electrode.



Example 1: Zn (s) | Zn²⁺ (aq) || Cu²⁺ (aq) | Cu (s)

 $E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano} = +0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$

**NOTE: use numbers straight from table! Do not change sign **

Measured E°_{cell} = 1.10 V.

Example 2: Voltaic cell: $Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2 Br^{-}(aq)$ E_{cell}° = 1.83 V. If E_{Zn}° = -0.76 V, what is E_{Br}° for the half-reaction below? $Br_2(aa) + 2e^- \rightarrow 2Br^-(aa)$ $E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano}$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-};$ it is the anode $\therefore E^{\circ}_{cell} = E^{\circ}_{Br} - E^{\circ}_{Zn} \therefore 1.83 \text{ V} = E^{\circ}_{Br} - (-0.76 \text{ V}) = E^{\circ}_{Br} + 0.76 \text{ V}$ $\therefore E^{\circ}_{Br} = 1.83 \text{ V} - 0.76 \text{ V}$ $\therefore E^{\circ}_{Br} = 1.07 \text{ V}$ <u>CHECK</u>: $E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano} = 1.07 \text{ V} - (-0.76 \text{ V}) = 1.83 \text{ V}$ (Correct!) Example 3: E°_{cell} = 1.39 V for the reaction below. What is E° for $VO^{2+} \rightarrow V^{3+}$? $Br_2(aq) + 2 V^{3+}(aq) + 2 H_2O(I) \rightarrow 2 VO^{2+}(aq) + 4 H^+(aq) + 2 Br^-(aq)$ $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ \therefore the cathode $\therefore E^{\circ}_{cat} = 1.07 V$ $E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{ano} \therefore 1.39 \text{ V} = 1.07 \text{ V} - E^{\circ}_{anode}$ $E^{\circ}_{\text{anode}} = 1.07 - 1.39 = -0.32 \text{ V}$ ∴ E°_{VO²⁺→V³⁺} = - 0.32 V



Relative Strengths of Oxidizing and Reducing Agents

 $E^{\circ}_{half-cell}$ values represent how easy or difficult it is to add electrons \therefore comparing $E^{\circ}_{half-cell}$ gives us strengths of oxidizing/reducing agents.

e.g.	$\mathcal{C}u^{2+}(aq)$ + 2 $e^{-} ightarrow \mathcal{C}u(s)$	E° = + 0.34 V
2	2 H ⁺ (aq) + 2 e ⁻ \rightarrow H ₂ (q)	E° = 0.00 V
	Zn^{2+} (aq) + 2 $e^{-} \rightarrow Zn$ (s)	E° = - 0.76 V

The bigger (more +ve, or less -ve) the E°, the easier is the reduction The smaller (more -ve, or less +ve) the E°, the harder is the reduction

Conversely,

The bigger (more +ve, or less -ve) the E°, the harder is the oxidation The smaller (more -ve, or less +ve) the E°, the easier is the oxidation

 \therefore reducing strength: Zn > H_2 > Cu oxidizing strength: Cu^{2+} > H^+ > Zn^{2+}

General Rule: Strength of reducing agent increases as $E^{\circ}_{half-rxn}$ becomes smaller (down Table 21.2 or Appendix D). Strength of oxidizing agent increases as E° half-rxn becomes bigger (up Table 21.2 or Appendix D).



Table 21.2 Selected Standard Electrode Potentials (298 K)

