

Counting rules

Two methods of electron counting are used and both give the same result.

- The neutral counting approach assumes the molecule or fragment being studied consists of purely covalent bonds. It was popularized by [Malcolm Green](#) along with the L and X ligand notation.^{[2][3]} It is usually considered easier especially for low-valent transition metals.^[citation needed]
- The "ionic counting" approach assumes purely ionic bonds between atoms. One can check one's calculation by employing both approaches.

It is important, though, to be aware that most chemical species exist between the purely covalent and ionic extremes.

Neutral counting

- This method begins with locating the central atom on the periodic table and determining the number of its valence electrons. One counts valence electrons for main group elements differently from transition metals.
 - E.g. in period 2: B, C, N, O, and F have 3, 4, 5, 6, and 7 valence electrons, respectively.
 - E.g. in period 4: K, Ca, Sc, Ti, V, Cr, Fe, Ni have 1, 2, 3, 4, 5, 6, 8, 10 valence electrons respectively.
- One is added for every [halide](#) or other anionic ligand which binds to the central atom through a sigma bond.
- Two is added for every lone pair bonding to the metal (e.g. each Lewis base binds with a lone pair). Unsaturated hydrocarbons such as alkenes and alkynes are considered Lewis bases. Similarly Lewis and Bronsted acids (protons) contribute nothing.
- One is added for each homoelement bond.
- One is added for each negative charge, and one is subtracted for each positive charge.

Ionic counting

- This method begins by calculating the number of electrons of the element, assuming an oxidation state

E.g. for a Fe^{2+} has 6 electrons

S^{2-} has 8 electrons

- Two is added for every [halide](#) or other anionic ligand which binds to the metal through a sigma bond.
 - Two is added for every lone pair bonding to the metal (e.g. each phosphine ligand can bind with a lone pair). Similarly Lewis and Bronsted acids (protons) contribute nothing.
 - For unsaturated ligands such as alkenes, one electron is added for each carbon atom binding to the metal.
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Electrons donated by common fragments [\[edit\]](#)

Ligand	Electrons contributed (neutral counting)	Electrons contributed (ionic counting)	Ionic equivalent
X (halide)	1	2	X^- ; X = F, Cl, Br, I
H	1	2	H^-
H	1	0	H^+
O	2	4	O^{2-}
N	3	6	N^{3-}
NR₃	2	2	NR ₃ ; R = H, alkyl, aryl
CR₂	2	4	CR ₂ ²⁻
Ethylene	2	2	C ₂ H ₄
cyclopentadienyl	5	6	C ₅ H ₅ ⁻
benzene	6	6	C ₆ H ₆

Examples

- CH_4 , for the central C

neutral counting: C contributes 4 electrons, each H radical contributes one each: $4 + 4 \times 1 = 8$ valence electrons

ionic counting: C^{4-} contributes 8 electrons, each proton contributes 0 each: $8 + 4 \times 0 = 8$ electrons.

Similar for H:

neutral counting: H contributes 1 electron, the C contributes 1 electron (the other 3 electrons of C are for the other 3 hydrogens in the molecule): $1 + 1 \times 1 = 2$ valence electrons.

ionic counting: H contributes 0 electrons (H^+), C^{4-} contributes 2 electrons (per H), $0 + 1 \times 2 = 2$ valence electrons

conclusion: Methane follows the octet-rule for carbon, and the duet rule for hydrogen, and hence is expected to be a stable molecule (as we see from daily life)

- H_2S , for the central S

neutral counting: S contributes 6 electrons, each hydrogen radical contributes one each: $6 + 2 \times 1 = 8$ valence electrons

ionic counting: S^{2-} contributes 8 electrons, each proton contributes 0: $8 + 2 \times 0 = 8$ valence electrons

conclusion: with an octet electron count (on sulfur), we can anticipate that H_2S would be pseudotetrahedral if one considers the two lone pairs.

- SCl_2 , for the central S

neutral counting: S contributes 6 electrons, each chlorine radical contributes one each: $6 + 2 \times 1 = 8$ valence electrons

ionic counting: S^{2+} contributes 4 electrons, each chloride anion contributes 2: $4 + 2 \times 2 = 8$ valence electrons

conclusion: see discussion for H_2S above. Both SCl_2 and H_2S follow the octet rule - the behavior of these molecules is however quite different.

- SF_6 , for the central S

neutral counting: S contributes 6 electrons, each fluorine radical contributes one each: $6 + 6 \times 1 = 12$ valence electrons

ionic counting: S^{6+} contributes 0 electrons, each fluoride anion contributes 2: $0 + 6 \times 2 = 12$ valence electrons

conclusion: ionic counting indicates a molecule lacking lone pairs of electrons, therefore its structure will be octahedral, as predicted by VSEPR. One might conclude that this molecule would be highly reactive - but the opposite is true: SF_6 is inert, and it is widely used in industry because of this property.

- TiCl_4 , for the central Ti

neutral counting: Ti contributes 4 electrons, each chlorine radical contributes one each: $4 + 4 \times 1 = 8$ valence electrons

ionic counting: Ti^{4+} contributes 0 electrons, each chloride anion contributes two each: $0 + 4 \times 2 = 8$ valence electrons

conclusion: Having only 8e (vs. 18 possible), we can anticipate that TiCl_4 will be a good Lewis acid. Indeed, it reacts (in some cases violently) with water, alcohols, ethers, amines.

- Ferrocene, $(C_5H_5)_2Fe$, for the central Fe:

neutral counting: Fe contributes 8 electrons, the 2 cyclopentadienyl-rings contribute 5 each: $8 + 2 \times 5 = 18$ electrons

ionic counting: Fe^{2+} contributes 6 electrons, the two aromatic cyclopentadienyl rings contribute 6 each: $6 + 2 \times 6 = 18$ valence electrons on iron.

conclusion: Ferrocene is expected to be an isolable compound.

These examples show the methods of electron counting, they are a *formalism*, and don't have anything to do with *real life* chemical transformations. Most of the 'fragments' mentioned above do **not** exist as such; they cannot be kept in a bottle: e.g. the neutral C, the tetraanionic C, the neutral Ti, and the tetracationic Ti are not *free* species, they are always bound to something, for neutral C, it is commonly found in graphite, charcoal, diamond (sharing electrons with the neighboring carbons), as for Ti which can be found as its metal (where it shares its electrons with neighboring Ti atoms), C^{4-} and Ti^{4+} 'exist' only with appropriate counterions (with which they probably share electrons). So these formalisms are only used to predict stabilities or properties of compounds