

Oxidation numbers

Know how to determine oxidation numbers for atoms in typical molecules & ions.

- ➔ This is how we will determine if a redox reaction is happening.
- ➔ On the exam, your ability to determine oxidation numbers may be tested directly through short-answer questions

Balancing redox reactions

Know how to balance a redox reaction as a sum of two half-cell reactions

As with any chemical equation, total charge and total number of each type of atom must be same on both sides

For a half-reaction, electron(s) appear as a reactant or product

Balance half-reactions in “acidic solution” first – if hydroxide (OH⁻) appears in overall reaction, convert to basic half-reaction

- ➔ This is how we will determine n , the number of electrons exchanged per mole reaction, in the problems below.
- ➔ This is how we identify which standard reduction potentials we can consult to express the standard cell potential.
- ➔ We can also make sure we have the right coefficients in the overall equation, to use in determining Q , below.

Voltaic cells

Know how to draw a basic picture of a voltaic cell: two half-cells with the **reduction** (in the chemical equation as written) appearing on the **right**

- ➔ This will help you get the right signs for cell potential E and for ΔG .

Standard cell potential

E_{cell} or just E is the **cell potential** – a measurement of the “electromotive force” created by the chemical reaction; measured as voltage difference between right and left electrodes: Volts = Joules / Coulomb

E_{cell}° or E° is the **standard cell potential**: the value of E when reactants & products are at standard concentrations – 1 atm or 1 M or pure substances. Does not imply a particular temperature.

Standard reduction potential (or standard electrode potential)

Standard reduction potentials E_{red}° are tabulated for a series of reduction half-cell reactions, usually at 298 K.

$E_{\text{cell}}^\circ = E_{\text{red}}^\circ + E_{\text{ox}}^\circ$ (standard cell potential as sum of half-cell electrode potentials)

But since $E_{\text{ox}}^\circ = -E_{\text{red}}^\circ$ for any half-cell reaction, and the species on the **right** is being **reduced** & left oxidized,

$E_{\text{cell}}^\circ = E_{\text{red}}^\circ(\text{right}) - E_{\text{red}}^\circ(\text{left})$ (standard cell potential as difference of two half-cell reduction potentials)

- ➔ E_{red}° and E_{ox}° do not change when half-cell reaction is multiplied by a coefficient – don’t need n to get E° !
- ➔ You must look up reduction potentials for half-cell with right phases and oxidation states for the problem at hand
- ➔ E_{red}° for (2 H⁺(aq) + 2e⁻ → H₂(g)) defined as 0.000 Volts

Expect to have to find E_{cell}° for a balanced (or not-yet-balanced!) redox reaction based on tabulated values, or a variation on this.

Electrochemistry & thermodynamics

One essential relationship, the rest follows from Chpt. 17. For all of these, you must know the number of electrons n , which means you must have a balanced chemical equation expressed as a sum of two half-reactions!!

$$\Delta G = -n F E \quad F = \text{Faraday's constant, Coulombs per mole of elementary charge}$$

E is the voltage at which the free energy change available from the chemical reaction and the electrical work are exactly balanced. $E > 0$ for spontaneous chemical reactions ($\Delta G < 0$).

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad \text{Nernst equation – cell potential as function of concentration}$$

Q is **reaction quotient** for overall reaction – make sure you know how to calculate it!

Three cases:

- | | | |
|--|---|--|
| 1) Standard conditions (1 atm, 1 M): $Q = 1, \ln Q = 0.$ | $\rightarrow \Delta G^\circ = -n F E^\circ$ | } Go between $E^\circ, \Delta G^\circ,$ and K
➔ Expect to do this |
| 2) Equilibrium: $Q = K, \Delta G = 0, E = 0.$ | $\rightarrow E^\circ = \frac{RT}{nF} \ln K$ | |

3) For all other conditions just use the Nernst equation. Several flavors but the first will always work.

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad \underbrace{E = E^\circ - \frac{RT}{nF} \ln(10) \log Q = E^\circ - \frac{RT}{nF} 2.303 \log Q}_{\text{If you don't like natural logarithms}} \quad \underbrace{E = E^\circ - \frac{0.059 \text{ Volts}}{n} \log Q}_{\text{At } T = 298 \text{ K only}}$$

- ➔ Typical problems: Determine E given all concentrations; determine missing concentration given E .