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Topic 9.10: Cell Potential Under Nonstandard Conditions

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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E° Describes Standard Conditions Only

A tabulated E° assumes standard conditions. Those are 1 M for aqueous species, 1 atm for gases, and 25 °C.

E° is a constant for the reaction, Ecell is not. E°cell never changes for a given cell reaction. The measured Ecell changes as the cell runs, because the concentrations inside it change.

The Nernst Equation

The Nernst equation corrects E° for the actual reaction quotient Q. It reads as below, where R = 8.314 J mol^{-1} K^{-1}, T is in kelvin, n is the moles of electrons in the balanced cell reaction, and F = 96,485 C mol^{-1}.

$$E = E^\circ - (RT/nF) \ln Q$$

At 25 °C the constants collapse into one number. RT/F = (8.314)(298)/96,485 = 0.0257 V. Converting ln to log base 10 multiplies by 2.303, giving the AP form below.

$$E = E^\circ - (0.0592/n) \log Q$$

The 0.0592 V factor belongs to 25 °C only. At any other temperature, go back to the ln form above and insert the given temperature in kelvin. A higher temperature makes the factor larger.

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Reading the Sign: What Q Does to E

The minus sign is the whole story. Q > 1 makes log Q positive and E falls below E°. Q < 1 makes log Q negative and subtracting a negative raises E above E°. Q = 1 gives E = E°.

A buildup of products weakens the cell; a buildup of reactants strengthens it. Products piling up push the reaction backward, while reactants in excess push it forward.

A tenfold change in Q shifts E by 0.0592/n volts. With n = 2, one decade of Q is worth 0.0296 V; with n = 1, the full 0.0592 V.

Building Q for a Cell

Q is written like an equilibrium constant expression. Products over reactants for the overall cell reaction as written, each raised to its stoichiometric coefficient. Solids and pure liquids are omitted; aqueous ions enter as molarities, gases as partial pressures in atm.

The zinc copper cell gives the standard example. For the reaction below, Q is the ratio below it. The solids vanish from the expression, so only the two ion concentrations matter.

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

$Q = [Zn^{2+}]/[Cu^{2+}]$

The hydrogen electrode shows how gases enter. For the half reaction below, Q is the ratio below it. With P_H_2 = 2.0 atm and $[H^+]$ = 1.0 M, Q = 2.0. Raising the hydrogen pressure raises Q and lowers E, like raising a product concentration.

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

$Q = P_H_2/[H^+]^2$

Q is the actual quotient, never K, unless the cell is at equilibrium.

A Cell Runs Down Toward Zero

As a galvanic cell operates, Q moves toward K and E falls.

At equilibrium, Q = K and E = 0. No net driving force remains, so the cell is dead. Setting E = 0 in the Nernst equation gives the relation below: a standard potential gives K in one line.

$\log K = nE°/0.0592$

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A moderate voltage implies an enormous K. The scale is logarithmic, so each 0.0592/n volts is another factor of 10 in K. Worked Example 3 below turns E° = 0.46 V with n = 2 into $K = 3.5 \times 10^{15}$.

A measured E works backward to Q. Rearranging gives the relation below. Worked Example 4 below turns a measured E = 0.95 V into $Q = 1.2 \times 10^{5}$.

$$\log Q = (E^\circ - E)/(0.0592/n)$$

E can cross zero. For E° = 0.34 V with n = 1 and $Q = 1.0 \times 10^{6}$, $E = 0.34 - 0.0592 \times 6 = -0.015$ V. E turns negative exactly when Q passes K.

Concentration Cells: Potential From Difference Alone

A concentration cell has identical half cells at different concentrations. Both half reactions are the same, so E° = 0, and the equation simplifies to the form below, with Q = [dilute]/[concentrated].

$$E = -(0.0592/n) \log Q$$

The spontaneous change is dilution. The concentrated ion is reduced at the cathode, while the metal is oxidized in the dilute compartment, the anode.

The copper example fixes the sign. For $Cu(s)|Cu^{2+}(0.0010\ M)||Cu^{2+}(1.0\ M)|Cu(s)$, Q = 0.0010/1.0 = 0.0010 and n = 2, so $E = -(0.0592/2) \log(0.0010) = +0.089$ V.

