

Lecture 14: E°_{cell} and ΔG

- Reading: Zumdahl: 11.3 (and 10.12)
- Outline: The voltage of a battery is determined by the Gibbs free energy of the chemical reaction that happens inside the battery.

$$E_{\text{cell}}^\circ \text{ and } w_{\text{rev}} \text{ (work)}$$

$$E_{\text{cell}}^\circ \text{ and } \Delta G_{\text{rxn}}^\circ \text{ and } K$$

- Electrochemistry is the avatar of Thermodynamics
- Problems (Zumdahl Ch 11 5th Ed.)
 - 33(!), 34b,c, 36 (Is ClO_3^- a problem?), 38, 39, 46, 47

$\mathcal{E}_{cell}^{\circ}$

A Cell (or Battery) EMF

- This is the symbol we use to represent the voltage of a battery or EMF cell (in Volts).
- The naught (superscript) means under standard thermodynamic conditions.
- We saw (previous lecture) how to construct a galvanic electrochemical cell (i.e. battery), capable of generating a flow of electrons.
- This flow of electrons (current) can perform work on the surroundings.

E_{cell} and work

- From the definition of electromotive force (EMF):

$$\text{Volt} = \text{energy (E,J)}/\text{charge (Q,C)}$$

$$1\text{ Volt} = 1\text{ Joule/Coulomb}$$

In English: 1 J of energy is available when

1 C of charge is transferred (or moves between) a potential difference of 1 V. Think of gravity: $P.E. = m \cdot (gh) \sim Q \cdot \mathcal{E}$

If all of this energy is converted to work that would be the maximum electrical work available due to the potential.

Q is the symbol for the amount of charge in Coulombs

$$\mathcal{E}_{\text{cell}} (V) = \frac{-W_{\text{max}}^{\text{elect}} (J)}{\Delta Q (C)}$$

$$-W_{\text{max}}^{\text{elect}} = -W_{\text{rev}}^{\text{nonPdV}} = \mathcal{E}_{\text{cell}} \cdot \Delta Q$$

Convention: If the battery potential is positive the system (battery) does work so (inside) it loses energy, hence the minus sign. ³

E°_{cell} example

How much work is done by a galvanic cell in which 1.5 moles of electrons are passed between a potential of 2 V (i.e. We have a 2V battery) under standard thermodynamic conditions?

$$\mathcal{E}^\circ_{\text{cell}} \cdot \Delta Q = -w_{\text{max}}^{\text{elect}}$$

$$2V \cdot 1.5 \text{ moles} = ??$$

↑

What do we do with this?

We need to know how much charge this is

The Faraday

How much charge does a mole of electrons have?

The “Faraday” (F) is the amount of charge contained in 1 mole of electrons.

$$F = 96,485 C / mol \sim 10^5 C / mol = 10^5 (J / mol) / V$$

$$e = 1.6 \cdot 10^{-19} C \text{ (Charge on a single electron)}$$

$$F = N_A e = 6 \cdot 10^{23} \cdot 1.6 \cdot 10^{-19} = 0.96 \cdot 10^5 C / mol$$

Now we can finish our problem and compute the work:

$$\Delta Q = n \cdot F = 1.5 \text{ moles} \cdot (0.96) 10^5 C / mole$$

$$W_{\max}^{\text{elect}} = -\mathcal{E}_{\text{cell}} \cdot \Delta Q = -n \cdot F \cdot \mathcal{E}_{\text{cell}}$$

$$\simeq -2V \cdot 1.5 \cdot 10^5 C = -3 \cdot 10^5 J = -300 kJ$$

A 1V battery can give about 100 kJ of work per mole of “reactant”.

Gibbs Energy and Work (at fixed P and T)

- Preparation to talk about batteries (next chapter)
- From Calorimetry: $\Delta H = \Delta H_{rxn} \cdot X$ to actually get heat (or an enthalpy change) you actually have to change the number of moles of something (X).
- Now to get work you need to consume some amount of reactant (X) :

$$W_{\max}^{electrical} = \Delta G = \Delta G_{rxn} \cdot X$$

- This shows that to do work you need a (chemical) potential times a (chemical) distance. And the work you get is proportional to the amount of stuff you use up.
- The “useful” work (text) is non-PdV work, and is electrical work; like a battery
- Calling the work useful and not useful (or PdV) work, which the book does, is not useful. (Sec 10.12-13).

