Oxidisation Numbers/Oxidisation States/Roman numerals in brackets in the name of a substance

A Year 1 Blog for the week commencing the 22nd of March 2020.

- I have elsewhere stressed that a **molecule** has no charges on it. There may indeed be areas of *partial separation of charge* (i.e. "∂-" and "∂+") such as those inside a water molecule, and the lone pairs of electrons on the Oxygen atom and the areas of electron density are what is responsible for the vast bulk of the reactions in which Water participates – but the two species inside every Water molecule are not ions. They are atoms of Oxygen and Hydrogen that are **sharing** pairs of bonding electrons!

- I want you to be **VERY** clear about that, because I am now going to introduce you to a part of Chemistry that at first sight seems to contradict what I have told you. **Please do not confuse** what you are about to learn with what you have already learnt viz. that **a MOLECULE can never have any charged particles inside it.** The reason for this is that it would then not be a molecule – it would have become an ionised species! A molecule and an ionic unit are two totally different things. In the former electrons are **shared**, and in the latter electrons are **transferred**!

- However, before I tell you about Oxidisation States and Oxidisation Numbers, let me say that the two things (Oxidisation States and Numbers) are just two different ways of describing the same situation. When a species has a particular Oxidisation State, then it has the Oxidisation Number belonging to that particular Oxidisation Sate. The two phrases (*Oxidisation States* and *Oxidisation Numbers*) therefore describe exactly the same situation except from a slightly different viewpoint. I shall refer to Oxidisation Numbers (rather than to Oxidisation States) for the rest of this note.

Oxidisation Numbers

- An Oxidisation Number (Ox No) refers to the **TOTAL number of electrons** that the atom of an element is **deemed** to have used when it **has reacted with** and formed bonds with other atoms in a *particular* type of substance.[1]

- **The use of the word "particular" in the description above is very important because an element can have different Oxidisation numbers in different types of substances, and some elements do indeed have many different Ox Nos** e.g. it is possible for Sulphur to have an Ox No of "+2" (e.g. in H_2S) or "+4" (e.g. in SO_2) or "+6" (e.g. in SO_3).

NB **In "uncombined elements"** (i.e. in metal ions in a piece of metal, in single atoms, and in multi-atomic molecules of an element such as H_2/P_4/S_8) **the *Ox No* is considered to be "zero"** e.g. *there is a double bond in an O_2 molecule and each atom of O has therefore used two electrons to form the molecule*, **but, even so, the Ox No of each atom of Oxygen in an O_2 molecule is still "ZERO"** – and perhaps even more importantly, despite the fact that every single metal species in a piece of metal is an *ion* and thus is a charged species, nevertheless, **the Ox No of every metal ion in a piece of pure metal is considered to be "ZERO"**! ***[NB Oxidisation numbers are just a set of conventions that chemists have agreed to accept.]***

- A nice and simple example of Ox Nos can be seen in a Water molecule, where each atom of Hydrogen uses its only electron to form the molecule of Water, and the Oxygen atom uses two of its six electrons (one to form one pair of bonding electrons with one atom of Hydrogen, and one to form another pair of bonding electrons with the other Hydrogen atom). Therefore, in a Water molecule,
  - Hydrogen has an *Ox No* of "+1", and
  - Oxygen has an *Ox No* of "-2".

[1] We are referring here to ionic and covalent bonds – but NOT to metallic bonds i.e. not to the bonds in a piece of a pure metal that has not combined with anything else.

- You will (or you should) now ask the question "But why was one of them a positive number and the other a negative number?", and the answer is that **if a substance has a NEUTRAL overall charge, then all the Oxidisation Numbers MUST add up to zero**, and there must therefore be some species with positive Oxidisation Numbers and others with negative Oxidisation Numbers. [NB I did warn you that *Oxidisation numbers are just a set of conventions that chemists have agreed to accept.]*

- The rule that governs which atom has a negative *Ox No* and which has a positive one is that in a given species **the atom of the element with the greatest electronegativity is given the negative Oxidisation Number**, and then everything else is adjusted to give the right answer (i.e. to give zero for a neutrally charged substance, or if the substance is an ion, then to give whatever charge the ion itself may have). Let us do a couple of Ox No calculations, and you will see how it works out. I will explain how to do the calculations in a moment, but for the moment let us just see how it works.
  Ox Nos for Water $[H_2O_1]^0$ gives $[(H^{1+})_2\ (O^{2-})_1]^0$ $2 \times (+1) + 1 \times (-2) = 0$
  Ox Nos for the dichromate ion $[Cr_2O_7]^{2-}$ gives $[(Cr^{6+})_2\ (O^{2-})_7]^{2-}$ $2 \times (+6) + 7 \times (-2) = -2$
  NB Please note how all the numbers add up, and that is the secret of doing the calculations for Ox Nos!

