Topic 9.9: Cell Potential and Free Energy

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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Every Potential Is Measured Against Hydrogen

The standard hydrogen electrode sets the zero of the table. By definition, the reduction below has E° = 0.00 V under standard conditions: 1 M H^+, 1 atm H_2, 25 °C. Every tabulated reduction potential is measured against this electrode.

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

A positive E° means reduction beats hydrogen. The copper half reaction below sits at +0.34 V, so Cu^{2+} is reduced more readily than H^+. The zinc half reaction below sits at −0.76 V, so Zn^{2+} is reduced less readily than H^+, and zinc metal is oxidized more readily than hydrogen gas.

$Cu^{2+} + 2e^- \rightarrow Cu$

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

A tabulated potential assumes 1 M concentrations for aqueous species, 1 atm for gases, and pure solids and liquids. Change the concentrations and the actual cell potential changes.

The Higher Reduction Potential Is Reduced

The cathode is the half reaction with the more positive E°. Put two half cells together and the species with the larger reduction potential is reduced at the cathode. The other half reaction runs backwards as oxidation at the anode. The strongest oxidizing agents sit at the top of the table, with the most positive potentials; the strongest reducing agents sit at the bottom.

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$E°_{cell} = E°_{cathode} - E°_{anode}$

Subtract, using the reduction potentials exactly as printed. For the zinc copper cell, $E°_{cell} = (+0.34) - (-0.76) = +1.10$ V. Subtracting a negative adds its magnitude.

Potentials are intensive: never scale them. Doubling the half reaction below leaves E° at +0.34 V. Scaling is needed only to balance electrons.

$Cu^{2+} + 2e^- \rightarrow Cu$

$2Cu^{2+} + 4e^- \rightarrow 2Cu$

Reversing the reaction flips the sign. The zinc copper cell forward has $E°_{cell} = +1.10$ V. Run backwards, the cathode and anode swap roles and $E°_{cell} = -1.10$ V.

$Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$

$\Delta G° = -nFE°$: Potential as Energy

Free energy and potential are the same quantity in different units. The link is below, where n is the moles of electrons transferred in the balanced redox equation and F = 96,485 C mol^{-1} is Faraday's constant. The negative sign is the hinge: a positive E° gives a negative ΔG°, and a negative E° gives a positive ΔG°.

$\Delta G° = -nFE°$

Check the units. A volt is a joule per coulomb, so (C mol^{-1}) × (J C^{-1}) gives J mol^{-1}. Answers are usually quoted in kJ mol^{-1}, so divide by 1000 at the end. For the zinc copper cell, n = 2 and $E°_{cell} = 1.10$ V, so $\Delta G° = -(2)(96{,}485)(1.10) = -212{,}267$ J mol^{-1}, about −212 kJ mol^{-1}.

n comes from the balanced equation, never from one ion's charge. In the reaction below, zinc loses 2 electrons and each silver ion gains 1, so n = 2.

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

The Sign Trio: E°, ΔG°, and K

Three quantities, one story. For a spontaneous reaction under standard conditions: $E° > 0$, $\Delta G° < 0$, $K > 1$. For a nonspontaneous reaction: $E° < 0$, $\Delta G° > 0$, $K < 1$.

The K link runs through the equation below. A negative ΔG° makes ln K positive, so K exceeds 1.

$\Delta G° = -RT \ln K$

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Even modest voltages imply enormous constants: at 298 K, RT ln 10 = 5.70 kJ mol^{-1}, meaning every 5.7 kJ mol^{-1} of free energy is one factor of 10 in K. The zinc copper cell at −212 kJ mol^{-1} has K of about 10^{37}.

E° and ΔG° describe standard conditions only. At equilibrium, the actual cell potential Ecell is zero and the actual free energy change ΔG is zero, even though E°cell and ΔG° are nonzero.

Voltage Alone Does Not Measure Spontaneity

Spontaneity is measured by ΔG°, and ΔG° depends on n as well as E°. A small voltage with many electrons can beat a large voltage with few. Cell X, with E°cell = 0.90 V and n = 1, gives ΔG° = −(1)(96,485)(0.90) = −86,837 J mol^{-1}, about −87 kJ mol^{-1}. Cell Y, with E°cell = 0.50 V and n = 4, gives ΔG° = −(4)(96,485)(0.50) = −192,970 J mol^{-1}, about −193 kJ mol^{-1}.

