

## Year 2, Organic Chemistry, Chapter 01:

### Lewis Structures, Resonance and Delocalisation

*Resonance/Delocalisation/Stability/Conjugation and Hyperconjugation/the Inductive and Mesomeric Effects/Activation and Deactivation all involve the **sharing** of electrons. Sometimes electron density is **increased** (e.g. '+M' or '+I') and at other times electron density is **decreased** (e.g. '-M' or '-I'). **The phrases "electron donating" and "electron withdrawing" are technically incorrect. In molecular species electrons are neither donated nor withdrawn, they are SHARED and ELECTRON DENSITY is thereby altered.***

- This Chapter is easy to understand, but it takes you to higher ground than we explored last year. I do not want you to get lost in detail, therefore right from the outset let me tell you where we will finish up.

#### LEWIS STRUCTURES

- *A Lewis Structure is just a theoretical construct. It does **NOT** mean that that is how a molecule will actually exist in reality.*

#### RESONANCE

- "Resonance" is the situation where more than one Lewis structure can be constructed for a given species. In such a situation none of the Lewis structures will exist in real life and, instead, the electrons that are involved in all the alternative Lewis structures become delocalised and a compromise of the differing Lewis structures is what exists in reality.

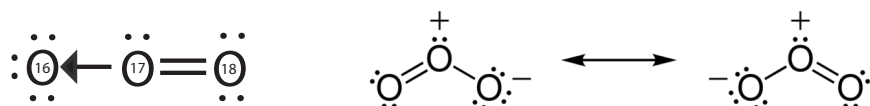
#### DELOCALISATION

- Resonance Lewis Structures do not depict the *actual* structure of any species. Chemists therefore asked themselves "How then can we explain the reality of these species?" and the answer that they came up with was "**Delocalisation**".
- I should like to stress here that the concept of "Delocalisation" is just a construct to try to explain why Resonance does not fit in with the observed facts about the species that we have been and shall be considering. In Science, we relentlessly pursue the explanation of **observed measurable reality** and we then have to put forward theory after theory (or one artificial construct after another) to try to explain the facts as we know them *at the time*. Delocalisation is a lovely elegant construct which will take us to Benzene and all the other Arenes (or as they are known, Aromatic species), *but it is just a construct*. There was a stage when Universities liked their Chemistry undergraduates to read a number of books before they went up to whichever College had accepted them, and one of the books used to be "Chemistry, Matter and the Universe" by Richard E. Dickerson and Irving Geis, and in it Dickerson & Geis say this at the beginning of Chapter 9

*"So far we have used two models for chemical bonding and molecular geometry: Lewis' electron pairs to explain how atoms are held together, and valence-shell electron-pair repulsion theory (VSEPR theory) to account for the geometry of bonding. These are simple ideas, but we have pushed them about as far as they will go. The cracks and seams in the bonding theory have begun to show through [and] the need for delocalized electrons is one example [,] and rather than trying to patch over the cracks, it is wiser to develop a better theory of bonding that will include the old ideas and permit us to go beyond them".*

and to that I would add that delocalisation is probably the last boundary to which non-Quantum Mechanical Chemistry can be pushed – so let us now look at Delocalisation.

- In Lewis Structures and in Resonance Structures, the electrons are shown as though they are fixed in certain places<sup>1</sup> e.g. in Ozone, at one moment in time there will be four electrons between “<sup>16</sup>O” and “<sup>17</sup>O”, and then a split-second later there will only be two electrons there – but if neither of these depictions is the case (and bond length measurements indicate something in between), then could the reality be something in between! Chemists thus came up with the construct that the real nature of the bond was that **some (or all) of the bonding electrons were spread over the WHOLE of the O<sub>3</sub> molecule and that they did not belong to any one atom in particular i.e. they were “delocalised”**. The structures of molecules therefore do NOT resonate/fluctuate between the different possible Resonance structures of the molecule, but instead they have a **single** structure which is a compromise of all the different possible Resonance structures.



- When we were studying metals last year we talked about the “sea of delocalised electrons” that there were in a piece of metal, and about the fact that no single atom in the piece of a metal kept a hold onto its own electron(s), but instead every atom shared in every delocalised electron in the piece of metal. Delocalisation here is much the same sort of concept (but with differences that we are going to explore in the Chapters that follow).
- That's it. That is all that we need to know about delocalisation for ‘A’ Level purposes. What we have now learnt about Resonance and the fact that in reality bond lengths do **NOT** keep fluctuating will very nicely allow us to discuss and to **understand** the nature of the Benzene ring when we come to it.

OK. I have now told you where we are going to finish up – so let us now cover the ground that we need to cover in order to get there.

<sup>1</sup> This is an extremely ham-fisted way of trying not to get bogged down in the complexities of Quantum Mechanics and Heisenberg's Principle of Uncertainty, and if you know a lot more about the subject than I do, then please forgive my amateurish phraseology. I am just a simple Chemist and not a Physicist.

- Welcome back. It is really good to see so many ‘old’ faces. If you have decided to do Second Year Chemistry, then it means that either you got the grades that you wanted and you now want to get ready to be admitted to do the degree of your choice at the University of your choice (and if so many congratulations – *and remember that you will have to submit all your applications in only a very few weeks from now*); or else, you did not get the grades that you wanted, and then over the Summer you realised that you had made a mistake, and now you want to put that right so that you *can* get admitted to the degree of your choice at the University of your choice. In that case, I offer my congratulations to you also. Remember what I said to you 12 months ago. **The ability to learn from one’s mistakes is the true hallmark of intelligence. Make lots and lots of mistakes when you are young – provided that you learn from your mistakes and then not repeat them!** You do not have the time to make the same mistakes as you made last year, so please go back to the “Introduction” to this book and re-read it. Read the bit on “How to Study” carefully and do what it says. You obviously have brains (otherwise you would not be doing ‘A’ Levels), and by being here you clearly want to make a success of your life (because you are *most* unlikely to be doing ‘A’ Level Chemistry for “fun”) – and I promise you that in the next few weeks (if you put your mind to it) you can catch up with the people who got it right first time round.
- You are now less than twelve months away from your first day at University! The six years that you have spent here must now seem just like six weeks or even just like six days! Make the most of your last few months here as a youth, and then I hope that you have a very happy and successful life hereafter as an adult!
- We are now in our second year of Organic Chemistry (or “Chains & Rings”) and as I told you last year, we are going to be dealing with matters that are much more complicated than First Year stuff. Up to now you have, by and large, been children and you were *taught* how to do things. When you leave here you will stop being children and you will enter the world as adults. Up to now you have been **taught**, but when you leave here you will have to **learn**. The difference is that being taught is a childish passive thing, whilst **learning is an adult self-regulatory activity**. I therefore want you to use this your last year at school to make that transition. Don't just sit there like primitive evolutionary sponges, but instead go out and develop your thirst for knowledge. Do **not** be satisfied with just hearing/reading what I and your other teachers tell you, but go out and read around your subjects. Develop your brain. How well you do in your life when you leave here will be heavily dependent on whether or not you have learnt how to use your brain to control all your activities. **You, and only you will determine how successful and happy a life you have hereafter. Use your brain and you should have a very happy and a very successful life.**
- Please remember that, last year, I told you that there is a big jump between GCSE work and ‘A’ Level work. This year you will see that exemplified, and then when you get to University, you will see the next big jump set in motion.
- Last year we learnt the basics of ‘A’ Level Chemistry, and this year we are now going to build on those foundations of Chemistry. The level of Organic Chemistry that we will encounter this year is a **great deal** more complex (to understand fully) than the stuff that we did last year, so let us start with an understanding of some of the things that will help make it easier to understand much of what you will have to master in the next few months.
- I am going to start with **Lewis Structures** because you need to understand Lewis Structures in order to understand **Resonance**, and you need to understand Resonance in order to *understand Delocalisation* – and you cannot understand anything about Benzene and other Arene (or Aromatic) rings unless you understand Delocalisation. (**Benzene** is an Arene ring, and a huge amount of Organic Chemistry in Medicine centres on Benzene and its derivatives.)
- Mind you, I have had students who have scored very high marks in their A2 Chemistry exams who did not bother to *understand* what they were doing. They just learnt everything off by heart. They were clever but **lazy** and I am absolutely certain that in later life they will not have done well,

