

radical (free radical)

A *molecular entity* such as $\cdot\text{CH}_3$, $\cdot\text{SnH}_3$, $\text{Cl}\cdot$ possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, in the ‘isolobal analogy’ the similarity between certain paramagnetic metal ions and radicals becomes apparent.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective ‘free’ in the general name of this type of *chemical species* and molecular entity, so that the term ‘free radical’ may in future be restricted to those radicals which do not form parts of radical pairs.

Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ - or π -radicals.

In the past, the term ‘radical’ was used to designate a *substituent group* bound to a molecular entity, as opposed to ‘free radical’, which nowadays is simply called radical. The bound entities may be called *groups* or substituents, but should no longer be called radicals.

See also *biradical*.

1994, 66, 1155; 1995, 67, 1362; see also 1990, 62, 2209