_	Half-reaction	<i>E</i> ° (V)	
	$F_2(g) + 2e^- \Longrightarrow 2F^-(aq)$	+2.87	
	$Cl_2(g) + 2e^- \Longrightarrow 2Cl^-(aq)$	+1.36	
	$MnO_2(g) + 4H^+(aq) + 2e^- \implies Mn^{2+}(aq) + 2H_2O(I)$	+1.23	
	$NO_{3}^{-}(aq) + 4H^{+}(aq) + 3e^{-} \implies NO(g) + 2H_{2}O(I)$	+0.96	Sti
ent	$Ag^+(aq) + e^- \Longrightarrow Ag(s)$	+0.80	enc.
age	Fe ³⁺ (<i>g</i>) + e ⁻ → Fe ²⁺ (<i>aq</i>)	+0.77	yth o
zing	$O_2(g) + 2H_2O(I) + 4e^- \Longrightarrow 4OH^-(aq)$	+0.40	of re
kidiz	Cu ²⁺ (<i>aq</i>) + 2e ⁻ ← Cu(<i>s</i>)	+0.34	duc
	2H⁺(<i>aq</i>) + 2e⁻ ← H ₂ (<i>g</i>)	0.00	sing
ith c	$N_2(g) + 5H^+(aq) + 4e^- \Longrightarrow N_2H_5^+(aq)$	-0.23	age
eng	Fe²+(<i>aq</i>) + 2e⁻ ⇒ Fe(<i>s</i>)	-0.44	Pht
Sti	2H ₂ O(<i>I</i>) + 2e⁻ ↓ H ₂ (<i>g</i>) + 2OH⁻(<i>aq</i>)	-0.83	
	Na⁺(<i>aq</i>) + e⁻ < Na(s)	-2.71	
	Li⁺(<i>aq</i>) + e⁻ ↓ Li(<i>s</i>)	-3.05	



Standard Electrode (Half-Cell) Potentials

Strength of Oxidizing and Reducing Agents

> Increasing oxidizing strength



Increasing reducing strength



Predicting Direction of Spontaneous Reactions

E° values are related to ΔG . we can use them to predict spontaneity

$$Cu(s) + Zn^{2+}(aq) \xrightarrow{?} Cu^{2+}(aq) + Zn(s)$$

weaker weaker stronger stronger

ox. ag. ox. ag. red. ag.

** stronger red/ox agents win, and push the reaction towards the other side **

 \therefore spontaneous direction is right-to-left (i.e. K_c < 1)

red. ag.

i.e., e^{-'}s grabbed by stronger oxid. agent (Cu^{2+}) converting it to Cu (s). i.e., electrons flow from the smaller $E^{\circ}_{half-rxn}$ to the larger $E^{\circ}_{half-rxn}$

(Note: negative numbers are smaller than positive numbers!)



Sample Problem 21.4

$$\begin{array}{ll} \mathsf{NO}_3^-(\mathsf{aq}) + 4 \ \mathsf{H}^+(\mathsf{aq}) + 3 \ \mathsf{e}^- \to \mathsf{NO}(\mathsf{g}) + 2 \ \mathsf{H}_2\mathsf{O}(\mathsf{I}) & \mathsf{E}^\circ = \ 0.96 \ \mathsf{V} \\ \mathsf{N}_2(\mathsf{g}) + 5 \ \mathsf{H}^+(\mathsf{aq}) + 4 \ \mathsf{e}^- \to \mathsf{N}_2\mathsf{H}_5^+(\mathsf{aq}) & \mathsf{E}^\circ = - \ 0.23 \ \mathsf{V} \\ \mathsf{MnO}_2(\mathsf{s}) + 4 \ \mathsf{H}^+ + 2 \ \mathsf{e}^- \to \mathsf{Mn}^{2+}(\mathsf{aq}) + 2 \ \mathsf{H}_2\mathsf{O}(\mathsf{I}) & \mathsf{E}^\circ = \ 1.23 \ \mathsf{V} \\ \end{array}$$

Reducing strength: $N_2H_5^+ > NO > Mn^{2+}$ Oxidizing strength: $MnO_2 > NO_3^- > N_2$

.: Spontaneous Reactions are:

(1) $3 N_2 H_5^+ (aq) + 4 NO_3^- (aq) + H^+ (aq) \rightarrow N_2 (g) + 4 NO + 8 H_2O (I)$ (2) $2 NO (g) + 3 MnO_2 (s) + 4 H^+ \rightarrow 2 NO_3^- (aq) + 3 Mn^{2+} (aq) + 2 H_2O (I)$ (3) $N_2 H_5^+ (aq) + 2 MnO_2 (s) + 3 H^+ \rightarrow N_2 (g) + 2 Mn^{2+} (aq) + 4 H_2O (I)$

> E°_{cell} (1) = 0.96 V - (-0.23 V) = 1.19 V E°_{cell} (2) = 1.23 V - (0.96 V) = 0.27 V E°_{cell} (3) = 1.23 V - (-0.23 V) = 1.46 V



Standard Electrode (Half-Cell) Potentials

Strength of Oxidizing and Reducing Agents

> Increasing oxidizing strength



Increasing reducing strength



