

Oxidation Numbers

- Refers to the charge on a chemical species
 - Ion – charge on ion
 - Atom – charge = 0
 - Polyatomic ion or compound – what the charge on *each* individual atom would be if it were an ion.

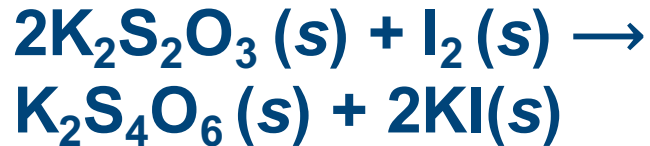
Determining the charge for an ion

- For Groups IA-VIIIA the “usual” charge of an ion is based on its position
 - +1, +2, +3, +/-4, -3, -2, -1, 0
- For Group B (transition metals), use the Stock system
 - Roman numerals represent charges
 - Ex. Fe(II) ion = Fe^{2+}

“Rules” for oxidation numbers

- The sum of the oxidation numbers must equal the overall charge on the species (0 if neutral)
- Can usually use the groups of the periodic table to determine oxidation numbers for ions.
 - IA = +1, IIA = +2, IIIA = +3, IVA = +/-4, VA = -3, VIA = -2, VIIA = -1, VIIIA = 0.
- F is usually -1 (as are most halogens)
- H is usually +1 (except if combined with IA or IIA metal to form a hydride, in which case it will be -1)
- O is usually -2 (except if combined to form a peroxide (-1) or superoxide (-1/2))

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in the following equation:



1 IA										18 VIIIA									
1 H Hydrogen 1.008																		2 He Helium 4.002602	
3 Li Lithium 6.94	4 Be Beryllium 9.0121831																		
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305																		
State of matter (color of name) GAS LIQUID SOLID UNKNOWN		Subcategory in the metal-metalloid-nonmetal trend (color of background)																	
		Alkaline metal		Alkaline earth metal		Metalloid		Noble gas											
		Lanthanide		Actinide		Polyatomic nonmetal		Unknown chemical properties											
		Transition metal		Post-transition metal		Diatomic nonmetal													
Atomic Number → 1 Name → Hydrogen Symbol → H Atomic Weight → 1.008																			
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.750	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293		
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)	
87 Fr Francium (223)	88 Ra Radium (226)	89 - 103 Actinoids		104 Rf Rutherfordium (267)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (269)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (285)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)	

57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.0377	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

Redox reactions (an introduction)

- Redox reactions involve a simultaneous *reduction* and *oxidation*.
- Reduction – gain of electrons
 - oxidation number is decreased
- Oxidation – loss of electrons
 - Oxidation number is increased
- Disproportionation – redox reaction where the same species is both oxidized and reduced.
 - Ex. $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

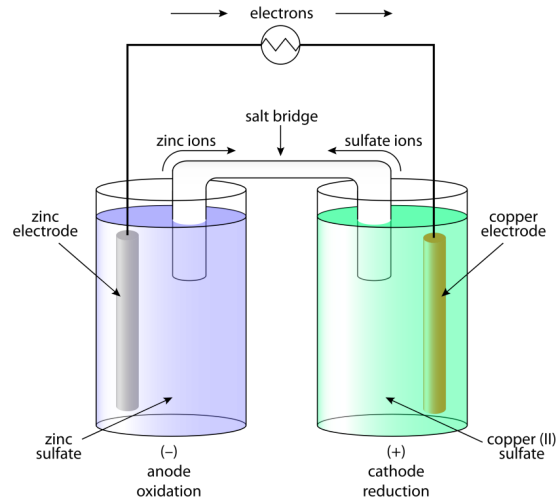
Agents

- Reducing agent – causes a reduction
 - Gets oxidized
 - Usually metal
- Oxidizing agent – causes an oxidation
 - Gets reduced
 - Usually nonmetal

Types of electrochemical cells

Galvanic/Voltaic

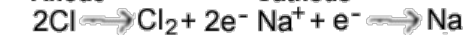
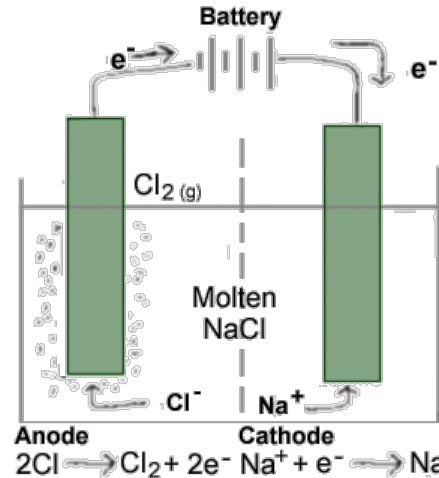
- Produces electricity as a result of a spontaneous reaction



https://en.wikipedia.org/wiki/Galvanic_cell

Electrolytic/Battery

- Electricity is used to carry out a non-spontaneous reaction



<https://www.chem.tamu.edu/class/major/s/tutorialnotefiles/electrolytic.htm>

Standard potentials

- Since all electrochemical cells contain two electrodes, we can only measure the overall potential, which is the combination of the potential of the anode and that of the cathode.
- We can define a reference electrode to have a voltage of 0 V so that all values are relative to this number.
- The standard hydrogen electrode (SHE) is $\text{H}_2(\text{g})$ adsorbed on Pt, an inert metal:



