Rules for assigning Oxidation Numbers

(1) always zero in the pure element, eg, H-H, Cl-Cl, Na

(2) equal to the charge on a monatomic ion
Na^+ +1 Ba^{2+} +2 Cl^- −1 etc.

(3) in a neutral molecule, the total must = 0
H—Br (+1) + (−1) = 0 PBr_5 P(+5) + 5Br(−1) = 0

(4) in a complex ion, the total must = charge on ion
NH_4^+ (−3) + 4(+1) = +1 BF_4^- (+3) + 4(−1) = −1
ClO_4^- (+7) + 4(−2) = −1

(5) priority rules based on the electronegativity scale are used in assigning O.N.'s in a compound
  (a) fluorine is always −1
  (b) group I metals (Na, K, etc.) always +1
  (c) group II metals (Ca, Mg, etc.) always +2
  (d) H is always +1 except when combined with a metal to form a hydride e.g LiH is $[Li^+]$ $[H^-]$ H is -1
  (e) O is always −2 except when combined with fluorine e.g. OF_2, where O is +2 (F is more electronegative and -1)
  OR in peroxides, which contain the O−O bond
  e.g H—O—O—H hydrogen peroxide, where O is −1.
  Na_2O_2 is 2 Na^+ $[O - O]^{2-}$ O is −1
  (f) other halogens (Group VII) are always −1, except when combined with fluorine or oxygen
  BrF_5 Br is + Cl_2O Cl is +

(6) to assign oxidation numbers to all carbon atoms in organic molecules, two further rules must be added to those given above:

i) one carbon atom bonded to another is ignored in calculations of oxidation numbers.

ii) when a C atom is bonded to a heteroatom such as O or N, the oxidation number assigned to O or N is divided equally among each of the atoms bonded to them. Thus the C atom in CH_3OH has an oxidation number of -2 because each H is +1 and the O contributes a -1 portion of its -2 oxidation number to each of the attached H and C atoms.