The silver example shows the n = 1 case. For $Ag(s)|Ag^{+}(0.10\ M)||Ag^{+}(1.0\ M)|Ag(s)$, Q = 0.10 and n = 1, so $E = -0.0592 \times \log(0.10) = +0.059$ V. As the cell runs, the two sides even out and E falls to zero. As the cell runs, the two sides even out and E falls to zero.

Worked Examples

Example 1: Product buildup trims the voltage. A cell has E° = 1.10 V, n = 2, and Q = 10 at 25 °C. $E = 1.10 - (0.0592/2) \log 10 = 1.10 - 0.0296 = 1.07$ V.

Example 2: Reactant excess lifts the voltage. A cell has E° = 0.76 V, n = 2, and Q = 0.010 at 25 °C. $\log Q = -2$, so $E = 0.76 - (0.0296)(-2) = 0.76 + 0.0592 = 0.82$ V. The intermediate step makes the double negative visible.

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Example 3: Equilibrium constant from a standard potential. A cell has E° = 0.46 V with n = 2 at 25 °C. At equilibrium E = 0, so log K = nE°/0.0592 = (2)(0.46)/0.0592 = 15.54, and K = $10^{15.54}$ = 3.5×10^{15}. A moderate voltage implies an enormous K because the scale is logarithmic.

Example 4: Measured potential worked back to Q. A cell with E° = 1.10 V and n = 2 shows a measured E = 0.95 V at 25 °C. log Q = (E° − E)/(0.0592/n) = (1.10 − 0.95)/0.0296 = 5.07, so Q = $10^{5.07}$ = 1.2×10^{5}.

Traps That Cost Marks in Topic 9.10

Using K instead of Q in the Nernst equation. The equation takes the actual reaction quotient under current conditions. Only at equilibrium does Q equal K, and then E = 0.

Sign errors with log Q, or forgetting n. For Q < 1, log Q is negative, and subtracting a negative raises E. Write out the intermediate step. The 0.0592 V is divided by n, the moles of electrons in the balanced equation: using n = 1 when the reaction transfers 2 electrons doubles the correction term.

Writing Q backwards. Q is products over reactants, matching the cell reaction as written. For the zinc copper cell, Q = $[Zn^{2+}]/[Cu^{2+}]$, not the inverse. Solids and pure liquids never appear in Q, and every term is raised to its stoichiometric coefficient.

Putting the concentration cell cathode on the dilute side. Reduction happens where ions are concentrated. The concentrated compartment is the cathode; the dilute compartment is the anode.

Confusing E = 0 with E° = 0. Every cell at equilibrium has E = 0, but E° is zero only for concentration cells.

Using the 0.0592 factor at a temperature other than 25 °C. The factor is specific to 298 K. At another temperature, use the ln form below with T in kelvin.

$E = E° - (RT/nF) \ln Q$

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Key Relationships to Remember

- $E = E° - (RT/nF) \ln Q$, with $R = 8.314$ J mol^{-1} K^{-1}, T in kelvin, n from the balanced cell reaction, $F = 96{,}485$ C mol^{-1}
- At 25 °C, $RT/F = 0.0257$ V and the working form is $E = E° - (0.0592/n) \log Q$; the 0.0592 V factor is specific to 298 K
- $Q > 1$ lowers E below E°; $Q < 1$ raises E above E°; $Q = 1$ gives $E = E°$
- A tenfold change in Q shifts E by exactly 0.0592/n volts
- Q is products over reactants for the overall cell reaction as written, solids and pure liquids omitted, ions as molarities, gases as partial pressures in atm, each raised to its coefficient
- As a cell runs, Q moves toward K and E falls; at equilibrium $Q = K$ and $E = 0$, so $\log K = nE°/0.0592$
- A measured E gives Q by $\log Q = (E° - E)/(0.0592/n)$
- Concentration cells have $E° = 0$, $E = -(0.0592/n) \log([\text{dilute}]/[\text{concentrated}])$, cathode on the concentrated side, anode on the dilute side, E falling to zero as the concentrations equalize

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Topic 9.10 Quiz: Cell Potential Under Nonstandard Conditions

Topic 9.10 Worksheet

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