because if you want to be good (or indeed excel) in your chosen field of endeavour, then you **do** have to *understand* what you are doing. I have total confidence in the gentleman who services my cars in Gerrards Cross – but I would **not** say the same of *some* of my students who have gone on to become doctors!<sup>2</sup>

## Lewis Structures

- Please remember what I told you last year about help with Lewis structures. Dr Wayne Breslyn of the University of Maryland has an absolutely outstanding set of videos on the Lewis structures of differing molecules, and you can start with his general explanation on <https://www.youtube.com/watch?v=1ZlnzyHahvo>, or you could type into your search engine “Wayne Breslyn, Lewis Structure, and then the name of the organic molecule in which you are interested, youtube” (where the name of the organic molecule is the one you are looking at e.g. “Carbon Monoxide”).
- When you were doing GCSE Chemistry (or GCSE Science) you learnt how to draw dot-and-cross diagrams, and in the Foundation Module in your first year in the Sixth Form I introduced you to bond-line diagrams, but I did not tell you much about the rules that govern the creation of such diagrams. These diagrams are very similar to Lewis structures, and I am therefore now going to set out a simplified set of rules to enable you to draw Lewis structures.<sup>3</sup>
- In what follows when I talk about “valence” electrons, please could you remember that for ‘A’ Level purposes (ignoring the Transition Metals), a **“valence” electron is an electron in the outermost shell of an atom that is available for bonding/reaction purposes** e.g. for atoms of the elements in Period 2, the elements in Group I have 1 valence electron/those in Group II have 2/those in Group III have 3/and so on. The Transition Metals are a different kettle of fish, but I am not going to talk about Transition Metals here because they are not part of *this* section of the A2 Syllabus. (They form part of the Inorganic Chemistry syllabus.)
- The following table shows the number of valence electrons for the initial elements in the Periodic Table.

Element	Number of valence electrons	
<sub>1</sub> H	1s <sup>1</sup>	1
<sub>2</sub> He	1s <sup>2</sup>	2
<sub>3</sub> Li	1s <sup>2</sup> , 2s <sup>1</sup>	1
<sub>4</sub> Be	1s <sup>2</sup> , 2s <sup>2</sup>	2
<sub>5</sub> B	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>1</sup>	3
<sub>6</sub> C	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>2</sup>	4
<sub>7</sub> N	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>3</sup>	5
<sub>8</sub> O	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>4</sup>	6
<sub>9</sub> F	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>5</sup>	7
<sub>10</sub> Ne	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>6</sup>	for ‘A’ Level purposes Neon does not react
<sub>11</sub> Na	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>6</sup> , 3s <sup>1</sup>	1
<sub>12</sub> Mg	1s <sup>2</sup> , 2s <sup>2</sup> 2p <sup>6</sup> , 3s <sup>2</sup>	2
..... and so on.		

<sup>2</sup> The thought of a doctor who does not know what she/he is doing is terrifying (but that is also true of a car mechanic/bus driver/airline pilot/nurse/whatever).

<sup>3</sup> The full set of rules is rather more complicated.

### Simplified rules for drawing Lewis structures for molecules (and uncomplicated ionic units)

- 1 Count up the number of valence electrons that there are for each atom (and this can be obtained by looking at the Periodic Table to see to which Group a particular atom belongs). If you are dealing with a negatively charged anion then add one extra electron for each negative charge on the species, and if you are dealing with a positively charged cation then subtract one electron for each positive charge on the species.

**NB You now have the total number of electrons, “X”, that you must account for.**

- 3 Identify the central atom – this will be the atom of the least electronegative element in the species, and it will usually be the first atom that is written in the formula of the species (e.g. Aluminium in  $\text{AlCl}_3$ /or Iron in  $\text{FeBr}_3$ /or Beryllium in  $\text{BeCl}_2$ /or whatever).

**NB Hydrogen is often written first in the name of a species (e.g.  $\text{H}_2\text{SO}_4$ ), but an H atom cannot be the central atom in a species.**

- 4 Draw in all the other atoms (often referred to as “terminal” or “peripheral” atoms) around that central atom.
  - 5 Draw a bond line (or a pair of electrons) between every peripheral atom and the central atom – and keep in mind that every bond line represents **two bonding electrons** (and sometimes the bond will be a **dative** bond).<sup>4</sup>
  - 6 Now draw in pairs of electrons on every peripheral atom to make four pairs (a complete octet) of electrons on **every peripheral atom in the species** (except for Hydrogen and Helium which can have only one pair of electrons to achieve stability).
  - 7 Now count up all the electrons that you have put into the Lewis structure so far (and remember that each bond-line represents **two electrons**) and let us call this number “Y”.
  - 8 If  $X > Y$ , then place the remaining electrons on the central atom in pairs (but sometimes you may have only one electron left over – and even that must go on the central atom).
  - 9 If the central atom now does not as yet have **8 electrons** around it, then move a lone pair of electrons from one of the peripheral atoms so that it now lies **between** that peripheral atom and the central atom. There was already a bond-line representing two electrons between the peripheral atom and the central atom, and you have just placed a second pair of electrons between them, **so there is now a double bond between the two atoms.**
  - 10 If you still do not have eight electrons on the central atom then repeat step 9. If this step needed to be executed (e.g. for a Cyanate, “ $\text{C}\equiv\text{N}$ ”) then there will now be a triple bond between the two atoms (*in a Cyanate there are three bonds between the C and the N atoms*).
- In a moment when you see how the rules are applied, you will realise how they work.
  - OK, I am going to stop there because I said that I was going to give you a **simplified** set of rules for drawing Lewis structures<sup>5</sup>, and we now have sufficient rules to draw the things that you encounter at ‘A’ Level.

---

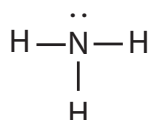
<sup>4</sup> It is permissible to use pairs of dots instead of bond lines in Lewis Structures. Dative bonds are not particularly important in Lewis Structures.

<sup>5</sup> I have not talked about formal charges as yet, and I do not want to do so for the moment.

