Unit 1 – Deck 3

ELECTROCHEMISTRY

Electrochemical cells and their potentials





Unit 1 Reading

Chemical Principles by Atkins Jones & Laverman Chapter K & 13



Inorganic Chemistry Housecroft & Sharpe Chapter 8





Topics





Electricity

Electricity from electrons:

- 1. There are + and charges
- 2. Charge much balance
- 3. Charge can flow like fluid
- 4. Current is measure of + flow
- 5. Charge flow through wires as e⁻

Electricity from ions:

1. Molten Salt: NaCl@800°C 2. Dissolved Salts

 K_{sp} $NaCl(s) \rightleftharpoons Na^{+}(aq)$

1885 - Svante Arrhenius

Electrochemistry

DEF: Interactions of molten salts/electrolyte solutions in an electric field

Charge: Property of subatomic particles p^+ and e^{-} Unit = Coulomb (C) $1e^{-} = 1.6 \times 10^{-19}C$ $\times 6.022 \cdot 10^{23}$ Faraday (F): 1 mol $e^- = 96485$ C



Current – the flow of electrons Unit of Current : C/s = A (Amp)

Engineering Units of Charge: mAh (milliamp hour) Or Ah (amp hour)

Voltage – Potential (V) \neq Energy (J) Unit of Potential: Volt (V) : J/C $\Delta G = -nFE$

Engineering Units of Energy: Wh (watt-hour) or kWh (kilowatt-hour)

 $\frac{\text{Charge}}{\text{Energy}} \quad 1 \text{ A } h = \frac{1 \text{ C } h}{s}$ $\frac{1 \text{ Charge}}{1 \text{ V } * 1 \text{ A } h} = \left(\frac{1 \text{ J}}{C}\right) \frac{1 \text{ C } h}{s}$

Energy = Volts • Charge

Watt is a unit of Power: 1 Watt (W) = 1 J/s $Power = \frac{Energy}{time}$

$$\frac{h}{s} = \left(\frac{1J}{s}\right)(1h) = 1Wh$$

Electrochemical Potential

Electrochemical Potential : A voltage measured between two different electrodes in chemically distinct environments @ Zero Current (V_{oc})

Electrochemical potentials fall between _____ V and _____ V





Carbon

NaCI (/)

V

Anode

300 °C

 $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$

Example: The Downs Process

Carbon

Cathode

Carbon

NaCI (/)

Anode

300 °C

 $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$

Example: The Downs Process

Carbon

Cathode



Question: If you push 10 A of current through the cell how long will it take you to make 23 g of Na?



Stoichiometry in electrochemical cells How much (g) Zn $2ZnO \rightarrow 2Zn + 0_{2}$ if you apply x amps for y hours?

1. Write the (and balance) the half reactions

2. Determine how much charge in mol e⁻ you have

3. Use molecular mass and the stoichiometry of the half reactions to get grams of Zn



F: 96485 C/mol

Stoichiometry in electrochemical cells How many hours to make x g Zn $2ZnO \rightarrow 2Zn + 0_{2}$ if your cell is running at y amps?

1. Write the (and balance) the half reactions

2. Determine how much charge in mol e- you need

3. Convert mole e⁻ to Amp•hours, divide by given current to get time of reaction in hours



F: 96485 C/mol

Poll: How much Ag can be deposited? Your phone's battery has a charge capacity of 3.2 Ah. Converting this

charge instead to make silver:

AglAg,SO₄ II CuSO₄ I Cu

copper consumed?