- The insertion of Oxidisation numbers for the atoms in Water **does not mean** that each H atom has a ***CHARGE*** of +1, and it does not mean that the O atom has a *charge* of -2!
  All that an Oxidisation Number does, is to tell you how many electrons an atom is deemed to use to form the particular substance under consideration.

- **It really is vitally important that you understand this point.** For example, you will remember that I told you that it is (I believe) impossible for an ion with a charge of "+4" or "-4" (such as a Pb^{4+} ion) to be formed in nature (because once the first three electrons have been removed from an atom, the remaining electrons are held so tightly by the protons in the nucleus that it becomes impossible to remove another electron naturally). However, man can artificially form a Pb^{4+} ion – *but nature cannot do so*!

- You will sometimes see the species "Pb^{4+}" written in a document – but this does not mean that the author is referring to a "Pb^{4+}" **ion**. Instead, what he is referring to is the **Oxidisation Number** of Lead inside the compound under consideration.

- There is one thing that I now want to re-emphasise viz. that where there is a neutral overall charge in a substance (e.g. in any molecule, or in a neutrally charged ionic *unit* such as NaCl or MgO), then the sum of all the Oxidisation Numbers must be zero!

  For example, in Water the sum of the Oxidisation Numbers is given by
  Species H H O
  Ox Nos (+1) + (+1) + (-2) = 0 overall charge!
  [Oxygen is the more electronegative species therefore it has the negative Ox No.]

  and in common table salt (Sodium Chloride), the sum of the Oxidisation Numbers is given by
  Species Na Cl
  Ox Nos (+1) + (-1) = 0 overall charge!
  [Chlorine is the more electronegative species and thus **it** has the negative Ox No.]

<u>**SUMMARY**</u>

- An **Oxidisation Number** (Ox No) refers to the *TOTAL number of electrons* that the atom of an element is deemed to use when it reacts and forms bonds with other atoms in a particular substance, and an **Oxidisation State** is the State in which an entity has a particular Oxidisation Number. For example if an entity has an Ox No of "+4", then it has an Oxidisation State of "+4" (as in "the Oxidisation State of Sulphur in SO_2 is "+4").

- **Please note that an Oxidisation Number is NOT a charge! It is NOT an indication that any electrons have been lost or gained!** Ox Nos can be used to describe atoms in both an ionic substance and in a molecular substance.

THE RULES FOR CALCULATING OXIDISATION NUMBERS

Please note the following general rules

- In a neutrally charged entity i.e. in a molecular substance (such as H_2SO_4) or in an ionic substance (such as NaCl or $MgCl_2$), **all the Ox Nos in the entity must add up to zero**.

- In an "uncombined" element, the Ox No of the element is always "zero".

- The Ox Nos of the elements in an entity are determined by the element with the greatest electronegativity in that entity, and we have already learnt that
  - *the Electronegativity of elements increases in going* ***across*** *a Periodic Table, and*
  - *the Electronegativity of elements increases in going* ***up*** *a Periodic Table.*

- **Fluorine** is thus the most electronegative element known to man (which is the same thing as saying that its atoms have a greater propensity to attract electrons than do the atoms of any other element), therefore **the Ox No of Fluorine never alters – it is always "-1"**.

- **Oxygen** is in Group VI and it is the second most electronegative element known to man therefore the Ox No of Oxygen is always "–2" except
  a) when it forms a compound with Fluorine (when its Ox No is determined by Fluorine), and
  b) when it forms the compound Hydrogen Peroxide (H_2O_2) with Hydrogen. Hydrogen has only one electron therefore it is not possible for it to have an Ox No of more than "+1", therefore in H_2O_2 **Oxygen** can have an Ox No of nothing more than "-1".[2]

- The Ox No of **Hydrogen** is always "+1", *except when it reacts with a metal element to form a Metal Hydride* e.g. NaH or CaH_2, and then Hydrogen has an Ox No of "–1". The total of the Ox Nos for the Hydrogen atom or atoms and the metal must add up to zero, and Hydrogen is considered to be more electronegative than metals, therefore each H atom is considered to have an Ox No of "-1" e.g. in CaH_2 the Ox Nos are $(Ca^{2+})_1(H^{1-})_2$.

