

When working with ionic substances, determine oxidation states separately in the two ions.

1) All atoms in a pure element have oxidation state 0.

This is true whatever the state of the element, whether it be a monatomic, diatomic, or polyatomic gas, a liquid, a metallic solid or a nonmetallic solid, or a polyatomic molecule.

Examples: Xe(g); N₂(g); O₂(g); O₃(g); Br₂(ℓ); Hg(ℓ); Fe(s); K(s); B(s); C(s); I₂(s); P₄(s); S₈(s).

2) The oxidation state of the element in a monatomic ion is equal to the charge on the ion.

This holds both for separated ions in aqueous solution and for ions bound in solid salts.

Examples: Cu⁺, +1; Cu²⁺, +2; Fe²⁺, +2; Fe³⁺, +3; Br⁻, -1; O²⁻, -2; S²⁻, -2; N³⁻, -3.

Some metals form only one common ion, have only one significant positive oxidation state.

Examples: Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺; Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺; Al³⁺; Ni²⁺; Zn²⁺, Cd²⁺; Ag⁺; Pb²⁺.

3) The oxidation state of hydrogen, H, in any ion or molecule (other than H₂) is +1, with two exceptions:

(i) The oxidation state of hydrogen is -1 in metal hydrides, for example, NaH, CaH₂, LiAlH₄. Metal hydrides are ionic compounds, in which the metal ions are in their characteristic positive oxidation states. For instance, solid NaH consists of Na⁺ ions and H⁻ ions.

(ii) The oxidation state of hydrogen is taken as -1 when hydrogen is covalently bonded to the semimetal boron, B, in (a) the neutral boron hydrides, for example, B₄H₁₀, B₅H₉, B₁₀H₁₄, and (b) the borohydride anions, for example, BH₄⁻, B₁₂H₁₂²⁻.

4) The oxidation state of oxygen, O, in any ion or molecule (other than O₂ or O₃) is -2, with three exceptions:

(i) The covalent molecule OF₂, in which the oxidation state of O is +2 because the oxidation state of F is always -1 (except in F₂). F is the only element more electronegative than O.

(ii) Peroxides, for example, H₂O₂, Na₂O₂, BaO₂, in which the oxidation state of O is -1. Peroxides can be covalent or ionic. Peroxide ion, O₂²⁻, has an O-O covalent single bond.

(iii) Superoxides, for example, KO₂, RbO₂, CsO₂, in which the oxidation state of O is -½. Superoxide ion, O₂⁻, has an O-O covalent single bond.

5) a. In all covalently bonded molecules or ions that do not contain hydrogen or oxygen, the more electronegative element is assigned its common negative oxidation state: -3 for N or P; -2 for S, Se, or Te; -1 for F, Cl, Br, I.

The more electronegative element is to the right or straight above in the periodic table.

Examples: In BN, the oxidation states are B +3, N -3; in CS₂, they are C +4, S -2;

in ICl₃, they are I +3, Cl -1; in PBr₃, they are P +3, Br -1; in PF₆⁻, they are P +5, F -1.

b. If the molecule or ion does contain H and/or O as well as several other elements, assign +1 to H, assign -2 to O, and assign the most common negative oxidation state to the most electronegative other element, in order to assign the remaining oxidation state.

Examples: HCN: H +1, N -3, C +2; HPO₄²⁻: H +1, O -2, P +5; POCl₃: O -2, Cl -1, P +5.

6) The sum of all the oxidation numbers must equal the total charge on an ion or molecule, namely, the ionic charge for an ion, or zero for a neutral molecule.

Examples: HPO₄²⁻: H +1, O -2, P +5; MnO₄⁻: O -2, Mn +7; SO₂: O -2, S +4.

Remember that assigning oxidation states does not imply that any atoms are present as ions within a covalently bonded molecule or polyatomic ion. In covalently bonded species, oxidation numbers are simply one convenient formal bookkeeping convention to keep track of the bonding electrons and the electrons transferred. Formal oxidation states can even be fractional.

BALANCING OXIDATION-REDUCTION REACTIONS IN AQUEOUS SOLUTION

Recommended single procedure that works for both acidic and basic solutions

I. Write balanced **half-reactions** for the oxidation and the reduction, following the steps below.

For each half-reaction, initially written in skeletal form:

1. Determine the **oxidation states** of the element that is being oxidized or reduced, in the form in which it appears as a reactant and in the form in which it appears as a product.
2. Balance the **number of atoms** of the element being oxidized or reduced.
3. Calculate the total **number of electrons** lost or gained in the half-reaction, and add that number of electrons to the correct side of the half-reaction.

Multiply the change in oxidation state by the total number of atoms of the element being oxidized or reduced; this number of electrons is transferred for each unit of half-reaction. Add that number of electrons to the right side of the half-reaction for an oxidation (loss of electrons, increase in oxidation state) or to the left side of the half-reaction for a reduction (gain of electrons, decrease in oxidation state).

4. Calculate the net **charge**, including the added electrons, on each side of the half-reaction. At this point, in general, the net charge on each side of the half-reaction will be different.
 - (a) If the reaction is occurring in an **acidic** or in a **neutral** solution, balance the net charge, including electrons, by adding $\text{H}^+(\text{aq})$ ions [or $\text{H}_3\text{O}^+(\text{aq})$ ions, if you prefer] to one side.
 - (b) If the oxidation-reduction reaction is occurring in **basic** solution balance the net charge, including electrons, by adding $\text{OH}^-(\text{aq})$ ions to one side.
5. Balance the total number of **O atoms** on each side of the half-reaction by adding H_2O to one side. (This step will simultaneously balance the number of H atoms on each side.)
6. The half-reaction should now be complete and balanced. Before proceeding any further:
 - (a) Check that the numbers of atoms of every element are the same on each side.
 - (b) Check that the total net charge is the same on each side of the half-reaction.If everything is not in balance, go back to the beginning and find the error.

II. **Combine** the two half-reactions to yield the net overall oxidation-reduction reaction equation.

1. Multiply each half-reaction by an appropriate integer such that the total number of electrons **lost** in the oxidation equals the total number of electrons **gained** in the reduction.
2. Add the multiplied amounts of the two half-reactions together, and then cancel the equal numbers of electrons that now appear on each side of the net oxidation-reduction equation. **No electrons should appear in any overall balanced oxidation-reduction equation.**
3. Check to see if H^+ , or OH^- , or H_2O appears on both sides of the equation. If so, **simplify** so that any H^+ , or OH^- , or H_2O that remains represents the net change in that substance, and appears on only **one side** of the overall net oxidation-reduction equation.
4. The overall oxidation-reduction reaction should now be complete and balanced. Test this:
 - (a) Check that the numbers of atoms of every element are the same on each side.
 - (b) Check that the total net charge is the same on each side of the overall equation.