The Nernst equation

- We know that $\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \ln Q$
- Dividing both sides by $-vF$, and using the equation we just derived: $E = -\frac{\Delta G_{rxn}^{\circ}}{vF} - \frac{RT}{vF} \ln Q$
- The 1st term represents the standard emf E° : $\Delta G_{rxn}^{\circ} = -vFE^{\circ}$
- This leaves us with the Nernst equation:

$$E = E^{\circ} - \frac{RT}{vF} \ln Q$$

- At a temperature of 25°C, $RT/F=25.7$ mV, so we can write the equation as:

$$E = E^{\circ} - \frac{25.7 \text{ mV}}{v} \ln Q$$

- Sometimes it is also kept in SI units but with a common logarithm:

$$E = E^{\circ} - \frac{0.0591}{v} \log Q$$

The Nernst equation

- At equilibrium, $Q=K$, $\Delta G_{\text{rxn}}=0$ and so $E=0$. Substituting this into the Nernst equation gives:

$$0 = E^\circ - \frac{RT}{vF} \ln K$$

- Rearranging a bit,

$$\ln K = \frac{vFE^\circ}{RT}$$

- This means that we can calculate equilibrium constants by measuring cell potentials.
- This has important practical consequences, as a typical voltmeter can easily measure fractions of a volt, which translate into enormous K 's (10^{30} or greater) which can't be determined otherwise (at least not easily)

Final thoughts on electrochemical cells

- Note that for a spontaneous reaction, $\Delta G < 0$ and so $E > 0$. That is, we can determine which half reaction occurs at the anode and which occurs at the cathode by looking at the corresponding potentials and rewriting them (remember we always have to flip one since they are both given as reductions!) so that the overall voltage is positive.

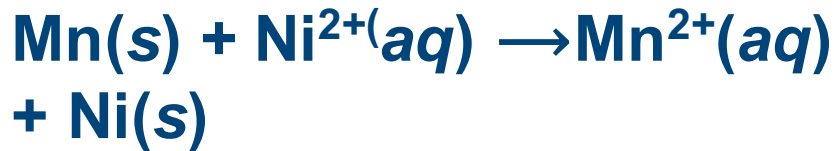
**For the reaction listed,
determine its standard cell
potential at 25 °C and
whether the reaction is
spontaneous at standard
conditions.**



$$E^{\circ} = -0.257 \text{ V}$$



$$E^{\circ} = -1.185 \text{ V}$$



Quantitative electrolysis

- The quantity of reactant consumed (or product formed) during electrolysis can be calculated using stoichiometry
 - Related to molar mass of substance ($n = m/M$)
 - Related to number of electrons transferred in the electrode reaction (ν)
 - Related to the quantity of electric charge used ($Q = It$)

Example

- We can use electrolysis to determine the gold content of a sample. The sample is dissolved, and all the gold is converted to $\text{Au}^{3+}(\text{aq})$, which is then reduced back to $\text{Au}(\text{s})$ on an electrode of known mass. What mass of gold will be deposited at the cathode in 1.00 hour by a current of 1.50 A?

Solution

- First find the total charge:

$$Q = (1.5 A)(1.00 \text{ hour}) \left[\frac{1 \frac{C}{s}}{1 A} \right] \left[\frac{60 \text{ min}}{1 \text{ hour}} \right] \left[\frac{60 s}{1 \text{ min}} \right] = 5.40 * 10^3 C$$

- Next find the moles of e⁻s transferred:

$$v = \frac{Q}{F} = \frac{5.40 * 10^3 C}{96485 C/mol} = 0.0560 \text{ mol } e^-$$

Solution

- Use stoichiometry to determine the moles of Au produced:

$$n = 0.0560 \text{ mol } e^{-} \left(\frac{1 \text{ mol Au}}{3 \text{ mol } e^{-}} \right) = 0.0187 \text{ mol Au}$$

- Finally calculate the mass of Au deposited:

$$m = n * M = 0.0187 \text{ mol Au} \left(\frac{197.0 \text{ g}}{1 \text{ mol Au}} \right) = 3.68 \text{ g Au}$$