- OK, let me now ask you to work out (or research) for yourselves what Oxidisation numbers all the following species have.

- When they are involved in an ionic substance, what are the
  a) Oxidisation Numbers of the Group I Metals viz. Li/Na/K/Rb/etc?
  b) Oxidisation Numbers of the Group II Metals viz. Be/Mg/Ca/etc?
  b) Oxidisation Numbers of the Group VII Non-Metals (the Halogens) viz. F/Cl/Br/I/etc?
  c) Please find out what the main Oxidisation Numbers of Pb/Fe/Cu/Ni/Zn are.
  f) Please find out what the main Oxidisation Numbers of Al/Fe/Cr are?

NB Nearly all the Metals in the middle of the Periodic Table are called "Transition Metals" and there is no way of knowing in advance[3] what their Oxidisation Numbers are going to be *because they are capable of having many different Oxidisation Numbers*.

- Do not spend more than 15 minutes on finding out the answers. **I do mean that!** 15 minutes and no more! Your time is the most precious thing that you have (after your individual personality), and I am trying to teach you good learning habits. You *can easily* spend hours on the Web, but it may not be the most efficient way of using your time. Always concentrate on the job in hand and make sure that you are using your precious time effectively. Another two hours on the Web may in fact be *less efficient* than spending ten minutes reading the remainder of this note.

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[2] This must be so, because H_2O_2 is a molecular substance therefore the Ox Nos for H_2O_2 must all add up to zero, and if each H atom has an Ox No of "+1", then the **TOTAL** for the two O atoms must be "-2" – therefore **each** O atom must have an Ox No of "-1". I hope that you are now beginning to understand how the Oxidisation conventions work, and how they make a coherent set of rules.

[3] I could have used the Latin phrase *"a priori"*, and in English this means "in advance of" or "beforehand".

ANSWERS

- The Oxidisation Numbers (or the main Ox Nos where there is more than one Ox No)
  a) for the Group I Metals (Li/Na/K/Rb/etc) is "+1"
  b) for the Group II Metals (Be/Mg/Ca/etc) is "+2"
  b) for the Group VII Halogens (F/Cl/Br/I/etc is) "-1", and
  c) the Main Ox No of Pb/Fe/Cu/Ni/Zn is "+2"
  d) the Main Ox No of Al/Fe/Cr is "+3". *[Actually, Iron has two main Ox. Nos. viz. "+2" and "+3".]*

SLIGHTLY MORE DIFFICULT QUESTIONS

- Could you now please calculate the Ox No indicated as "n" in the following species, and could you note that in Algebra you can denote an unknown quantity as "x" / "y" / "z" / "n" /etc. Here I have chosen to use "n" as my unknown because an "x" can easily be confused with the multiplication sign "x".

- $S^{n}O_4^{2-}$ — the salt of the acid H_2SO_4.
- $P^{n}O_4^{3-}$ — the salt of the acid H_3PO_4.
- $C^{n}O_3^{2-}$ — the salt of the acid H_2CO_3.
- $N^{n}O^{3-}$ — the salt of the acid HNO_3.
- $H_2S^{n}O_4$ — this is the acid H_2SO_4.
- $[Cr^{n}{}_2O_7]^{2-}$ — the salt of the acid $H_2Cr_2O_7$.
- $S^{n}O_2$ — this is the gas sulphur dioxide
- $HN^{n}O_3$ — this is the acid HNO_3

and, to get you started I will do the algebra for you for two examples i.e. $H_2S^{n}O_4$, and $S^{n}O_2$.

Calculation for $H_2S^{n}O_4$

Step 1 : establish which element is the most electronegative : Answer = Oxygen
Step 2 : establish the Ox No for this element : Answer = –2
Step 3 : establish the Ox No for the other unknown i.e. Hydrogen : Answer = +1
Step 4 : now put in the known Ox Nos and the square brackets and the charge on the whole species $= [(H^{1+})_2 \; S^{n} \; (O^{2-})_4]^{0}$
Step 5 : equate the Ox Nos inside the brackets with the number outside the brackets remembering to use **as many atoms as there are for each Ox No**
e.g. in H_2SO_4: two for H, one for S, and four for O viz.
$[2x(+1) + 1x(n) + 4x(-2)] = 0$, therefore $[2 + n - 8] =0$, therefore $n = +6$.