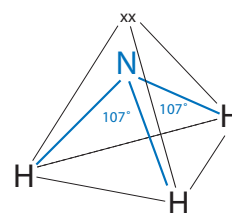
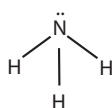
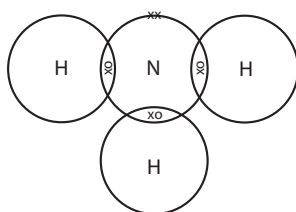
- Let us now draw some of the Lewis structures for species that you will encounter at 'A' Level<sup>6</sup> and, because it is just possible that you might also be asked something about (VSEPR) shapes in your Second Year exams (you learnt about VSEPR in your first year), let me also include the *shapes* of the species that I use for the Lewis Structures.
- Please remember that the examiners can and will test you on things that you learnt last year! Under the new exam rules in the 'A' Level exams you will be tested either directly or indirectly on everything that you have learnt in the last two years.*

### Ammonia NH<sub>3</sub>

- N has 5 valence electrons therefore  $1 \times 5 = 5$
- H has 1 valence electron therefore  $3 \times 1 = 3$
- There is no charge on NH<sub>3</sub> therefore  $X = 5 + 3 = 8$
- 6 electrons go between N and the three Hs.
- Put the remaining 2 electrons on the central atom.
- The resulting Lewis Structure is



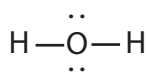
- or using dot-and-cross and VSEPR diagrams you would have



The "bond angle" is the angle between each H-N-H bond. Each of these THREE bond angles is 107°.

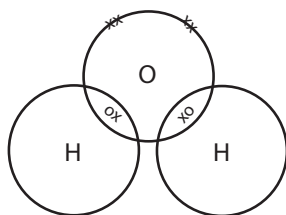
### Water H<sub>2</sub>O (NB H cannot be a central atom)

- O has 6 valence electrons therefore  $1 \times 6 = 6$
- H has 1 valence electron therefore  $2 \times 1 = 2$
- There is no charge on H<sub>2</sub>O therefore  $X = 6 + 2 = 8$
- 4 electrons go between O and the two Hs
- Put the remaining 4 electrons as 2 lone pairs on the central atom.
- The resulting Lewis Structure is

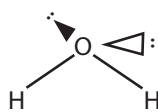


- and using dot-and-cross and VSEPR diagrams you would have

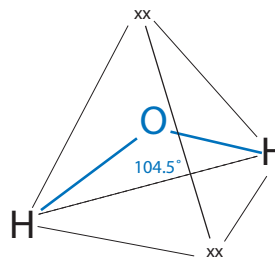
<sup>6</sup> At GCSE Level you will already have drawn simple molecules that do not have a central atom (e.g. H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>/ and the Halogens), but I am not going to go into more complicated species that have no central atom.



A water molecule has a THREE dimensional structure – a fact not conveyed by this diagram.



In theory, this diagram should show the 3D nature of the species.

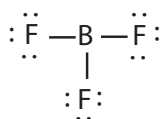


The "bond angle" is the angle in the H-O-H bond. The bond angle is 104.5°.

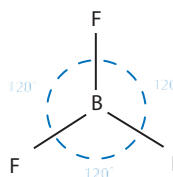
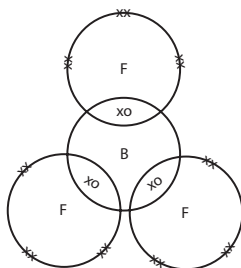
NB The bond angle in  $\text{NH}_3$  is  $107^\circ$ , in  $\text{CH}_4$  is approximately  $109.5^\circ$  (i.e. Ammonia **plus**  $2.5^\circ$ ), and in Water it is approximately  $104.5^\circ$  (Ammonia **minus**  $2.5^\circ$ ).

### Boron Trifluoride

- B has 3 valence electrons therefore  $1 \times 3 = 3$
- F has 7 valence electrons therefore  $3 \times 7 = 21$
- There is no charge on  $\text{BF}_3$  therefore  $X = 3 + 21 = 24$
- 6 electrons go between B and the three Fs.
- Complete the octet on each of the Fs (and that uses up another 18 electrons).
- That uses up all the 24 electrons.
- The resulting Lewis Structure is



- This clearly does not show you whether there are any dative bonds in the species (but there are none), and using dot-and-cross and VSEPR diagrams you would have



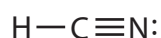
NB I hope that you remember that symmetrical species (even those with polarised bonds) cannot be polarised species – and very often it is the polarisation of a species that is responsible for its reactions (as we will see when we come to study the reactions of those species that react with Benzene).

- OK, let us do a couple of examples where you need to introduce multiple bonds into your Lewis structure.
- $\text{BF}_3$  has something called a “diminished octet”, and so does  $\text{AlCl}_3$  and so do many other molecules. However, I do not want to talk about diminished octets at this juncture. (Nor do I want to talk about “expanded octets”).

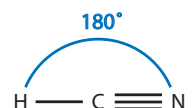
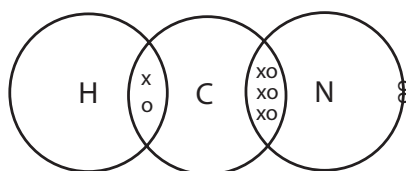
## HCN

and please remember that even though the molecule is written with an H as the first atom, H cannot be the central atom of a molecule.

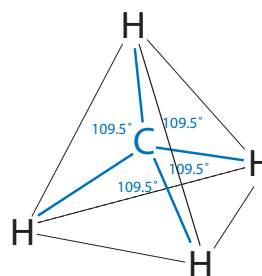
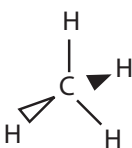
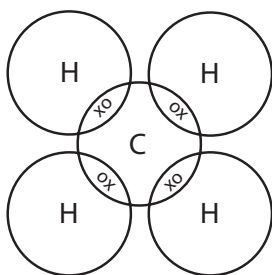
- C has 4 valence electrons therefore  $1 \times 4 = 4$
- N has 5 valence electrons therefore  $1 \times 5 = 5$
- H has 1 valence electron therefore  $1 \times 1 = 1$
- There is no charge on HCN therefore  $X = 4 + 5 + 1 = 10$
- 2 electrons go between H and C, and 2 electrons go between C and N. That leaves 6 electrons.
- 6 go onto N to complete the octet, and that uses up all the 10 electrons.
- There are only 4 electrons on the central atom, therefore move 2 (TWO) lone pairs of electrons on the N to the space between the N and the C (to now form 3 bonds between C and N), and that now leaves just one lone pair of electrons on the N.
- The resulting Lewis Structure is



and using dot-and-cross and VSEPR diagrams you would have



- There are no dative bonds in HCN.
- OK, could **you** do the Lewis structure for the non-polar molecule Methane  $\text{CH}_4$  (and it is very easy), and in the diagrams in the middle and on the right below I have tried to show Methane in 3-D.



The "bond angle" is the angle between each  $\text{H}-\text{C}-\text{H}$  bond. Every bond angle here is  $109.5^\circ$ .

- Before we tackle Resonance, it would help if we were to try to draw the Lewis structures (and let us also do the VSEPR diagrams) for  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^+$  and  $\text{HSO}_4^-$  (and the latter two species will be involved in the reactions of Benzene). That will open up the path to Resonance for us, and then we can talk about Delocalisation. Unfortunately, you cannot easily get from Lewis Structures to Benzene, so I will get to Benzene (and all the Arenes) via **Resonance and Delocalisation**.

