Rules for Assigning Oxidation States

Note: Any contradiction in rules is resolved by a rule that is higher on the list.

Oxidation State is assigned <u>per atom</u>.

If the species is an ionic compound and doesn't show a charge, it is frequently useful and sometimes necessary to use the charge of one ion to predict the charge of the other ion and then if needed, apply the rules below separately.

1. The oxidation state of any atom in a free (uncombined) element is 0. This includes diatomic elements.

2. The total of the oxidation states of all the atoms in a neutral molecule or formula unit is 0. For an ion, this total is equal to the charge on the ion, both in magnitude and sign.

3. Monovalent metal cations will have an oxidation state equal to their normal charge, i.e., alkali metals (group IA) are +1, alkaline earth metals (IIA) are +2, aluminum is +3, silver is +1, zinc is +2, etc.

4. In its compounds the oxidation state of hydrogen is +1; that of fluorine is -1.

5. In its compounds oxygen has an oxidation state of -2.

6. In their binary compounds with metals, the elements of group VIIA have an oxidation state of -1; those of group VIA, -2; and those of group VA, -3.

Example 1: H_2O Apply Rule 4, so **H=+1**.
Apply Rule 2, so **O=-2** since 2×(+1) + (-2) = 0

Example 2: H_2O_2 Apply Rule 4, so **H=+1**
Apply Rule 2, so **O=-1** since 2×(+1) + 2×(-1) = 0

Example 3: NaH First Apply Rule 3 since it is higher than Rule 4, so **Na=+1**
Rule 2 contradicts Rule 3, so Apply Rule 2, so **H=-1** since +1 + (-1) = 0

Example 5: $KMnO_4$ This is ionic with multiple atoms, so separate into ions: K^+ + MnO_4^-
Na^+ Apply Rule 3 so **K=+1**
MnO_4^- Apply Rule 5, so **O=-2**
Apply Rule 2, so **Mn=+7** since (+7) + 4×(-2) = -1

- Element by itself : 0
- Group 1A : always +1
- Group 2A : always +2
- Halogens : usually −1, positive with oxygen
- Monatomic ion: ion charge
- $\boxed{H}$: +1 with nonmetals, −1 with metals
- $\boxed{O}$: usually −2, −1 in peroxide (H_2O_2)
- $\boxed{F}$: always −1

Sum of ON's for a <u>neutral</u> compound = 0
Sum of ON's for a polyatomic <u>ion</u> = ion charge

Half-Reaction Method for Balancing Redox Equations in Acid/Base Media

1. Split the equation into two half-reaction equations (use oxidation numbers, if needed).

2. Balance redox atoms.

3. Balance all other atoms or ions (except H and O). These atoms must have same ox # on both sides of half-reactions. Ions must have same charge on both sides of the half-reactions. These are usually spectator ions.

4. Balance O by adding H_2O on opposite side.

5. Balance H by adding H^+ on opposite side.

7. Balance total charge on each side by placing the appropriate number of electrons on the more positive (less negative) side.

8. If needed, multiply half-reactions by appropriate factors to make electrons gained and lost equal. Determine *n* if needed for Nernst equation.

9. Add half-reactions to get overall reaction. Simplify if needed (must adjust *n* for Nernst).

10. If BASIC, add OH^- (equal in number to H^+) to both sides. Combine H^+/OH^- to form H_2O Cancel any H_2O's appearing on both sides of half-reactions. Simplify if needed (must adjust *n* for Nernst).

Arrow Method for Balancing Simple Redox Equations

Note: If equation contains hydrogen and/or oxygen on one side and not the other, it is <u>not a simple redox equation</u>.

1. Assign oxidation numbers to all the atoms in the equation.

2. Draw arrows connecting species containing atoms which have changed oxidation state. If this is a disproportionation reaction, “clone” the reactant for figuring purposes, then combine and simplify at the end.

3. Compute the total number of electrons lost or gained for both the oxidized and reduced REACTANTS. (Be sure to balance the corresponding redox <u>product</u> atoms.)

   # electrons = Coefficient x Subscript x ($OxSt_{react}$ - $OxSt_{prod}$)
   Note: + = gain; - = loss

4. Make the total loss and gain of electrons the same by multiplying coefficients by appropriate factors and, if needed, determine *n* (the number of electrons transferred).

5. Balance all other atoms. These atoms must have same ox # on both sides of half-reactions and were neither oxidized nor reduced. These are usually spectator ions/atoms.