Calculation for SO_2

Step 1 : establish which element is the most electronegative : Answer = Oxygen
Step 2 : establish the Ox No for this element : Answer = –2
Step 3 : now put in the known Ox Nos and the square brackets and the charge on the whole species $= [S^{n}(O^{2-})_2]^{0}$
Step 4 : equate the Ox Nos inside the brackets with the number outside the brackets remembering to use **as many atoms as there are for each Ox No**
$[1x(n) + 2x(-2)] = 0$, therefore $[n - 4] =0$, therefore $n = +4$.

- Could you please note that you have now seen that Sulphur has two different Ox Nos "+6" in Sulphuric Acid, and "+4" in Sulphur Dioxide.

- **In your First Year 'A' Level exam, you will almost certainly get a question that involves a knowledge of the calculations that involve Ox Nos, so let me go through the rules again and do some more examples.**

Calculating Oxidisation Numbers

1 First put a square bracket around the species given, and then put in the Ox No of the whole of that species outside the top of the right hand square bracket.
[NB If the species is a molecular substance, then it must have an Ox No of zero.]
2 Then put in all the known Ox Nos e.g. Oxygen has to be "–2" except (a) when in a compound with Fluorine, or (b) when in Hydrogen Peroxide.
3 Put in an "n" for the unknown Ox No, and then solve for "n".
4 Remember to use "**-n**" or "**+n**" for numbers when solving for "x", but "**n-**" or "**n+**" **when the Ox No is shown as a power** (or index number) in the species.

A) SO_4^{2-}

1 SO_4^{2-} becomes $[SO_4]^{2-}$
2 $[S^n(O^{2-})_4]^{2-}$
3 Therefore [1 x (n) + 4 x (-2)] = -2
Therefore n + (-8) = -2
Therefore n - 8 = -2
Therefore n = -2 + 8
Therefore n = +6
- The Ox No of Sulphur in a Sulphate ion is "+6".

B) $Cr_2O_7^{2-}$

1 $Cr_2O_7^{2-}$ becomes $[Cr_2O_7]^{2-}$
2 $[(Cr^n)_2 (O^{2-})_7]^{2-}$
3 Therefore [2 x (n) + 7 x (-2)] = –2
Therefore 2n + (–14) = –2
Therefore 2n – 14 = –2
Therefore 2n = +12
- The Ox No of Chromium in the Dichromate Ion is "+6".
[We will use the dichromate ion a lot in Organic Chemistry in our second term.]

C) MnO_4^-

1 MnO_4^- becomes $[MnO_4]^-$, and this could also have been (but is NOT) written as $[MnO_4]^{1-}$
2 $[Mn^n(O^{2-})_4]^-$
3 Therefore [1 x (n) + 4 x (-2)] = -1
Therefore n + (-8) = -1
Therefore n - 8 = -1
Therefore n = -1 + 8
Therefore n = +7
- The Ox No of Manganese in a Manganate ion is "+7".

- In your second year I will tell you that the MnO_4^- ion (from Sodium Permanganate $Na^+MnO_4^-$ or from Potassium Permanganate $K^+MnO_4^-$) with an Oxidisation Number of "+7" is a more powerful Oxidising Agent than the Dichromate ion $Cr_2O_7^{2-}$ (again from either Sodium Dichromate or from Potassium Dichromate) – and you may see why this so if you look at the Oxidisation numbers of their ions. One of them is "+7" and the other is "+6". In other words, the Manganate ion is deemed to have lost more of its electrons and thus is more anxious than a Dichromate ion to steal someone else's electrons.

NB Remember **OILRIG**. If you gain electrons you are being **REDUCED**, and if you are being reduced the other species must be losing electrons therefore it is being **OXIDISED**. Both Manganate and Dichromate ions are thus **OXIDISING** agents, and we will use $K_2Cr_2O_7$ to oxidise Alcohols into Aldehydes/Ketones/ or Carboxylic Acids in Organic Chemistry next term. (The Americans use the word "Semester" where we use the word "Term".)