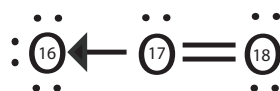


## Ozone, O<sub>3</sub>

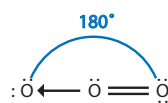
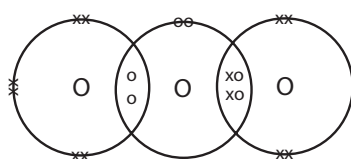
- There are three Oxygen atoms in O<sub>3</sub> therefore (by definition) the central atom has to be an O atom. You will remember from your First Year that the factor that defines an element is the number of **protons** in the nuclei of its atoms, and that some elements have atoms with differing numbers of neutrons in their nuclei (and this makes them all isotopes of that element). Oxygen (*on earth*) has the isotopes <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O – therefore for this exercise let us *totally unrealistically* say that (instead of having all three atoms of just one isotope) we have one atom of each isotope and that <sup>17</sup>O is the middle atom. That will make it nice and easy to identify the atom to which we are referring. (By the way, every isotope of Oxygen will still have 6 valence electrons.)

- <sup>16</sup>O has 6 valence electrons therefore  $1 \times 6 = 6$
- <sup>17</sup>O has 6 valence electrons therefore  $1 \times 6 = 6$  and let <sup>17</sup>O be the central atom
- <sup>18</sup>O has 6 valence electrons therefore  $1 \times 6 = 6$
- There is no charge on O<sub>3</sub> therefore  $X = 6 + 6 + 6 = 18$

- Draw a bond line between the central atom and each of the peripheral atoms (and that takes 4 electrons leaving 14 electrons).
- Complete the octet on the peripheral atoms (and that will take another 12 electrons leaving just 2 electrons).
- Place the remaining 2 electrons as a lone pair on the central atom.
- There is now a complete octet on each of the peripheral atoms, but only 6 electrons on the central atom, therefore move one lone pair of electrons from one of the peripheral atoms so that it now lies between itself and the central atom. This completes the octet on all the three atoms (and creates a double bond between one peripheral atom and the central atom).
- Can you remember that in your First Year I told you that you must always love and treat your children equally and that if you lend your son your car to take his girlfriend out on a Saturday night, then you **must** also lend your daughter the car to take her boyfriend out if she asks to borrow it, **and more importantly you must lend your daughter the car to take her girlfriend out if she is a lesbian**. Well, I hope that you can see that <sup>17</sup>O is not treating <sup>16</sup>O and <sup>18</sup>O *equally* in the Lewis Structure above. <sup>17</sup>O cannot treat <sup>16</sup>O and <sup>18</sup>O differently because to all intents and purposes the two are identical. <sup>17</sup>O cannot have a double bond between one peripheral atom and not the other, **and that is what Resonance is all about** – and we will come to it very soon, but for the moment let us draw the Lewis Structure that we have obtained by sticking to the rules. I hope that by now you are beginning to see why I am taking the route of Lewis Structures/Resonance/Delocalisation to get to Benzene and all the other Arenes. If not, everything will soon become clear.
- The resulting (unfair, because <sup>17</sup>O is treating <sup>16</sup>O and <sup>18</sup>O differently) Lewis Structure has a dative bond and also a double bond in it



and using dot-and-cross and VSEPR diagrams you would have



- In fact, even though the rules of Lewis structures make it look as though there has to be a dative bond (a “coordinate bond”), once you get into the minutiae of atomic and molecular orbitals, it turns out that there is not a dative bond in  $O_3$ , but I am not going to go there today – and if I put the following text (in blue) here, then you will understand why.
- I do NOT expect you to understand the text in blue below. I put it here merely to explain why you go wrong if you follow the Lewis rules. **I would not even bother to read the text in blue if I were you.** In your shoes I would just move swiftly on to Sulphur Dioxide. The spellings in the text below are in American English because Mr Swenson at the US Department of Energy is an American gentleman.

Why would it be energetically favorable for  $O_2$  to be a di-radical rather than a double-bond? (di-radical: two radicals in one molecule, a single bond, with one half-filled lone pair on each oxygen atom.) And yet, due to its paramagnetism, we know (that) it has a large percentage of the di-radical electron-arrangement, and the bond strength is too low to be a double bond. If  $O_2$  does not have a clean Lewis structure model, (then) I will not expect  $O_3$  to do it either.

If both bond lengths are the same, how can you choose two O atoms to be the central ones? I can rationalize, saying (that) you are imagining a certain stage in a reaction where one O atom approaches an  $O_2$  molecule. Then your question becomes, why is an arrangement with two good single-bonds and two radical electrons at the ends have lower energy than one double bond and one coordination-bond? (is that your “dative” bond?) Two things: oxygen is small and tight with its electrons. Another oxygen will not get much from trying to attach itself with a coordination (dative) bond. Those bonds are more likely to work when a small highly electronegative divalent atom (only oxygen, really) takes advantage of a larger, less electronegative atom with a large number of lone-pair electrons (sulfur, chlorine, iodine...) Also, two single-bonds usually have higher bond-strength (more energy-advantage) than one double-bond. It almost makes sense, really, that  $O_3$  should be single-bonded.

The O atom in the center position of  $O_3$  has two single bonds. Its Lewis octet is filled. It has too low an atomic number to have “d” orbitals, which are usually what allows for expansion beyond the Lewis octet. So the radical electrons at the ends are mostly “stranded” by themselves, they cannot use the central atom as a bridge to form a shared orbital, another bond. They could use an empty higher orbital of the oxygen, but I think these are energetically similar to being out in free space. So the radical electrons must either jump directly to each other, eventually bending the molecule to make an equilateral  $O_3$  ring, or they stay by themselves. 3-member rings are extremely strained, and it seems that is not what  $O_3$  prefers to be. Bear in mind that either of these states (bridging over central, or ring-closed) might actually be present in some small percentage. Only a first-principles molecular-orbital calculator would know for sure. Is that my old classmate, or the leading-edge software he sells, or neither at this time? Regrettably I do not know the exact status.

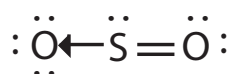
Why  $O_2$  is not more double-bonded is what bothers me. Lewis octets just are not a very good summary of the full picture in the case of oxygen-oxygen bonding.

Jim Swenson (US Dept of Energy) <https://stab-iitb.org/newton-mirror/askasci/chem03/chem03464.htm>

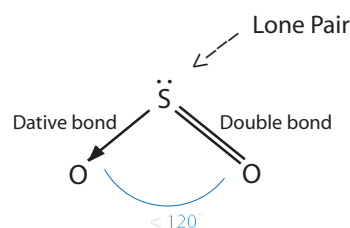
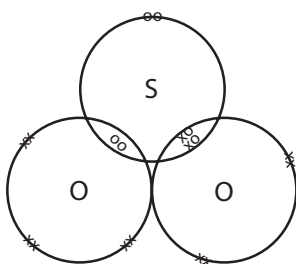
- I am fairly certain that you will have found that extremely difficult to follow, but it **will** have brought home to you that Lewis Structures do not always give you the complete picture of a structure.