With n held equal, the larger voltage wins. The larger E° gives the more negative ΔG° and the larger K.

Worked Examples

Example 1: The silver iron cell, end to end. E°(Ag^{+}/Ag) = +0.80 V beats E°(Fe^{2+}/Fe) = −0.44 V, so silver ions are reduced at the cathode and iron metal is oxidized at the anode. Cell potential: E°cell = (+0.80) − (−0.44) = +1.24 V, positive, so the cell is galvanic. Balancing electrons gives the reaction below, so n = 2 and ΔG° = −(2)(96,485)(1.24) = −239,283 J mol^{-1}, about −239 kJ mol^{-1}.

$Fe(s) + 2Ag^{+}(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$

Example 2: Cell notation for aluminum and nickel. E°(Al^{3+}/Al) = −1.66 V and E°(Ni^{2+}/Ni) = −0.25 V. Nickel has the more positive reduction potential, so it is reduced at the cathode and aluminum is oxidized at the anode. Cell notation puts the anode on the left and the cathode on the right:

$Al(s)|Al^{3+}(aq)||Ni^{2+}(aq)|Ni(s)$

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Cell potential: E°cell = (−0.25) − (−1.66) = +1.41 V, so the cell is galvanic,
even though both reduction potentials are negative: what matters is the
difference.
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Example 3: Free energy from a potential. A cell has E°cell = +0.62 V with n = 3. ΔG° = −(3)(96,485)(0.62) = −179,462 J mol^{-1}, about −179 kJ mol^{-1}.

Example 4: Potential from a free energy, and the negative case. A reaction has ΔG° = −237 kJ mol^{-1} with n = 2. Converting −237 kJ mol^{-1} to joules, E°cell = −ΔG°/(nF) = 237,000/((2)(96,485)) = +1.23 V. For contrast, a cell with E°cell = −0.25 V and n = 2 gives ΔG° = −(2)(96,485)(−0.25) = +48,243 J mol^{-1}, about +48.2 kJ mol^{-1}, so it is nonspontaneous as written.

Traps That Cost Marks in Topic 9.9

Flipping the anode's sign before subtracting. The equation below uses reduction potentials as printed. Flip the sign and then subtract and the answer is wrong.

E°cell = E°cathode − E°anode

Scaling a potential with its half reaction. Doubling a half reaction doubles the electrons and the free energy, never the potential.

Using one ion's charge for n. n is the moles of electrons in the balanced equation, found from the half reactions after balancing.

Leaving ΔG° in joules. F is in C mol^{-1} and E° in V, so the product is J mol^{-1}. Divide by 1000 for kJ mol^{-1}, or the answer is wrong by a factor of 1000.

Confusing E°cell with Ecell at equilibrium. At equilibrium Ecell = 0 and ΔG = 0, while E°cell and ΔG° keep their standard values. A negative E°cell is not a broken cell: it means the reaction as written is nonspontaneous and needs an external supply, so the setup is electrolytic.

Judging spontaneity by voltage alone. Compare ΔG° values when n differs; a smaller voltage with more electrons can be more spontaneous.

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Key Relationships to Remember

- Standard hydrogen electrode: $2H^+ + 2e^- \rightarrow H_2$ has E° = 0.00 V by definition; standard conditions are 1 M, 1 atm, 25 °C
- The half reaction with the more positive reduction potential is reduced at the cathode; the other is oxidized at the anode; electrons flow through the wire from anode to cathode
- E°cell = E°cathode − E°anode, using reduction potentials exactly as tabulated; potentials are intensive and are never scaled by coefficients
- Reversing a cell reaction flips the sign of E°cell and of ΔG°, with magnitudes unchanged
- $\Delta G° = -nFE°$, F = 96,485 C mol^{-1}; n is the moles of electrons in the balanced equation; convert J mol^{-1} to kJ mol^{-1} by dividing by 1000
- Sign trio: E° > 0 goes with ΔG° < 0 and K > 1; E° < 0 goes with ΔG° > 0 and K < 1, linked by $\Delta G° = -RT \ln K$
- At 298 K, RT ln 10 = 5.70 kJ mol^{-1}, so every 5.7 kJ mol^{-1} of ΔG° is one factor of 10 in K
- At equilibrium, Ecell = 0 and ΔG = 0, while E°cell and ΔG° keep their standard values
- Spontaneity is compared with ΔG°, not E° alone; with equal n, the larger E° gives the larger K

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