- how much silver, in grams, can be deposited. How much would be



Ag: 107.9 g/mol Cu: 63.5 g/mol

F: 96485 C/mol



Electrochemical cells under the hood

CONDUCTIVITY

OHMS LAW V=IR V~I

NORMALIZE TO DIMENSIONS TO GET INTRINSIC PROPERTY OF SOLUTION:



CONDUCTIVITY $\sigma = \frac{1}{p} - \frac{1}{r} \frac{1}{r} = \frac{1}{r} \frac{1}{r}$

HOW EASY IT IS FOR A VOLTAGE TO DRIVE CHARGE THROUGH A SOLUTION OR MATERIAL SIEMAN SIEMAN Sieman Sieman Sieman





Under the hood - Electrodes

Electrode *must* move electrons









Under the hood - Electrolytes

Electrolytes *must* move ions and only ions



10⁻⁵ to 10⁻¹ S/cm

4) IONS IN SOLUTION

"ELECTROLYTES" NaCl in H20



REACTS / MOVES IN ELECTRUSTATICALLY BOUND E - FIELD "CONTACT ION PAIR" INVISIBLL TO E-FIELD APPEARS TO BE CHARGE NEUTRAL



[Naci] / M



 $CT \implies Na(OH_{a})_{c} + CT$ CHARGE SEPARATED



Under the hood - Electrolytes

Electrolytes *must* move ions and only ions









Under the hood - Terminology

- another (electrolyte)

- (V=IR)
- DEF Siemen | SI unit of conductivity equal to 1/Ohm.
- material or solution $\sigma = \frac{1}{R}$
- that forms multiple layers of ions of opposite charges. an electrochemical cell

DEF Electrochemical Cell | A device that forces electrons through one path (circuit) and ions through

DEF Metal | Material in which electrons flow freely. Conductivity increases a temperature decreases DEF Semiconductor | Material the conducts electrons but not freely. Need heat to conduct electrons (themal excitation). Conductivity increases a temperature increases. DEF Ohm | SI unit of resistance. Units of R in Ohms law relating current observed to voltage applied

DEF Conductivity | A measure of how easy it is for charge (ionic or electronic) to flow through a

DEF Contact Ion Pair | A + and a – charged pair of ions that are in solution but electrostatically bond to one another and "appear" to be charge neutral in the presence of an externally applied voltage. DEF Electrical Double Layer | The layer of ions right at an electrode surface under applied voltage

DEF Dendrite | Tree-like metallic structures that sometimes form when electrodepositing a metal in



Galvanic cell A spontaneous redox reaction occurs and generates an electric current

Electrolytic cell A nonspontaneous reaction reaction to occur

Spontaneity in Electrochemical Cells

However, we can use an electric current to cause a chemical



Galvanic Cells





 $n = \# e^{-}$ transferred (equiv) F = 96485 C/mol E = Potential in units of V = J/C

<u>Cell Potential</u>



If $E_{cell}^{\circ} > 0$ then Spontaneous

 $\Delta G = \Delta H - T \Delta S$ $\Delta G = -RTln(K_{eq})$

 E° defined for $\frac{1}{2}$ rxn's for interoperability



Electrolytic Cells

<u>A Non-Spontaneous Reaction</u>

- $\Delta G > 0$ E < 0
- Electrical Potential



Cell Potential

 $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$

Chemical Potential

Induce rxn to make/break a chemical compound



Pt I H⁺ (1 M) II OH⁻ (1 M) I Pt $4H^+ + 4OH^- \rightarrow O_2 + 2H_2 + 2H_2O$

Galvanic vs. Electrolytic Cells

Galvanic cells are spontaneous reactions that generate electricity. Electrolytic cells are galvanic cells being forced to run backward.

In both cases Oxidation occurs at the anode and reduction occurs at the cathode. Electrons flow from the anode to the cathode

Differences Galvanic: anode is (-), cathode is (+) Electrolytic: anode is (+), cathode is (-)

Summary

Galvanic cell (spontaneous) E_{cell}° is positive ΔG° is negative K > 1

Electrolytic cell (nonspontaneous) E_{cell}° is negative ΔG° is positive K < 1

Free Energy of the Cell

Example: What is K_{eq} for the reaction?

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



$E_{cell}^{\circ} = 1.10 V$

Voltage and Equilibrium Constants

equilibrium constant?

How Much Na is left once the reaction has reached equilibrium?