**Sulphur Dioxide** ( $_{16}\text{S}$   $1s^2$ ,  $2s^2$   $2p^6$ ,  $3s^2$   $3p^4$  has 6 valence electrons, *exactly the same as Oxygen*)

- S has 6 valence electrons therefore  $1 \times 6 = 6$
- O has 6 valence electrons therefore  $2 \times 6 = 12$
- There is no charge on  $\text{SO}_2$  therefore  $X = 12 + 6 = 18$
- 2 electrons go between S and each of the two O atoms = 4 (leaving 14).
- Another **12** electrons go to complete the octet on each of the peripheral O atoms (that leaves **2** electrons to go on the central atom, S).
- There are only 6 electrons on the central atom, therefore move one of the lone pairs of electrons on one of the O atoms so that it is now between O and S (to now form 2 bonds between S and one of the O atoms).
- The resulting (unfair, and “unfairness” leads to Resonance) Lewis Structure has a double bond and also a dative bond in it



and using dot-and-cross and VSEPR diagrams you would have

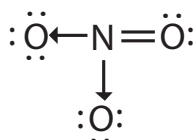


The bond angle is less than  $120^\circ$  because the lone pair is repelling the bonded pairs.

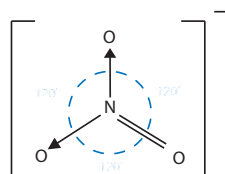
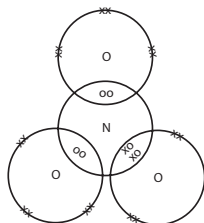
### $\text{NO}_3^-$

- We talked about nitric Acid,  $\text{HNO}_3$ , a number of times last year, and the Nitrate ion  $\text{NO}_3^-$  is Nitric Acid from which the proton has been dissociated.
- N has 5 valence electrons therefore  $1 \times 5 = 5$
- O has 6 valence electrons therefore  $3 \times 6 = 18$
- There is a negative charge therefore  $1 \times 1 = 1$
- Therefore the total number of electrons  $X = 5 + 18 + 1 = 24$
- 2 electrons go between N and each of the three O atoms (= 6 electrons leaving 18).
- Another **18** electrons go to complete the octet on each of the peripheral O atoms (=24).
- There are only 6 electrons on the central atom, therefore move one of the lone pairs of electrons on one of the O atoms so that it is now between O and N (to now form 2 bonds, i.e. a double bond between N and one of the Os).
- The resulting (unfair, because N is not treating each O atom equally) Lewis Structure has one double bond and also two dative bonds in it.<sup>7</sup>

<sup>7</sup> And here I am not at all bothered whether or not there really are two dative bonds in the structure. All that I am doing is sticking to the simplified Lewis rules.



- or using dot-and-cross and VSEPR diagrams you would have



- $\text{NO}_3^-$  is an anion with a single negative charge therefore, by convention, in diagrammatic form the charge is shown outside square brackets.
- In reality, there is no difference between any of the electrons – whether they be the N atom's electrons, the O atoms' electrons, or the electron that the dissociated proton left behind. An electron is just an electron, therefore it is difficult to say which bonds are dative bonds – and this underlines the point of Resonance when we come to it.
- You might at this stage say to me that a double bond will have more electron density in it than a single bond and the bond with the greater electron density will push the bonds with lesser electron density away from it, therefore the bond angles will not be  $120^\circ$ , but when we get to Resonance you will see why I left the bond angles at  $120^\circ$ . **(It has been established that the bond angles in  $\text{NO}_3^-$  are in fact  $120^\circ$  which is where Delocalisation will come in.)**

### $\text{NO}_2^+$

(The Nitronium ion results from the removal of the  $\text{OH}^-$  ion from Nitric acid,  $\text{HNO}_3$ .)

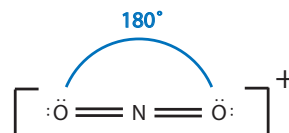
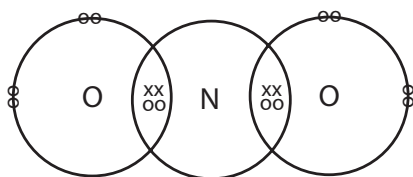
- N has 5 valence electrons therefore  $1 \times 5 = 5$
- O has 6 valence electrons therefore  $2 \times 6 = 12$
- (A positive sign indicates a **lack** of an electron, therefore we must **remove** one electron.)
- There is one “+ve” charge on  $\text{NO}_2^+$  therefore  $1 \times -1 = -1$
- Therefore  $X = 5 + 12 - 1 = 16$
- Draw a bond line between each peripheral O atom and the central N atom. That takes **4** electrons.
- Complete the octet on each of the peripheral O atoms. That takes another **12** electrons (=16).
- Each of the O atoms has a complete octet, but the central N atom does not, therefore move one of the lone pairs of electrons from each one of the O atoms so that it is now between the N atom and itself so that the N atom has a complete octet.
- There will now be a double bond between the N atom and each one of the O atoms, and to use my anthropomorphism<sup>8</sup> about “fairness” the resulting Lewis Structure is fair<sup>9</sup>.
- We could have created a triple bond between N and one of the O atoms, but in Chemistry symmetry is a preferred solution.

<sup>8</sup> “Anthropomorphism” is the attribution of human motivation, characteristics, or behaviour to inanimate objects, animals, or natural phenomena.

<sup>9</sup> Please remember that “unfair” is not a word that chemists use. I am at this stage just trying to get across to you that N cannot treat each one of its (identical) O atoms differently.



- Using dot-and-cross and VSEPR diagrams you would have

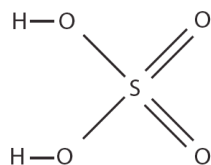


NB As you can see, you cannot tell which bonds are dative bonds from Lewis Structures. You need to use dot-and-cross diagrams to do that. However, mathematically it does NOT matter whether or not a bond is “dative”.

### HSO<sub>4</sub><sup>-</sup>

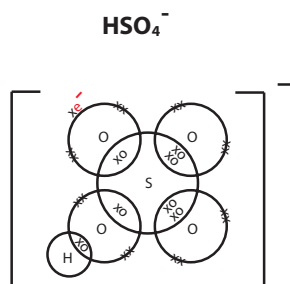
(where S is the central atom, and it would be most unlikely for one of the 4 O atoms to be so)

- HSO<sub>4</sub><sup>-</sup> is a Sulphuric Acid molecule where one of the protons has been dissociated. If you draw an H<sub>2</sub>SO<sub>4</sub> molecule first, then it becomes much easier to do the Lewis structure. (Please could you check that in the dot-and-cross diagram below, each H atom has 1 electron/each O atom has 6 electrons/the S atom has 6 electrons/and that every O atom and the S atom is sharing in 8 electrons. (However, you will find that the S atom is sharing not in 8 electrons, but in 12 electrons. This is known as an “expanded octet”.)



