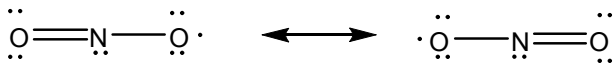
Exceptions to the NAS rule for Lewis structures:
Odd-Electron Cases

1) NO_2

N = 8 + 8*2 = 24
A = 5 + 6*2 = 17
S = N-A = 7

#bonds = S/2 = 7/2 = 3.5 ← not an integer, so NAS fails

To draw NO_2, let's try 3 bonds. Since each bond is 2 electrons, this will account for 6 electrons. With A=17, we will have 11 electrons left over, making 5 lone pairs and 1 odd electron.



(Note that there are other possibilities – the odd electron could have been placed on the other O or on the N (try drawing these!). But, those possibilities yield structures whose atoms have formal charges which are nonzero, and thus less favorable than these 2 resonance structures where all the formal charges are zero.)

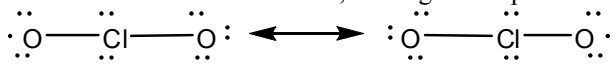
If you try 4 bonds for NO_2, that will account for 8 electrons since each bond is 2 electrons. With A=17, we will have 9 electrons left over, making 4 lone pairs and 1 odd electon. You will find that 4 lone pairs can be placed, but then there is no place for the last odd electron since each atom will already have a full octet. So, there cannot be four bonds in NO_2.

2) ClO_2

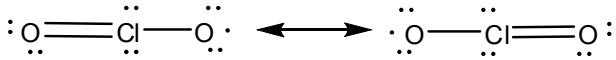
N = 8 + 8*2 = 24
A = 7 + 6*2 = 19
S = N-A = 5

#bonds = S/2 = 5/2 = 2.5 ← not an integer, so NAS fails

To draw ClO_2, let's try 2 bonds. Since each bond is 2 electrons, this will account for 4 electrons. With A=19, this will leave 15 electrons left over, making 7 lone pairs and 1 odd electron.



But, if we try 3 bonds…. Since each bond is 2 electrons, this will account for 6 electrons. With A=19, this will leave 13 electrons left over, making 6 lone pairs and 1 odd electron.



Since chlorine is in the 3rd row, it can expand its octet and this is okay. The formal charges in this case are all zero, indicating that this is the best possible set of resonance structures. (You could draw other forms – e.g. the odd electron on Cl instead of O – but this leads to nonzero formal charges and structures which are less favorable than the case drawn here.)