For the electrochemical cell below what is the

Na | NaPF₆ in THF || Zn(PF₆) in THF || Zn





$E_{cell} = +1.95 V$





Standard Reduction Potentials

E Cell: A value for a galvanic or electrolytic cell (a combination of two E° values)

E°: A value for a half-reaction that corresponds to a single electrode



Standard Conditions

Temperature = 298 K

Pressure = 1 bar

Solutions = Aqueous & 1 Molarity

Solids are in their standard state



There are four standard conditions that you need to know:

Standard Hydrogen Electrode (SHE)

A platinum wire immersed in a 1M solution of hydronium ions

A sensible definition but impractical to measurement tool. Other simpler reference electrodes are more reliable.

$2H^+(aq, 1M) + 2e^- \rightleftharpoons H_2(g, 1bar)$

H₂ at 1 bar

Pt wire

 $1 \text{ M H}^+(aq)$

Pt electrode H₂ outlet



$E^{\circ} = 0.0 V$

Pt electrode surface



Standard Potentials

When combining two half-reactions to form a redox reaction, the halfreaction with *the higher standard reduction potential will be reduced* in a spontaneous reaction.

For full table of standard potentials: Atkins Appendix 2B

Increasing strength of oxidant

Half Reaction						
F ₂	+	2e ⁻	+	2F ⁻		
Pb ⁴⁺	+	2e ⁻	+	Pb^{2+}		
Cl ₂	+	2e ⁻		2 <i>C l</i> ⁻		
Ag^+	+	e –		Ag		
Fe ³⁺	+	e [–]	+	Fe ²⁺		
Cu ²⁺	+	2e ⁻	1	Cu		
2 <i>H</i> ⁺	+	2e ⁻		H ₂		
Fe ³⁺	+	3e ⁻	4	Fe		
Pb ²⁺	+	2e ⁻	+	Pb		
Fe ²⁺	+	2e ⁻		Fe		
Zn^{2+}	+	2e ⁻	-	Zn		
Al ³⁺	╋	3e ⁻		Al		
Mg^{2+}	• +	$2e^{-}$		Mg		
Li^+	+	<i>e</i> ⁻		Li		

Potential +2.87 V +1.67 V +1.36 V Incr + 0.80 V eas +0.77 V guis +0.34 V stren 0.00 V gtl -0.04 V Of -0.13 V reductan -0.44 V -0.76 V -1.66 V -2.36 V -3.05 V

PO

Which is a stronger Reductant?

- Fe²⁺ or Pb²⁺ ?
- Ag or Zn?

Which is a stronger oxidant?

- $H^+ \text{ or } A|^{3+}$
- Cu²⁺ or Ag⁺

For full table of standard potentials: Atkins Appendix 2B

of oxidant strength Increasing

Half Reaction						
F ₂	+	2e ⁻		2F ⁻		
Pb ⁴⁺	+	2e ⁻	2	Pb^{2+}		
Cl ₂	+	2e ⁻	 	2 <i>Cl</i> ⁻		
Ag^+	+	e –	-	Ag		
Fe ³⁺	+	e [–]		Fe ²⁺		
Cu ²⁺	+	2e ⁻		Cu		
2 <i>H</i> ⁺	+	2e ⁻		H ₂		
Fe ³⁺	+	3e ⁻		Fe		
Pb ²⁺	+	2e ⁻		Pb		
Fe ²⁺	+	2e ⁻	-	Fe		
Zn^{2+}	+	2e ⁻	 	Zn		
Al ³⁺	+	3e ⁻		Al		
Mg^{2+}	- +	$2e^{-}$		Mg		
Li^+	+	e^{-}	\	Li		

Potential +2.87 V +1.67 V +1.36 V Increasing + 0.80 V +0.77 V +0.34 V strength 0.00 V -0.04 V Of -0.13 V reductant -0.44 V -0.76 V -1.66 V -2.36 V -3.05 V



Calculating Cell Potentials

If you have 2 compounds from The Electrochemical Series you can determine: The full balanced redox reaction & $\Delta E_{rxn} \rightarrow Spontaneity$ (galvanic vs electrolytic)

Compare the two half-reactions: Identify the best oxidizing agent 1. 2. Identify the reduction half-reaction Flip the direction of the oxidation half-reaction. Make sure to flip the 3. sign of the standard potential too! Add the two potentials to determine the standard cell potential

- 4.



