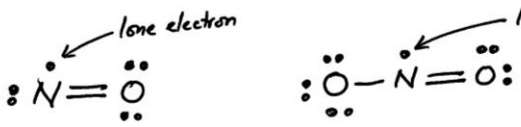
ODD NUMBER OF VALENCE ELECTRONS

(b) Odd Number of Valence Electrons

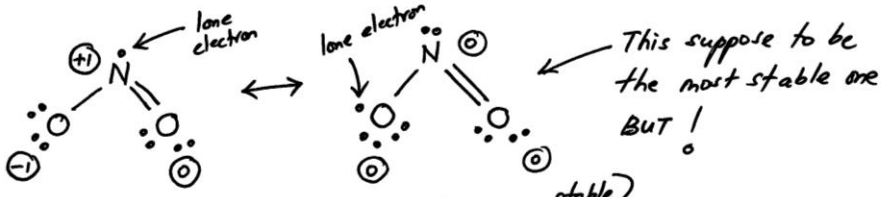
All the molecules have contained only pairs of valence electrons. However, there are a few stable molecules that have an odd number of valence electrons. Such species called FREE RADICALS, contain a lone (unpaired) electron, which makes them paramagnetic and extremely reactive.

For example : NO has $11e^-$ and NO_2 has $17e^-$

The most plausible Lewis structures for these molecules are :



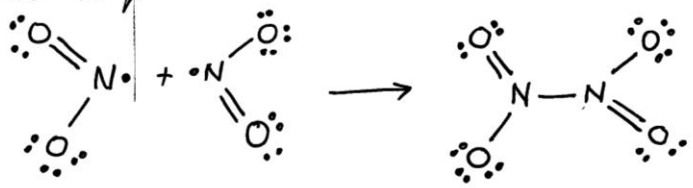
Check on resonance structure of NO_2.



Structure (I) Structure (II)

Structure II is more stable than structure I because structure II has no FC.

BUT, given the way NO_2 reacts; the two NO_2 molecule collide, the lone electron on N atom react with each other to pair their lone electrons to form N_2O_4.



Limitation of Formal Charge Rule!

Apparently, in this case, the lone electron spends most of its time on N, so formal charge, FC is not very useful for picking the most important resonance form.

When gaseous NO and NO_2 are released in vehicle exhaust, colorless NO react with O_2 in the air to form brown NO_2. NO_2 decomposes in the presence of sunlight to give NO and O, both of which are free radicals.

$$NO_2 \xrightarrow[\text{sunlight}]{h\nu} NO + O$$

O: free atom

$$O + O_2 \longrightarrow O_3 \text{ (ozone)}$$

O_3: air pollutant

$$NO_2 + NO_2 \xrightarrow{\text{dimerizes}} N_2O_4$$

As expected, NO and NO_2 are paramagnetic (odd number of electron).

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