- For HSO<sub>4</sub><sup>-</sup>
  - S has 6 valence electrons therefore  $1 \times 6 = 6$
  - O has 6 valence electrons therefore  $4 \times 6 = 24$
  - H has 1 valence electron therefore  $1 \times 1 = 1$  (there is only one H atom in HSO<sub>4</sub><sup>-</sup>)
  - There is a “-ve” charge therefore  $1 \times 1 = 1$
  - Therefore  $X = 6 + 24 + 1 + 1 = 32$
- Draw a bond line between an O atom and the single H atom. That takes 2 electrons (leaving 30).
- Draw a bond line between each of the 4 peripheral O atoms and the central S atom. That takes 8 electrons (leaving 22 electrons).
- Complete the octet on each of the three peripheral O atoms that is not bonded to an H atom. That would take another 22 electrons. (NB The O atom that is bonded to the H atom needs only 2 electrons to complete its octet.)
- I have to stop there because I have not taught you anything about something called “**formal charges**” (as yet), but could you please accept that the bond line diagram above is correct and that the central Sulphur atom is sharing in not 8 electrons to form an octet but 12 electrons to form an **expanded octet**. However, if you dissociate one electron from the above bond-line diagram then you would get the diagram on the left overleaf, and if you were to dissociate two electrons from a molecule of Sulphuric Acid you would get the diagram on the right.

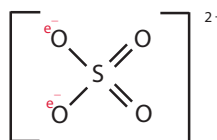
The electron shown in red on the top left hand O atom is the one that the dissociated proton left behind, but it is not possible to distinguish one electron from another therefore it is NOT correct to show it thus (and that is why I have shown it in red).



The electron left behind by the dissociated proton is correctly shown outside the brackets.

**SO<sub>4</sub><sup>2-</sup>**

Instead of using a dot-and-cross diagram, I have used a bond-line diagram.



Here I have shown in red the electron that each H atom left behind when it was dissociated as a proton.

- OK, that gives you a good grounding in Lewis Structures, therefore let me now remind you of what I told you about “Formal Charges” in Chapter 14 of Foundation Chemistry last year.

### Formal charges

**Formal Charges must be calculated for EACH INDIVIDUAL ATOM as well as for the whole species. The objective of the exercise will be to draw a Lewis structure that minimises the formal charges for the individual atoms and for the whole species.**

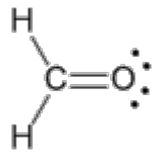

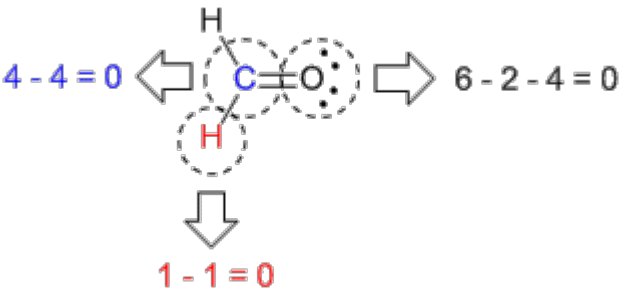
- Most of the entries for Chemistry in Wikipedia are from eminent people in their fields, and Wikipedia is therefore a reasonable starting point if you want to look something up. On Formal Charges, Wikipedia says “In Chemistry, a **formal charge (FC)** is the charge assigned to an atom in a molecule, assuming that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity. When determining the best Lewis structure (or predominant resonance structure) for a molecule, the structure is chosen such that the formal charge on each of the atoms is as close to zero as possible.”
- I have already told you earlier that, in Chemistry, the place in a species where it will react with another species is often determined by the spot where there is a concentration of electrostatic charge in the species, and “Formal Charges” are a good rule-of-thumb method for calculating where there could be such a concentration of electrostatic charge.
- The rules for the calculation of Formal Charges are as follows

The FC = (No. of valence electrons) - (half the No. of bonded electrons) - (No. of NON-bonded electrons)

and this is the same as

FC = (No of **valence e<sup>-</sup>**) - (½ the number of **bonding e<sup>-</sup>**) - (total number of **lone electrons**).

- The following example for the substance Formaldehyde comes from the University of Calgary.
- **The Diagrammatic or visual method** visually compares the number of valence electrons in an isolated neutral atom (which can be determined from the older style group number of the [periodic table](#)) with the atom in the molecule. It is a visual equivalent of the equation based method described above.
  - Draw a circle around the atom of interest
  - Count the number of electrons in the atoms circle (electrons in covalent bonds are shared)
  - Formal charge = group number of atom of interest - electrons in the circle of atom of interest

	Example molecule of interest
	Formal charge on oxygen: Group number = 6 Number of covalent bonds = 2 Number of lone pair electrons = 4
	Formal charges for all the different atoms

ALL the Formal Charges are 'zero' therefore the structure is correct.

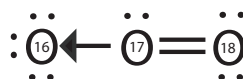
- OK, you now know all the rules, so could you please draw the Lewis structures for

H<sub>2</sub>O  
 CO<sub>2</sub>  
 SO<sub>2</sub>  
 O<sub>3</sub>  
 BF<sub>3</sub>  
 HNO<sub>3</sub>  
 H<sub>2</sub>SO<sub>4</sub>  
 H<sub>3</sub>PO<sub>4</sub>

- OK, now let us start talking about Resonance, and then we can talk about Delocalisation.

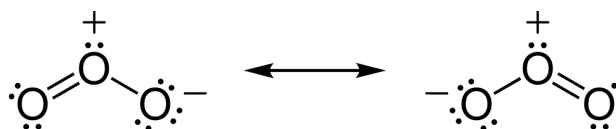
# Resonance

- “Resonance” is the situation where more than one Lewis structure can be constructed for a given species. In such a situation none of the Lewis structures will exist in real life and, instead, the electrons that are involved in the alternative Lewis structures become delocalised and a compromise of all the differing Lewis structures is what exists in reality.
- I have told you about the necessity (when you are old enough to have children of your own) to love and treat all your children equally<sup>10</sup>; but, “love” is not a valid concept in Chemistry, and if to all intents and purposes there is no difference between two atoms in terms of molecular orbitals<sup>11</sup>, then a third atom bonded to each of them must treat them equally, or if it is possible to draw more than one Lewis structure for the same species (excluding all forms of isomerism) then *none* of the different Lewis structures will be the structure of the species in real life.
- I have gone to great lengths to draw the Lewis Structures for O<sub>3</sub>, SO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> for you because these species are just three examples of the *unfairness* of treatment that seems to be accorded by a central atom to its peripheral atoms – and we know that **this cannot happen in Chemistry**. Actually, there is no such thing as fairness or unfairness in Chemistry (because these are just human notions of decent behaviour). In Chemistry, logic or mathematics determines how different species “behave” (which is also itself an anthropomorphic term), and if logically or mathematically two species are “equal” then in Chemistry they must and they **will** be treated equally.
- Let us look at the Lewis Structures of all three of the species O<sub>3</sub>, SO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, and ask what it is that needs to be done to achieve equality of treatment.
- In the case of Ozone, the Lewis Structure is



and (forgetting, for the moment, dative bonds because it does not matter mathematically where an electron comes from) you might say that there should be a double bond between <sup>16</sup>O and <sup>17</sup>O just as often as there is one between <sup>17</sup>O and <sup>18</sup>O – and in fact that is a perfectly acceptable way of being “fair”.

- In fact, both representations need to be shown to represent Ozone correctly, and these different depictions are called the *Resonance Structures* of Ozone. The positive sign denotes the O atom that has ‘donated’ both the bonding pair of electrons and it is therefore ‘short’ of an electron, whilst the negative sign denotes the O atom that has received an electron which forms one of the bonding electrons in the dative or “coordinate” bond.