- Easy, isn't? OK, now that we have talked about Oxidisation/Reduction/and Oxidisation Numbers, let us talk about "Ionic half-equations", but before we do so, I must introduce you to the use of Roman numerals in Chemical formulae.

- You will often see the names of some substances written with a Roman numeral in the name. This is a practice that confuses a number of students – but now that we have discussed Oxidisation States/Numbers, it becomes very easy to explain what is meant when Roman numerals are used.

- Let us first of all look at an example of the use of Roman numerals in conjunction with different substances that contain the element Phosphorous, *and please do remember that the number at the top right of square brackets indicates the charge on the species inside the brackets*. [NB Please do not worry about the names of these substances/species! They are there merely to tell you what the species actually are.]

Substance	**Substance with all its Oxidisation Numbers**	**Ox No for Phosphorous**	**Roman numeral for Phosphorous**
Phosphorous (III) Oxide, P_2O_3	$[(P^{3+})_2(O^{2-})_3]^0$	+3	III
Phosphorous (V) Oxide, P_2O_5	$[(P^{5+})_2(O^{2-})_5]^0$	+5	V
Trioxophosphoric (V) Acid, HPO_3	$[(H^{1+})_1(P^{5+})_1(O^{2-})_3]^0$	+5	V
Tetraoxophosphoric (V) Acid, *H_3PO_4*	$[(H^{1+})_3(P^{5+})_1(O^{2-})_4]^0$	+5	V
(NB This acid, i.e. H_3PO_4, is commonly called just "Phosphoric Acid" or sometimes "Phosphoric (V) Acid")			
Heptaoxodiphosphoric (V) Acid, $H_4P_2O_7$	$[(H^{1+})_4(P^{5+})_2(O^{2-})_7]^0$	+5	V
A "phosphate (V)" ion	$[(P^{5+})_1(O^{2-})_4]^{3-}$	+5	V
A "heptaoxodiphosphate (V)" ion	$[(P^{5+})_2(O^{2-})_7]^{4-}$	+5	V
A "trioxophosphate (V)" ion	$[(P^{5+})_1(O^{2-})_3]^{-}$	+5	V

NB Here, "tri-"/"tetra-"/"hepta-"/etc come from the Greek words for numbers and reveal how many Oxygen atoms are present in the substance. [NB Please do not worry about Greek names at this stage.]

- If you compare the entries in the last two columns above, then you will see exactly what the Roman numerals signify i.e. **they signify the Oxidisation Number of the element in that particular substance**. Here P has an Ox No of "3" in only one of the above examples and "5" in all the others, and earlier in this note we saw examples of S having Ox Nos of "+2", "+4", and "+6". **Roman numerals are used as a method of helping to identify exactly which substance is under consideration by enumerating its Oxidisation Number.**

PLEASE NOTE

1 You do not have to be an *excellent* mathematician to be a good chemist, but you do have to be a *competent* mathematician to be a good chemist – therefore could I urge you to do all the calculations that you find necessary to verify all the Ox Nos in the table above *(and all that we are talking about here is doing very simple Algebraic calculations)*. If you need to do so, please go back and look at the worked examples, and then do the calculations involved here.

2 For every "salt" there is a corresponding acid (and *'vice versa'*).[4] I hope therefore that you have noticed that **the negative charge on a salt corresponds EXACTLY to the number of protons that have been dissociated**. When I was learning 'A' Level Chemistry, I could never remember the formula for "Carbonic Acid" because I could never remember whether it was HCO_3 or H_2CO_3 – and if you have the same problem, then here is a nice little way of solving the problem (and if you like it reverses the logic of the above sentence). Think of Calcium Carbonate (the formula for which is $CaCO_3$), then remember that Calcium is in Group II therefore a Carbonate salt must have the formula CO_3^{2-} (because it comes from $Ca^{2+}CO_3^{2-}$) – and then hey presto, it follows that Carbonic Acid must have the formula H_2CO_3! Isn't that nice and simple and elegant! Isn't Chemistry so nice and simple when you start to know what you are doing! *Mind you, that will be true for everything that you do in life! It does **not** take a genius to be a rocket scientist or a brain surgeon. You just need to know what you are doing (and the same is true for a road-sweeper).*

[4] "*Vice versa*" is Latin for "the other way round".