

Connection between *E_{cell}*, ΔG , and K

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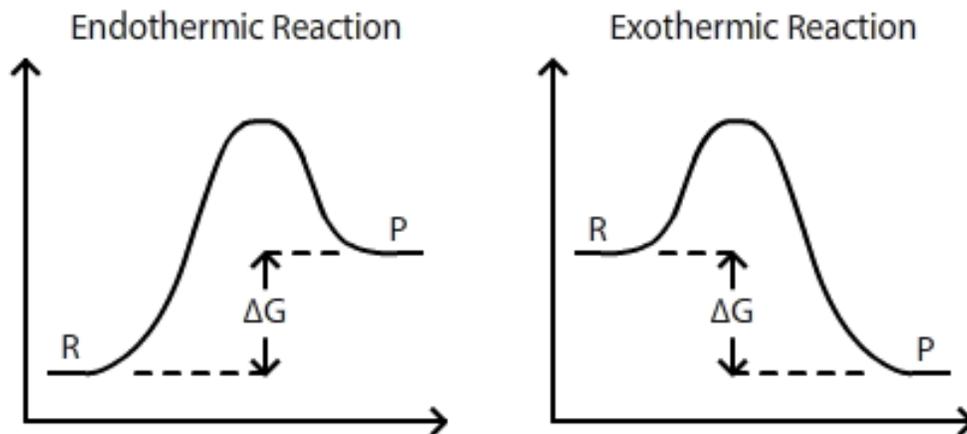
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The connection between cell potential, Gibbs free energy and constant equilibrium are directly related in the following multi-part equation:

$$\Delta G^{\circ} = -RT \ln K_{\text{eq}} = -nFE_{\text{ocell}}$$

ΔG : Gibbs Free Energy

ΔG is the change of Gibbs (free) energy for a system and ΔG° is the Gibbs energy change for a system under standard conditions (1 atm, 298K). On an energy diagram, ΔG can be represented as:



Graphic by Shamsheer Singh

Where ΔG is the difference in the energy between reactants and products. In addition ΔG is unaffected by external factors that change the kinetics of the reaction. For example if E_a (activation energy) were to decrease in the presence of a catalyst or the kinetic energy of molecules increases due to a rise in temperature, the ΔG value would remain the same.

E°_{cell} : Standard Cell Potential

E°_{cell} is the electromotive force (also called cell voltage or cell potential) between two half-cells. The greater the E°_{cell} of a reaction the greater the driving force of electrons through the system, the more likely the reaction will proceed (more spontaneous). E°_{cell} is measured in volts (V). The overall voltage of the cell = the half-cell potential of the reduction reaction + the half-cell potential of the oxidation reaction. To simplify,

$$E_{\text{cell}} = E_{\text{reduction}} + E_{\text{oxidation}} \quad \text{or} \quad E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

The potential of an oxidation reduction (loss of electron) is the negative of the potential for a reduction potential (gain of electron). Most tables only record the standard reduction half-reactions. In other words, most tables only record the [standard reduction potential](#); so in order to find the standard oxidation potential, simply reverse the sign of the standard reduction potential.

***Note: The more positive reduction potential of reduction reactions are more spontaneous. When viewing a cell reduction potential table, the higher the cell is on the table, the higher potential it has as an oxidizing agent.**

Difference between E_{cell} and E°_{cell}

E°_{cell} is the standard state cell potential, which means that the value was determined under standard states. The standard states include a concentration of 1 Molar (mole per liter) and an atmospheric pressure of 1. Similar to the standard state cell potential, E°_{cell} , the E_{cell} is the non-standard state cell potential, which means that it is not determined under a concentration of 1 Molar and pressure of 1 atm. The two are closely related in the sense that the standard cell potential is used to calculate for the cell potential in many cases.

$$E_{\text{cell}} = E_{\text{ocell}} - RTnF \ln Q$$

Other simplified forms of the equation that we typically see:

$$E_{\text{cell}} = E_{\text{ocell}} - 0.0257n \ln Q$$

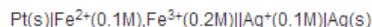
or in terms of log base 10, instead of the natural logarithm (base e)

$$E_{\text{cell}} = E_{\text{ocell}} - 0.0592n \log_{10} Q$$

Both equations apply when the temperature is 25°C. Deviations from 25°C requires the use of the original equation. Essentially, E° is E at standard conditions

Example 1

What is the value of E_{cell} for the voltaic cell below:



$E_{\text{cell}} = ?$

SOLUTION

To use the Nernst equation, we need to establish E°_{cell} and the reaction to which the cell diagram corresponds so that the form of the reaction quotient (Q) can be revealed. Once we have determined the form of the Nernst equation, we can insert the concentration of the species.