Example

$2H^+ + 2e^- \rightleftharpoons H_2$

 $Zn^{2+} + 2e^{-} \rightleftharpoons Zn$

Calculate the standard cell potential for an electrochemical cell made from a standard hydrogen electrode half cell and a zinc half cell.



$E^{\circ} = -0.76 V$





Question

Using a standard potentials, which of these reactions occurs spontaneously? A. $2 H^+ + Fe \rightarrow Fe^{2+} + H_2$ B. $6 H^+ + 2 Au \rightarrow 2Au^{3+} + 3H_2$

- C. Neither
- Both D.

2B STANDARD POTENTIALS AT 25°C Potentials in Electrochemical Order

Reduction half-reaction

Strongly oxidizing $H_4XeO_6 + 2 H^+ + 2 e^- \rightarrow XeO_3 + 3 H_2O$ $F_2 + 2 e^- \rightarrow 2 F^ O_3 + 2 H^+ + 2 e^- \rightarrow O_2 + H_2O$ $S_2O_8^{2-} + 2 e^- \rightarrow 2 SO_4^{2-}$ $Ag^{2+} + e^- \rightarrow Ag^+$ $Co^{3+} + e^- \rightarrow Co^{2+}$ $H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$ $Au^+ + e^- \rightarrow Au$ $Pb^{4+} + 2 e^- \rightarrow Pb^{2+}$ $2 \operatorname{HClO} + 2 \operatorname{H}^+ + 2 \operatorname{e}^- \rightarrow \operatorname{Cl}_2 + 2 \operatorname{H}_2 \operatorname{O}$ $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$ $2 \text{ HBrO} + 2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{Br}_2 + 2 \text{ H}_2\text{O}$ $MnO_4^- + 8 H^+ + 5 e^- \rightarrow Mn^{2+} + 4 H_2O$ $Mn^{3+} + e^- \rightarrow Mn^{2+}$ $Au^{3+} + 3e^- \rightarrow Au$ $Cl_2 + 2e^- \rightarrow 2Cl^ Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2C$ $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^ O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$ $MnO_2 + 4 H^+ + 2 e^- \rightarrow Mn^{2+} + 2 H_2O$ $\text{ClO}_4^- + 2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$ $Pt^{2-} + 2e^{-} \rightarrow Pt$ $Br_2 + 2e^- \rightarrow 2Br^-$

	E° (V)	Reduction half-reaction	E° (V)
		$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.01
	+3.0	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
	+2.87	$2 H^+ + 2 e^- \rightarrow H_2$	0, by c
	+2.07	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.04
	+2.05	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.08
	+1.98	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
	+1.81	$In^+ + e^- \rightarrow In$	-0.14
	+1.78	$\mathrm{Sn}^{2+} + 2 \mathrm{e}^- \rightarrow \mathrm{Sn}$	-0.14
	+1.69	$AgI + e^- \rightarrow Ag + I^-$	-0.15
	+1.67	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
	+1.63	$V^{3+} + e^- \rightarrow V^{2+}$	-0.26
	+1.61	$Co^{2+} + 2 e^- \rightarrow Co$	-0.28
	+1.60	$In^{3+} + 3 e^- \rightarrow In$	-0.34
	+1.51	$Tl^+ + e^- \rightarrow Tl$	-0.34
	+1.51	$PbSO_4 + 2 e^- \rightarrow Pb + SO_4^{2-}$	-0.36
	+1.40	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.37
	+1.36	$In^{2+} + e^- \rightarrow In^+$	-0.40
0	+1.33	$Cd^{2+} + 2 e^- \rightarrow Cd$	-0.40
	+1.24	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41
	+1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
	+1.23	$In^{3+} + 2 e^- \rightarrow In^+$	-0.44
	+1.23	$S + 2 e^- \rightarrow S^{2-}$	-0.48
	+1.20	$In^{3+} + e^- \rightarrow In^{2+}$	-0.49
	+1.09	$Ga^+ + e^- \rightarrow Ga$	-0.53



definition

Next Time

Section 8.3 Nernst Equation Tools and visualizations for analyzing cell potentials