ΔG and Work (Fixed T and P)

- Consider a reversible reaction, and work is the sum of the PdV part and extra work. Then

$$\begin{aligned}\Delta G &= \Delta H - \Delta(TS) = \Delta E + \Delta(PV) - T\Delta S \\ &= q_{rev} - P\Delta V + w_{rev}^x + P\Delta(V) - q_{rev} = w_{rev}^x\end{aligned}$$

$$\Delta G = w_{rev}^x = w_{rev}^{nonPdV}$$

We previously showed that the reversible work is the maximum work (as a negative number) you can get out of a system. Now see Gibbs energy is the same as the maximum non-PdV work (i.e. electrical) we can get from a chemical reaction when run at constant T and P.

E_{cell} and ΔG

- Since there is a relationship between ΔG and work, there is also a relationship between ΔG and E_{cell} .

$$\Delta G = w_{\text{max}}^{\text{elect}} = -\mathcal{E}_{\text{cell}} \cdot \Delta Q = -n \cdot F \cdot \mathcal{E}_{\text{cell}}$$

- The above relationship states that there is a direct relationship between Gibbs free energy and cell potential.
- For a galvanic cell (under standard conditions):

$$\mathcal{E}_{\text{cell}}^{\circ} > 0 \quad \text{Therefore, } \Delta G_{\text{rxn}}^{\circ} < 0 \quad (\text{spontaneous})$$

E_{cell} and ΔG_{rxn}

- We have a chemical reaction, and some of the reaction occurs (moles of each species are used up or created):

$$\Delta n(i) = c_{ss,i} \Delta X \quad \text{and} \quad \Delta G = \Delta G_{\text{rxn}} \Delta X$$

- Some electrons are transferred in the reaction.

$$\Delta n(e) = n(e) \Delta X \quad \text{and} \quad \Delta Q = F \Delta n(e)$$

- $n(e)$ is the stoichiometric coefficient for the number of electrons transferred for the reaction as written (even though the electrons are not written out in the net reaction)
- Putting all these connections together in the equation on the previous slide:

Reaction Energy

- The relation between the actual energy and the reaction energy in terms of the balanced equations gives a relation between the **reaction** Gibbs energy and the cell voltage:

$$\Delta G = -\mathcal{E}_{cell} \cdot \Delta Q = -\mathcal{E}_{cell} \cdot F \Delta n(e) = -\mathcal{E}_{cell} \cdot Fn\Delta X$$

$$\Delta G = \Delta G_{rxn} \Delta X = -\mathcal{E}_{cell} \cdot Fn\Delta X$$

$$\boxed{\Delta G_{rxn} = -n \cdot F \cdot \mathcal{E}_{cell}}$$

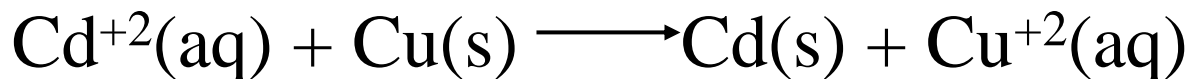
The stoichiometric coefficient $n(e)$.

- The Reaction Gibbs free energy is not the electrical work.
- Cannot equate reaction energy and work.
- To do work you actually have to have some amount of chemical reaction (specified as the number of moles of something that reacted).
- Identify the intensive and extensive quantities above.

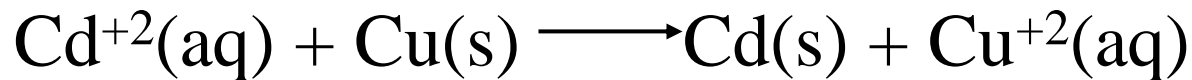
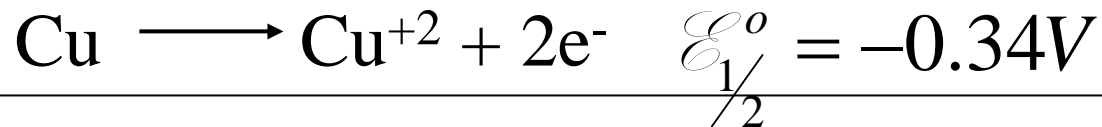
Determine E°_{cell} and $\Delta G^\circ_{\text{rxn}}$ for a Battery

For the following reaction, determine the overall standard cell potential and determine ΔG°

Note: The net reaction does not give n , and does not show how many electrons are used per reaction. To determine $n(e)$ we must break the reaction into its half reactions.