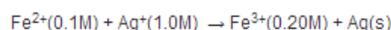
Solve:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$= E^{\circ}_{\text{Ag}/\text{Ag}} - E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}}$$

$$= 0.800\text{V} - 0.771\text{V} = 0.029\text{V}$$

Now to determine E_{cell} for the reaction



Use the Nernst equation

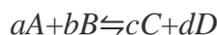
$$E_{\text{cell}} = 0.029\text{V} - (0.0592\text{V}/1)\log [\text{Fe}^{3+}]/[\text{Fe}^{2+}][\text{Ag}]$$

$$= 0.029\text{V} - 0.0592\text{V} \cdot \log [0.2]/[0.1] \cdot [1.0]$$

$$= 0.011\text{V}$$

K: The Equilibrium Constant

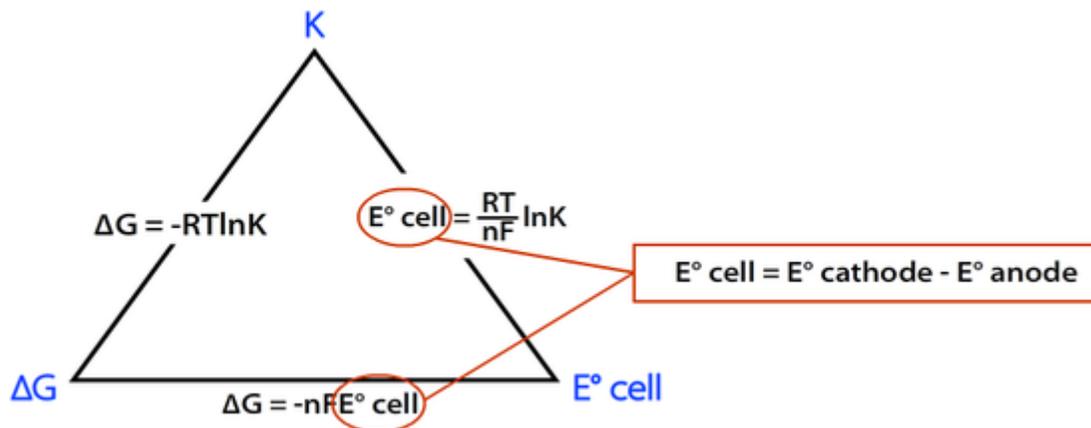
K is the equilibrium constant of a reaction and is given by the reaction quotient:



$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The Relationship Between The Three

The relationship between ΔG , K, and E° cell can be represented by the following diagram.



where

- $R = 8.314 \text{ J mol}^{-1} \text{ C}^{-1}$
 - $T = \text{Temp in K}$
 - $n = \text{moles of } e^- \text{ from balanced redox reaction}$
 - $F = \text{Faraday's constant} = 96,485 \text{ C/mol}$
- E°_{cell} can be calculated using the following formula:

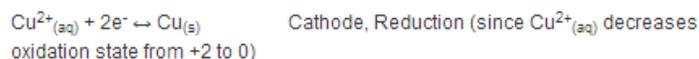
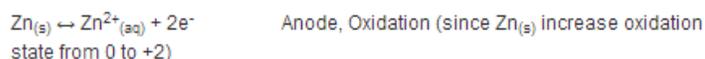
$$E^\circ_{\text{cell}} = E^\circ (\text{cathode}) - E^\circ (\text{anode}) = E^\circ (\text{Reduction}) - E^\circ (\text{Oxidation})$$

Example 2

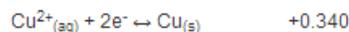
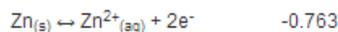
Question Find the E° cell for the following coupled half-reactions

SOLUTION

1. Determine the cathode and anode in the reaction



2. Determine the E° cell values using the standard reduction potential table



3. Use $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$$= 0.340 - (-0.763)$$

$$= 1.103 \text{ V}$$

Problems

1. Find E° cell for $2\text{Br}_{(aq)} + \text{I}_{2(s)} \leftrightarrow \text{Br}_{2(s)} + 2\text{I}_{(aq)}$
2. Find E° for $\text{Sn}_{(s)} \leftrightarrow \text{Sn}^{2+}_{(aq)} + 2e^-$
3. Find E° cell for $\text{Zn}_{(s)} | \text{Zn}^{2+}_{(aq)} || \text{Cr}^{3+}_{(aq)}, \text{Cr}^{2+}_{(aq)}$

(See answer key for solutions)

*If the E° values of the reaction is negative, then the reaction is NOT spontaneous and therefore the reverse reaction is occurring and the electrons are flowing in the opposite direction.

* These values are tabulated in the standard reduction potential table.