Source: Wikipedia

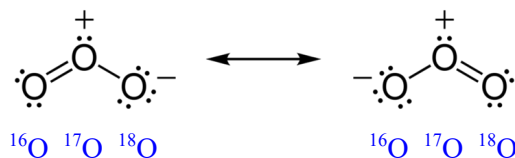
- The arrow with heads at each end is there to indicate that the two structures are Resonance structures, and the Resonance structures can be enclosed in brackets to indicate that they are all part of a group of structures none of which is the correct one.

<sup>10</sup> You may not love them all equally but you **MUST treat** them all equally.

<sup>11</sup> We will talk about Molecular Orbitals **very briefly** later on.



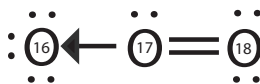
- A few moments ago I said “*forgetting, for the moment, dative bonds*” – but of course, we cannot forget dative bonds completely because in a dative bond, one atom is providing both the bonding electrons for the bond, and **in a sense therefore the atom that is providing both electrons (rather than providing just ONE of the pair of electrons that is needed to create a bond) has lost an electron** and the atom that has accepted the dative bond has gained an electron and you can therefore put a “+” sign on the atom that has lost the electron and a “-” sign on the atom that has gained the electron – and that is precisely what has been done in the Wikipedia diagram below



and if you refer to the dot-and-cross diagram, you will see why the “+ve” and “-ve” charges are where they are. In the resonance structure on the right above,  $^{17}\text{O}$  has created the dative bond with  $^{16}\text{O}$  and has therefore “lost” an electron (and has the “+ve” sign) while  $^{16}\text{O}$  has gained an electron (and has the “-ve” sign).



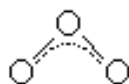
- Remember the Lewis Structure on page 13



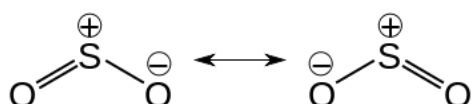
- Now, **it is NOT the case that the double bond keeps swapping between  $^{16}\text{O}$  and  $^{18}\text{O}$** ! That is merely a graphic (Resonance) representation of the reality that the diagram is trying to convey. If the double bond kept swapping, then the bond lengths of  $^{16}\text{O}-^{17}\text{O}$  and  $^{17}\text{O}-^{18}\text{O}$  would keep changing, whereas in reality the bond lengths are constant and they are neither as long as a single bond nor as short as a double bond (and the bond lengths can be measured by different methods e.g. X-ray diffraction crystallography<sup>12</sup>/infra-red spectroscopy/etc).
- OK, if the double bond does NOT keep swapping from one peripheral atom to the other, then can the double bond be on **both** peripheral atoms at the same time – and the answer to this question is “No” because whilst the two bond lengths in  $\text{O}_3$  are in fact identical, we know from experimental evidence that they are **not** as short as they would be if the two bonds were double bonds.

<sup>12</sup> You may remember that last year I told you that in 1955 at the age of 15 I met the great Sir (William) Lawrence Bragg. WLB was the pioneer of modern X-ray diffraction crystallography, and he was then followed by people such as Bernal/Dorothy Hodgkin (another Nobel Laureate)/Rosalind Franklin (from whom James Watson took information without due acknowledgement thereof, and then he and Francis Crick conceived the idea of the structure of DNA)/etc. Both Sir Lawrence and his father Sir William Henry Bragg were recipients of the Noble Prize for their work on X-ray diffraction crystallography. I met two of our former Prime Ministers and three of our Chancellors of the Exchequer during my nearly four decades in the City, but I was not particularly impressed by any of them – and yet I have never forgotten my childhood meeting with Sir Lawrence Bragg!

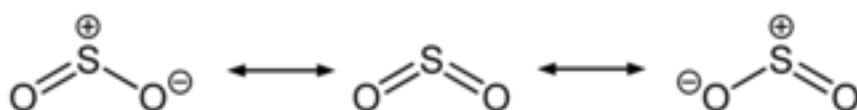
- Imperial College London says the following (but I have corrected a spelling mistake)  
*The  $O_3$  molecule is bent, with an O-O-O bond angle of  $117^\circ$ . The bond length in ozone ( $1.28\text{\AA}$ ) is intermediate between the single bond found in *hydrogen peroxide* HO-OH ( $1.49\text{\AA}$ ) and the double bond in *oxygen*  $O=O$  ( $1.21\text{\AA}$ ). From this, it is apparent that the bonding in  $O_3$  must have considerable double bond character, and so perhaps a good graphic description of its bonding is:*



- In a moment I am going to tell you that it is because of the inability to reconcile all the known facts that chemists arrived at the concept/construct of *delocalisation*, but before I do so, let us look at  $SO_2$  and  $NO_3^-$ .
- The Resonance structures (the different non-isomeric Lewis structures for the same molecule) for  $SO_2$  as shown by Wikipedia are



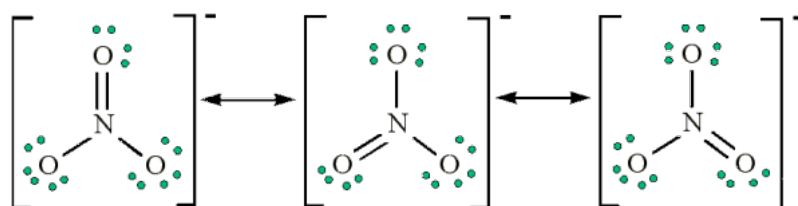
but they can also be shown as



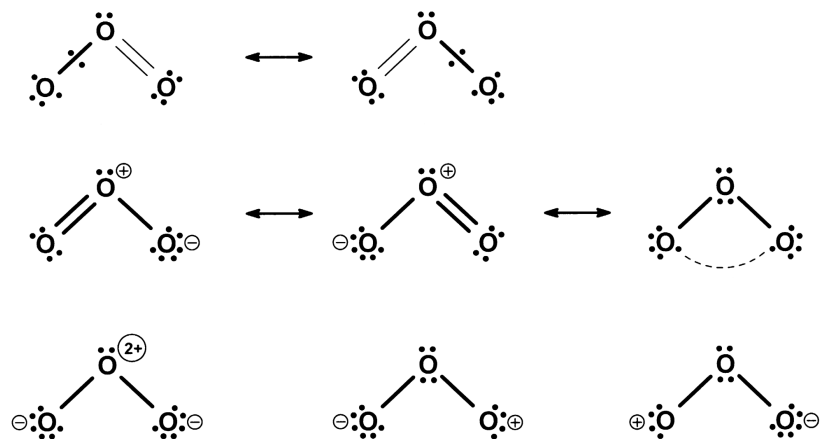
and the Resonance structures for the third species that I have chosen to look at,  $NO_3^-$  as shown by Mike Blaber at

<http://www.mikeblaber.org/oldwine/chm1045/notes/Bonding/Resonan/Bond07.htm>

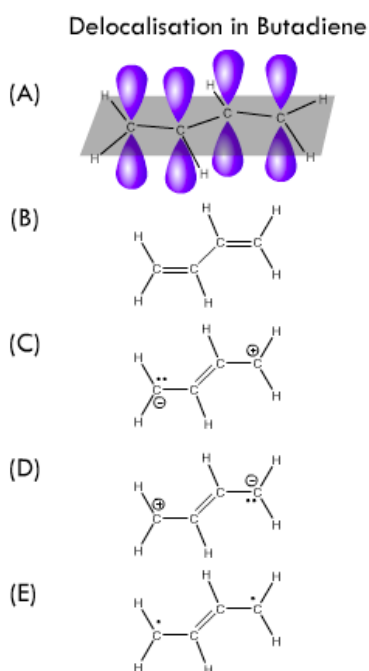
(an excellent Chemistry website) is



- I trust that you have now got the hang of Resonance, and appreciate that it tries to depict graphically the differing Lewis structures that are possible for exactly the same species. Actually, I have kept the explanation of Resonance as simple as possible because it is very easy to go into it in much greater depth as the following Resonance structures for Ozone from the University of Munich shows! By the way, if you read Jim Swenson's piece on page 8, then Mr Swenson was referring to some of the possible structures shown overleaf.