E°_{cell} an example



$$\mathcal{E}_{\text{cell}}^\circ = -0.74\text{V}$$

$$\begin{aligned} \Delta G_{\text{rxn}}^0 &= -nF\mathcal{E}_{\text{cell}}^\circ = -(2 e^- / \text{rxn}) \cdot (96000 \text{ C} / \text{mol } e^-) \cdot (-0.74 \text{ J} / \text{C}) \\ &= 150\text{kJ} / (\text{rxn}) \quad (\text{not spontaneous, not galvanic}) \end{aligned}$$

When adding half reaction to get a net reaction (where $n(e)$ drops out) then you can add the voltages. Warning: If $n(e)$ does not drop out, you cannot just add voltages.

E°_{cell} and K

$$\Delta G_{\text{rxn}} = -nF\mathcal{E}_{\text{cell}}$$

Under Standard conditions then:

$$\Delta G_{\text{rxn}}^0 = -nF\mathcal{E}_{\text{cell}}^0$$

Previously: $\Delta G_{\text{rxn}}^0 = -RT \ln K$

Therefore: $nF\mathcal{E}_{\text{cell}}^0 = -\Delta G_{\text{rxn}}^0 = RT \ln K$

$$\mathcal{E}_{\text{cell}}^0 = \frac{RT}{nF} \ln K$$

@ r.t. $T = 298.13\text{K}$ $RT = 2.48\text{kJ} / \text{mole}$

$$\frac{RT}{F} = 2.57 \cdot 10^{-2} \frac{\text{J} / \text{mole}}{\text{Coulombs} / \text{mole}} = 25.7\text{mV}$$

$\ln 10 = 2.303$

$25.7\text{mV} \cdot \ln 10 = 59\text{mV}$

$\mathcal{E}_{\text{cell}}^0 = \frac{25.7}{n} \ln K = \frac{59.1}{n} \log_{10} K \quad \text{mV}$

E°_{cell} and K

$$E^\circ_{\text{cell}} = \frac{25.7}{n} \ln K = \frac{59.1}{n} \log_{10} K \text{ mV}$$

- The above relationship states that by measuring E°_{cell} , we can determine K .
- The above relationship illustrates that electrochemical cells are a venue in which thermodynamics is readily evident (an avatar).

E°_{cell} and $\Delta G^\circ_{\text{rxn}}$ and K

- Developing the “full picture”

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K$$

$\Delta G^\circ_{\text{rxn}} = -n \cdot F \cdot \mathcal{E}^\circ_{\text{cell}}$

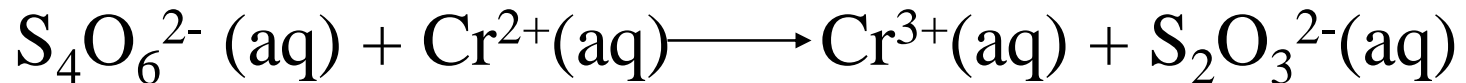
$\mathcal{E}^\circ_{\text{cell}} = \frac{0.0591 \text{ V}}{n} \cdot \log_{10} K$

$\mathcal{E}^\circ_{\text{cell}} = \frac{RT}{nF} \cdot \ln K$

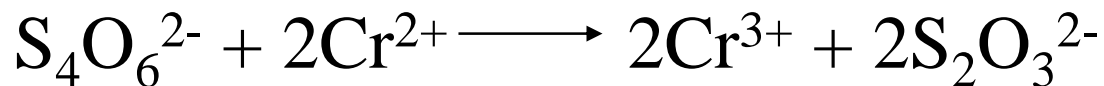
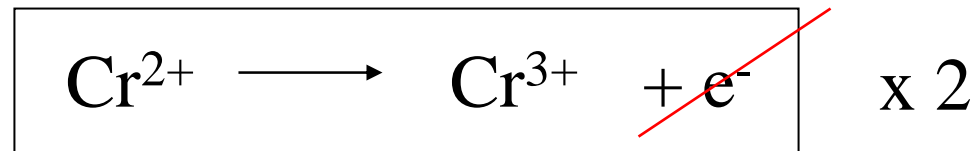
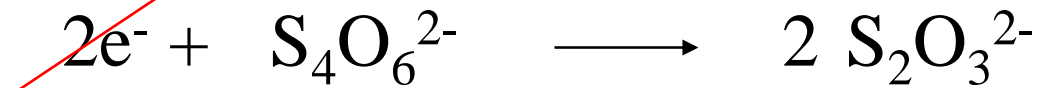
- It is important to see how all of these ideas interrelate.
- We can measure K directly under Standard State conditions; very very far away from Equilibrium