Summary Table

E°_{cell}	Delta G	Q & K Relationship	Reaction Direction	Spontaneity (as written)
>0	-	$Q < K$	Forward	Spontaneous
<0	+	$Q > K$	Backward	Non-spontaneous
=0	=0	$Q = K$	No Reaction	N/A

Example: Using $\Delta G = -RT \ln K$

Given $K = 2.81 \times 10^{-16}$ for a following reaction $\text{Cu}^{2+}_{(aq)} + \text{Ag}_{(s)} \rightleftharpoons \text{Cu}_{(s)} + 2\text{Ag}^+$ find ΔG .

Solution:

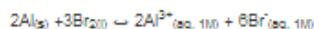
Use the following formula: $\Delta G = -RT \ln K$

$$= 8.314 \times 298 \times \ln(2.81 \times 10^{-16}) = -8.87 \times 10^5$$

$$= 8.871 \text{ kJ}$$

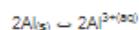
Example: Using $\Delta G = -nFE^\circ_{\text{cell}}$

Find ΔG for the following reaction:



Solution:

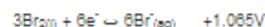
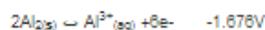
Step 1: Separate the reaction into its two half reactions



Step 2: Balance the half equations using O, H, and charge using e^-



Step 3: From the balanced half reactions, we can conclude the number of moles of e^- for use later in the calculation of ΔG . Determine the E° values using the standard reduction potentials, using the E° cell table.



Step 4: Determine $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

$$= 1.065 - (-1.676)$$

$$= 2.741 \text{ V}$$

Step 5: Once E°_{cell} has been calculated and the number of moles of electrons have been determined, we can use $\Delta G = -nFE^\circ_{\text{cell}}$

$$= (-6 \text{ mol } e^-)(96485 \text{ C/mol } e^-)(2.741 \text{ V})$$

$$= -1588\text{kJ}$$

This equation can be used to calculate E°_{cell} given K or K given E°_{cell} . If $T=298 \text{ K}$, the RT is a constant then the following equation can be used: $E^\circ_{\text{cell}} = (0.025693\text{V}/n) \ln K$

Example: Using $E^\circ_{\text{cell}} = (RT/nF) \ln K$

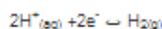
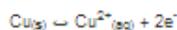
Given the E°_{cell} for the reaction $\text{Cu}_{(s)} + 2\text{H}^+_{(aq)} \rightleftharpoons \text{Cu}^{2+}_{(aq)} + \text{H}_{2(g)}$ is -0.34V , find the equilibrium constant (K) for the reaction.

SOLUTION

Step 1: Split into two half reaction



Step 2: Balance the half reactions with charges to determine n



Therefore $n=2$

Step 3: From the example above, $E^\circ_{\text{cell}} = -0.34\text{V}$

$$-0.34 = (0.025693/2) \ln K$$

$$K = e^{(-0.34 \times 2/0.025693)}$$

$$K = 3.19 \times 10^{-12}$$

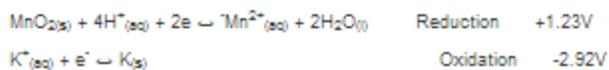
Example 1: I see you

Given the following reaction determine ΔG , K , and E°_{cell} for the following reaction at standard conditions? Is this reaction spontaneous?

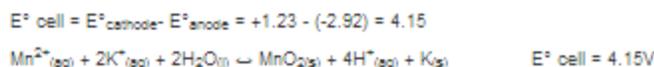


SOLUTION

Step 1: Separate and balance the half reactions. Label which one is reduction and which one is oxidation. Find the corresponding E° values for the half reactions.



Step 2: Write net balanced reaction in acidic solution, and determine the E° cell.

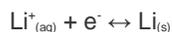
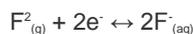


Step 3: Find ΔG for the reaction.

$$\begin{array}{l} \text{Use } \Delta G = -nFE^\circ_{\text{cell}} \\ = -2 \text{ mol e}^- \times 96458 \text{ C} \times 4.15 = -800.60\text{kJ} \\ \text{Therefore, since } E^\circ_{\text{cell}} \text{ is positive and } \Delta G \text{ is negative, this reaction is spontaneous.} \end{array}$$

Problems

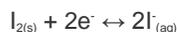
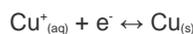
4. Find ΔG for the following combined half reactions:



5. Find the equilibrium constant (K) for the following reaction: (*Hint:* Find E°_{cell} first!)



6. Find E°_{cell} for the given reaction at standard conditions:



(See answer key for solutions)

Answers

1. +0.530 V

2. +0.137 V
3. +0.339 V
4. +1139.68 kJ
5. 6.4×10^{25}
6. +0.195 V

References

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