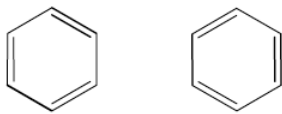
- Four Resonance structures are shown for Butadiene below and **not one of them is correct**. All four carbon atoms are in fact linked in the purple delocalized electron system [as shown in the first depiction (A)].



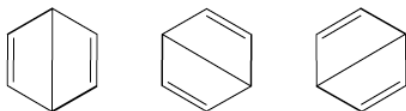
Source : Dickerson & Geis, "Chemistry, Matter and the Universe"  
<http://www.chem.ox.ac.uk/vrchemistry/foundation.html>

- Dickerson & Geis also show (in the same book) the following Resonance structures for Benzene and the delocalised structure for Benzene and Butadiene (page 20). NB The two Kekulé structures are different only if six C atoms are different (otherwise they would be the same structure viewed from the front and then viewed from the back).

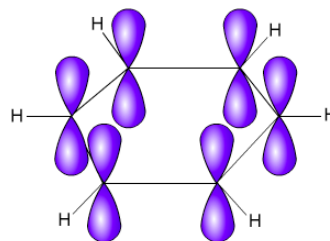
Possible  $\pi$  double-bonded structures in benzene



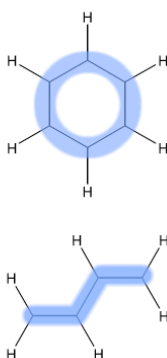
The two Kekulé structures



and the three Dewar structures with a less likely long central bond.



Six more electrons and six carbon p orbitals perpendicular to the plane of the benzene ring, are not used in the  $\sigma$ -bonding skeleton of benzene. These electrons would be sufficient for three more localised carbon-carbon bonds.



Comparison of the extent of delocalisation in benzene (top) and butadiene (bottom). None of the resonance structures for butadiene shown on the previous page are correct; the four electrons not used in  $\sigma$  bonding are delocalised over the entire four-carbon skeleton.

- If you are having trouble with working out the resonance structure for a standard species, then you could try <http://www.stolaf.edu/depts/chemistry/courses/toolkits/123/js/lewis/>.
- Let me remind you what I have said regarding Resonance

**“Resonance” is the situation where more than one Lewis structure can be constructed for a given species. In such a situation none of those Lewis structures will exist in real life and, instead, the electrons that are involved in the alternative Lewis structures become delocalised and a compromise of all the differing Lewis structures is what exists in reality.**

- OK, we have mentioned “Delocalisation” a number of times, so let us now talk about it next.

## DELOCALISATION

On page 1 I told you that

- We have now seen that differing Resonance Lewis Structures do not depict the actual structure of certain species. Chemists therefore asked themselves “How then can we explain the reality of these species?” and the answer that they came up with was “**Delocalisation**”.
- I should like to stress here that the construct of “Delocalisation” is just a construct to try to explain why Resonance does not fit in with the observed facts about the species that we have been considering. In Science, we relentlessly pursue the explanation of observed measurable reality and we then have to put forward theory after theory (or one artificial construct after another) to try to explain the facts as we know them at the time. Delocalisation is in fact a lovely elegant construct which is going to take us to Benzene and all the other Arenes (or as they are also known, Aromatic species), but it is just a construct. On page 1 of this Chapter I quoted Dickerson & Geis saying this at the beginning of Chapter 9 in “Chemistry, Matter and the Universe”

So far we have used two models for chemical bonding and molecular geometry: Lewis' electron pairs to explain how atoms are held together, and valence-shell electron-pair repulsion theory (VSEPR theory) to account for the geometry of bonding. These are simple ideas, but we have pushed them about as far as they will go. The cracks and seams in the bonding theory have begun to show through [and] the need for delocalized electrons is one example [,] and rather than trying to patch over the cracks, it is wiser to develop a better theory of bonding that will include the old ideas and permit us to go beyond them.

and to that I added that delocalisation is probably the last boundary to which non-Quantum Mechanical Chemistry can be pushed – so let us now look at Delocalisation.

- In Lewis Structures and in Resonance Structures, the electrons are shown as though they are fixed in certain places<sup>13</sup> e.g. in Ozone, at one moment in time there will be four electrons between <sup>16</sup>O and <sup>17</sup>O, and then a split-second later there will only be two electrons there – but if neither of these depictions is the case (and bond length measurements indicate something in between), then could the reality be something in between! Chemists thus came up with the construct that the real nature of the bond was that **some (or all) of the bonding electrons were spread over the WHOLE of the O<sub>3</sub> molecule and that they did not belong to any one atom in particular i.e. they were “delocalised”**. The structures of molecules therefore do NOT resonate/fluctuate between the different possible Resonance structures of the molecule, but instead they have a **single structure which is a compromise of all the different possible Resonance structures**.
- When we were studying metals last year we talked about the “sea of delocalised electrons” that there were in a piece of metal, and about the fact that no single atom in the piece of a metal kept a hold onto its own electron(s), but instead every atom shared in every delocalised electron in the piece of metal. Delocalisation here is much the same sort of concept.
- That's it. That is all that we need to know about delocalisation for ‘A’ Level purposes. What we have now learnt about Resonance, and the fact that in reality bond lengths do NOT keep fluctuating, will very nicely allow us to discuss and to **understand** the nature of the Benzene ring when we come to it.

---

<sup>13</sup> This is an extremely ham-fisted way of trying not to get bogged down in the complexities of Quantum Mechanics and Heisenberg's Principle of Uncertainty, and if you know a lot more about the subject than I do, then please forgive my amateurish phraseology.

- OK, we are now going to talk briefly about Hybrid Orbitals/Molecular Orbitals/Conjugation/Hyperconjugation/the Mesomeric and Inductive Effects/and Activation and Deactivation, and then we will have all the basic concepts that we need to cover the 'A' Level Syllabus topics on Benzene/Toluene/Phenol/and all the other Arenes – but please remember that you will NOT be tested on the stuff that I am giving you in the first four Chapters of this book. I am telling you about all this stuff only because I want you to actually **understand** the material in the 'A' Level Syllabus (rather than to learn it all “parrot fashion”).
- If you have persevered and worked your way through the whole of this Chapter, then I congratulate you. You have shown intelligence, determination, perseverance and strength of character. Well done! If you are also a nice person, then you have every chance of having a very successful and a very happy life.