An Example: determine E°_{cell} and K

- Balance, determine E°_{cell} and K for the following:

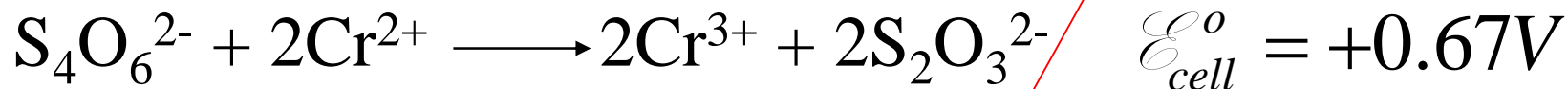
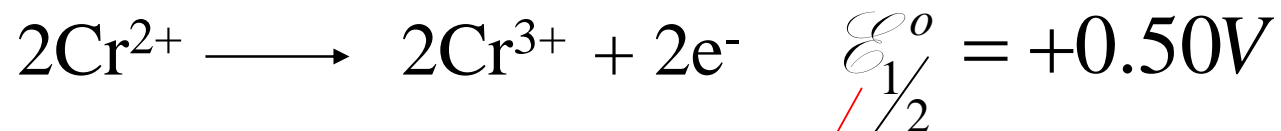
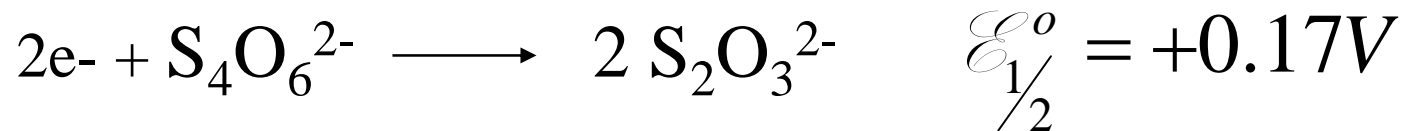


- Break the net reaction into its half reactions



A Battery Example

- Determining E°_{cell}



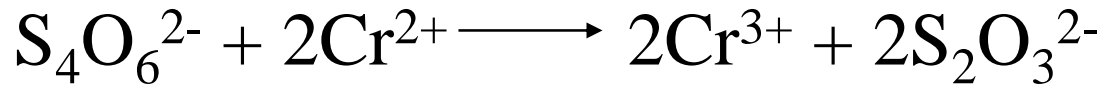
From the two half reactions we see:

$$n=n(e)=2$$

 This voltage is NOT doubled 17

Determining K for a Battery

$$\mathcal{E}_{cell}^o = +0.67V$$



$$\mathcal{E}_{cell}^o = \frac{0.025}{n} \ln K$$

$$\ln K = \frac{n \cdot \mathcal{E}_{cell}^o}{0.025} = \frac{2 \cdot 0.67}{0.025} = 52.3$$

$$K = e^{52.3} = 10^{22.7} = 5 \cdot 10^{22}$$

The larger the Battery Voltage; the larger the K; the larger the tendency to go to products; the greater the driving force for the reaction

Gibbs Energy from K

- Closing the loop (from the triangle relation of the full picture)
- Compute the Gibbs free energy of reaction:

$$\begin{aligned}\Delta G_{rxn}^0 &= -RT \ln K \\ &= -2.47 \cdot \ln(5 \cdot 10^{22}) \text{ kJ / mole} = -2.47 \cdot (52.3) \\ &= -129 \text{ kJ / rxn}\end{aligned}$$

$$\begin{aligned}\Delta G_{rxn}^0 &= -nF\mathcal{E}_{cell}^0 = -2 \cdot 96500 \cdot 0.67 \text{ J / rxn} \\ &= -129 \text{ kJ / rxn}\end{aligned}$$

The numbers are the same by the two methods (with some round off differences). The reaction is highly spontaneous.

Z11.33 Work and a Battery

How much work will you get from the Battery shown in 20b?

- See 11.20 the Cd/V Battery, all species at standard state.
- Develop the half reactions, find half-cell Voltages (EMFs) in Table and compute the cell EMF.
- Determine n (for electrons) and compute ΔG_{rxn}^o
- Now compute the work.
 - Insufficient Information !!!!!
 - If you use 0.1 moles of Cd (metal) how much work will you get?