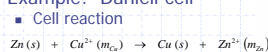


# Physical Chemistry

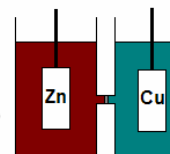
## Lecture 39 Electrochemical Cells

### Cells

- ◆ Devices that make chemical energy available as electrical energy
- ◆ Based on chemical reactions in solution
- ◆ Example: Daniell cell

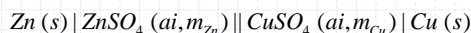


- Half-reactions occur at separate electrodes



### Cell diagrams and conventions

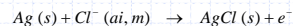
- ◆ Written cell description
- ◆ Based on convention of where oxidation and reduction occur
- ◆ Method for creating cell diagram
  - Write each phase from left to right with bars to indicate separations
  - Oxidation always occurs at the left electrode
  - Reduction always occurs at the right electrode
- ◆ Example: Daniell cell



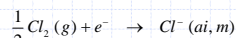
### Relation of cell diagram to cell reaction

- ◆ Write half-reactions for electrodes
- ◆ Sum half-reactions to obtain the cell reaction
- ◆ Example:  $\text{Ag (s)} | \text{AgCl (s)} | \text{HCl (m)} | \text{Cl}_2 (\text{g}), \text{Pt}$

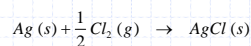
Left:



Right:



Overall:



### Voltage and free energy

- ◆ Chemical-potential change is energy
  - Free energy used to drive charges through an external circuit, where they do electrical work
- ◆ Work of moving a unit charge is voltage
- ◆ Relation between voltage,  $\mathcal{E}$ , and free-energy change is given by **Nernst's equation**

$$\mathcal{E} = - \frac{\Delta G}{nF}$$

- ◆ **Faraday's constant**,  $F$ , is the electrical charge on one mole of electrons = 96,485 coulombs

### Standard voltage

- ◆ Energy in changing from reactants at standard state to products at standard state is  $\Delta G^\theta$
- ◆ Relation between standard voltage,  $\mathcal{E}^\theta$ , and standard free-energy change is given by **Nernst's equation**

$$\mathcal{E}^\theta = - \frac{\Delta G^\theta}{nF}$$

## Half-cell voltages

- Free energy change in a half reaction is thought of as a separate quantity
- Requires a definition of the half-reaction that occurs with no free-energy change
  - Half-reaction free-energy change is referred to that reaction
  - Hydrogen half reaction is **assumed** to have zero free-energy change



## Standard half-cell voltages at 25°C and 1 atmosphere

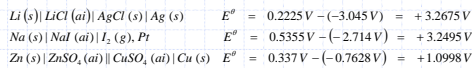
Electrode Diagram	Reaction	E <sup>θ</sup> (volts)
Li <sup>+</sup>   Li	Li <sup>+</sup> + e <sup>-</sup> → Li	-3.045
OH <sup>-</sup>   Ca(OH) <sub>2</sub>   Ca   Pt	½ Ca(OH) <sub>2</sub> + e <sup>-</sup> → OH <sup>-</sup> + ½ Ca	-3.02
OH <sup>-</sup>   H <sub>2</sub> , Pt	H <sub>2</sub> O + e <sup>-</sup> → ½ H <sub>2</sub> + OH <sup>-</sup>	-0.8281
Zn <sup>2+</sup>   Zn	½ Zn <sup>2+</sup> + e <sup>-</sup> → ½ Zn	-0.7628
SO <sub>4</sub> <sup>2-</sup>   PbSO <sub>4</sub>   Pb	½ PbSO <sub>4</sub> + e <sup>-</sup> → ½ Pb + ½ SO <sub>4</sub> <sup>2-</sup>	-0.3546
I <sup>-</sup>   AgI   Ag	AgI + e <sup>-</sup> → Ag + I <sup>-</sup>	-0.1522
D <sup>+</sup>   D <sub>2</sub> , Pt	D <sup>+</sup> + e <sup>-</sup> → ½ D <sub>2</sub>	-0.0034
H <sup>+</sup>   H <sub>2</sub> , Pt	H <sup>+</sup> + e <sup>-</sup> → ½ H <sub>2</sub>	0.0000
Br <sup>-</sup>   AgBr   Ag	AgBr + e <sup>-</sup> → Ag + Br <sup>-</sup>	+0.0711
Cu <sup>2+</sup> , Cu <sup>+</sup>   Cu	Cu <sup>2+</sup> + e <sup>-</sup> → Cu <sup>+</sup>	+0.153
Cl <sup>-</sup>   Hg <sub>2</sub> Cl <sub>2</sub>   Hg	½ Hg <sub>2</sub> Cl <sub>2</sub> + e <sup>-</sup> → Hg + Cl <sup>-</sup>	+0.2680
Cu <sup>2+</sup>   Cu	½ Cu <sup>2+</sup> → Cu	+0.337
I <sup>-</sup>   I <sub>2</sub> , Pt	½ I <sub>2</sub> + e <sup>-</sup> → I <sup>-</sup>	+0.5355
Mn <sup>2+</sup> , H <sup>+</sup>   MnO <sub>2</sub>   Pt	½ MnO <sub>2</sub> + 2 H <sup>+</sup> + e <sup>-</sup> → ½ Mn <sup>2+</sup> + H <sub>2</sub> O	+1.208

## Calculating standard cell voltages at 25°C and 1 atmosphere

- Cell voltage is measured by difference

$$E_{cell}^\theta = E_{right}^\theta - E_{left}^\theta$$

- Examples:

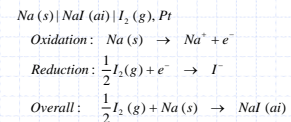
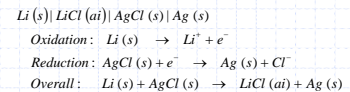


## Cell reactions from half-cell reactions

- Cell reaction is result of the two half-reactions

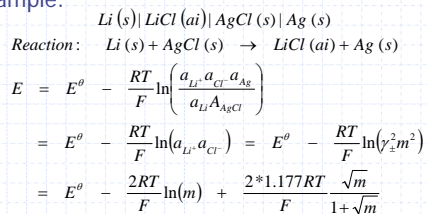
$$E_{cell}^\theta = E_{right}^\theta - E_{left}^\theta$$

- Examples:



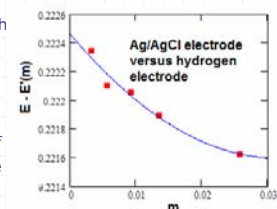
## Voltage at nonstandard conditions

- Cell voltage depends on ionic activities
- At low concentrations, activities described by the Debye-Hueckel law
- Example:



## Experimental determination of standard voltage

- Plot E – E' versus m
  - E' calculated from expected variation with concentration due to Debye-Hueckel theory
- Intercept at m = 0 gives E<sup>θ</sup>
- Example of voltage of the Ag/AgCl electrode versus NHE
- E<sup>θ</sup> = 0.2225 volts



## Summary

- ◆ Cells provide means to transform chemical energy to electrical work
- ◆ Diagrams specify cells
  - Oxidation occurs at left electrode
  - Reduction occurs at right electrode
- ◆ Half-cell reactions specify the processes at the electrodes
- ◆ Standard half-cell voltages used to calculate the standard voltage of a cell
- ◆ Voltages at other conditions determined by calculation of correction due to activity
  - Use Debye-Hueckel limiting law at low concentrations