

3.3: Polyatomic ions and their compounds

Polyatomic ions

Polyatomic ions are molecular ions composed of two or more atoms bonded by covalent bonds and acting as a single unit, but unlike molecules, they have a net charge on them.

The examples include cations like ammonium ion (NH_4^+), and hydronium ion (H_3O^+); and anions like hydroxide ion (OH^-), and cyanide ion (CN^-). Usually, the name of polyatomic cations ends with -ium, and the name of polyatomic anions end with -ide, except for oxyanions that have separate rules for their nomenclature.

Oxyanion

The oxyanions are oxides of nonmetals that are molecular ions. Examples include carbonate (CO_3^{2-}), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}). The following guidelines will help remember the names and charges of oxyanions in most cases.

📌 Oxyanions having elements from groups 14, 15, and 16

1. the 2nd-row elements C, and N have three oxygen, and 3-row elements P, and S have four oxygen, i.e., one oxygen more than the row number,
2. the name of the polyatomic anion is the name of the atom other than oxygen with the last syllable replaced with -ate, and
3. the charge on these oxyanions equals the number of valence electrons on the non-oxygen atom minus twice the number of oxygen atoms. For example: in (PO_4^{3-}), phosphorous has 5 valence electrons and there are 4 oxygen atoms, so the charge = valence electrons in the central atom - 2 x number of oxygen atoms = $5 - (2 \times 4) = -3$; in (SO_4^{2-}), sulfur has 6 valence electrons and there are 4 oxygen atoms, so the charge = $6 - (2 \times 4) = -2$; in (CO_3^{2-}), carbon has 4 valence electrons and there are 3 oxygen atoms, so the charge = $4 - (2 \times 3) = -2$; and in (NO_3^-), nitrogen 6 valence electrons and there are 3 oxygen atoms, so the charge = $5 - (2 \times 3) = -1$.
4. There is a 2nd set of oxyanions of the elements mentioned above with one less oxygen but the same charge and the last syllable of the name changed from -ate to -ite. For example: (NO_3^-) is nitrate and (NO_2^-) is nitrite; (PO_4^{3-}) is phosphate and (PO_3^{3-}) is phosphite; and (SO_4^{2-}) sulfate and (SO_3^{2-}) is sulfite.

📌 Oxyanions of halogens

Oxyanions of chlorine, bromine, and iodine are also common oxyanions with the following in common.

1. They have -1 charge,
2. a halogen with four oxygen is named by adding prefix "per-" to the name of the halogen with last syllable replaced with -ate, for example; (ClO_4^-) is perchlorate, (BrO_4^-) is perbromate, and (IO_4^-) is periodate.
3. a halogen with three oxygen is named as name of the halogen with last syllable replaced with -ate, for example; (ClO_3^-) is chlorate, (BrO_3^-) is bromate, and (IO_3^-) is iodate,
4. a halogen with two oxygen is named as name of the halogen with last syllable replaced with -ite; for example, (ClO_2^-) is chlorite, (BrO_2^-) is bromite, and (IO_2^-) is iodite,
5. a halogen with one oxygen is named by adding prefix "hypo-" to the name of the halogen with last syllable replaced with -ite; for example, (ClO^-) is hypochlorite, (BrO^-) is hypobromite, and (IO^-) is hypoiodite.

📌 Acids of oxyanions

Oxyanions are acids when their charge is neutralized with protons (H^+). Names of the acids are the names of oxyanions with -ate replaced with -ic acid and -ite replaced with -ous acid. For example: (HNO_3) is nitric acid and (HNO_2) is nitrous acid; (H_3PO_4) is phosphoric acid and (H_3PO_3) is phosphorous acid; and (H_2SO_4) sulfuric acid and (H_2SO_3) is sulfurous acid.

The prefixes "per-" and "hypo-" in the cases of oxyanions of halogens remain in the acid name. For example: (HClO_4) is perchloric acid; (HClO_3) is chloric acid; (HClO_2) is chlorous acid; and (HClO) is hypochlorous acid.

Oxyanions with one proton attached but charge one then not fully neutralized, i.e., they are still polyatomic anion are named beginning with hydrogen and ending with the name of the oxyanion. For example: (HSO_4^-) is hydrogen sulfate; (HSO_3^-) is

hydrogen sulfite; and (HPO_4^{2-}) is hydrogen phosphate.

Oxyanions with two protons attached but charge one them not fully neutralized, i.e., they are still polyatomic anion are named beginning with dihydrogen and ending with the name of the oxyanion. For example, $(\text{H}_2\text{PO}_4^-)$ is dihydrogen phosphate

Two oxyanions containing a transition metal as the central atom in common use as reagents are in chemistry are chromate (CrO_4^{2-}) and permanganate (MnO_4^-). Table 3.3.1 lists the formulas and names of some of the common polyatomic ions.

Table 1: Names of some of the common polyatomic ions

Formula	Name	Formula	Name
(NH_4^+)	Ammonium	(MnO_4^-)	Permanganate
(H_3O^+)	Hydronium	(BrO_4^-)	Perbromate
(HO^-)	Hydioxide	(IO_4^-)	Periodate
(CN^-)	Cynide	(CrO_4^{2-})	Chromate
(CO_3^{2-})	Carbonate	(CO_2^{2-})	Carbonite
(NO_3^-)	Nitrate	(NO_2^-)	Nitrite
(PO_4^{3-})	Phosphate	(PO_3^{3-})	Phosphite
(SO_4^{2-})	Sulfate	(SO_3^{2-})	Sulfite
(HCO_3^-)	Hydrogen carbonate	(ClO_4^-)	Perchlorate
(HSO_4^-)	Hydrogne sulfate	(ClO_3^-)	Chlorate
(HPO_4^{2-})	Hydrogenphosphate	(ClO_2^-)	Chlorite
$(\text{H}_2\text{PO}_4^-)$	Dihydrogenphosphate	(ClO^-)	Hypochlorite

Names of compounds containing polyatomic ions

Rules for naming ionic compounds containing polyatomic ions are the same as binary ionic compounds. That is, write the name of the cation followed by the name of the anion. For cations with variable charge, keep the roman numeral in the compound's name. For example, NaNO_3 is sodium nitrate, CaCO_3 is calcium carbonate, FeCO_3 is iron(II) carbonate, NH_4Cl is ammonium chloride.

Writing formulae of compounds containing polyatomic ions

The polyatomic ion acts as a single unit, i.e., they are molecular ions. The writing formula of compounds containing polyatomic ions is the same as writing the formula of a binary ionic compound, except that the polyatomic ions must remain intact as a unit. If a subscript is needed for the anion, place the polyatomic ion within small brackets and write the subscript outside the bracket. Just like the subscript to the right of the monoatomic anion tells how many atoms of the anions are there, the subscript to the right of the small bracket around a polyatomic anion tells how many polyatomic anions are there in the compound. For example, iron(III) nitrate is $\text{Fe}(\text{NO}_3)_3$; sodium carbonate is Na_2CO_3 ; ammonium phosphate is $(\text{NH}_4)_3\text{PO}_4$; potassium permanganate is KMnO_4 ; and calcium phosphate is $\text{Ca}_3(\text{PO}_4)_2$. Note that in $\text{Fe}(\text{NO}_3)_3$, there are three nitrate ions, i.e., one iron atom, three nitrogen atoms, and nine oxygen atoms, in the formula unit of the compound.

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