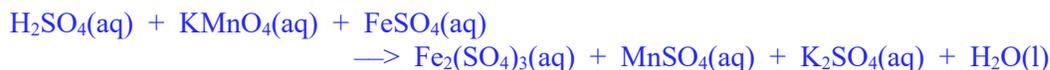


A Year 1 and Year 2 Blog on Ionic Equations, and Half-Equations: 6th October 2019

(This is merely a *summary* of some of the things that you need to know. *Everything in this blog, and more, can be found in my books.*)

- Let me start by asking you: “How easy would it be to balance the following equation where the stoichiometric numbers are unknown?”



- If your answer was “Not impossible, but not easy” – then sit back and enjoy the ride because this Blog will show you how to do it within minutes rather than hours.
- “Ionic Equations” are reaction equations that omit spectator ions, and “Ionic half-equations” (which are more correctly called “**Aquated** ionic half-equations” break ionic equations into their component Reduction and Oxidisation equations.

NB Getting the same number of electrons in each half-equation **IS THE KEY** to doing ionic half-equations. **THAT** is the essential part of the exercise because it is that which unifies the two half-equations. One half-equation must generate the same number of electrons as the other half-equation needs to complete its reaction, and given that we have already started to talk about the LOSS and the GAIN of electrons, can you see that we are actually talking about **OILRIG** and **REDOX** reactions!

Ionic Equations

- Ionic equations are extremely useful in that they allow us to penetrate to the very heart of an ionic/a redox reaction by getting rid of all the spectator ions in the reaction and thereby reveal the very essence of the ionic reaction. Ionic equations can, in turn, be broken down into ionic half-equations.

Ionic HALF-Equations

- Ionic HALF-equations are very useful in that they allow us
 - first of all **to break down a reaction into its component parts**, and then
 - **to use the number of electrons that has been revealed by the half-equation as a means of unifying those components by equating the number of reacting electrons in each half-equation.**
- *As we will see, this procedure allows us to balance ANY redox equation, but specifically it allows us to balance equations that would otherwise be extremely difficult to balance!*
- OK, let’s see how this works – but before we can talk about Ionic half-equations, we need to talk about Oxidising and Reducing agents.

Oxidising Agents¹ and Reducing Agents

- An Oxidising agent is something that allows something else to Oxidise; and (from **OILrig**), the substance that is being oxidised is losing electrons, therefore the oxidising agent must be absorbing/gaining electrons, therefore (from **oilRIG**) **the oxidising agent is itself being reduced while it acts as an oxidising agent.**
- Similarly, a Reducing agent is something that allows something else to be Reduced. The substance that is being reduced is **gaining** the electrons that the Reducing agent will **lose**, therefore **the reducing agent is itself being oxidised while it acts as a reducing agent.**
- In the last two years we have considered the Reduction or the Oxidisation of *largish species* such as Organic molecules, whereas in **Ionic half-equations** we will look at the Oxidisation or Reduction of an *individual element* (instead of looking at a whole species).
- OK, we can now talk about the principles of Ionic **half-equations**².

A simple chemical reaction

- It is possible to start with one of the simpler reactions in Chemistry (say the reaction between Sodium and Oxygen) to demonstrate the mechanics of half-equations. The reaction that takes place between Sodium and Oxygen can be stated as

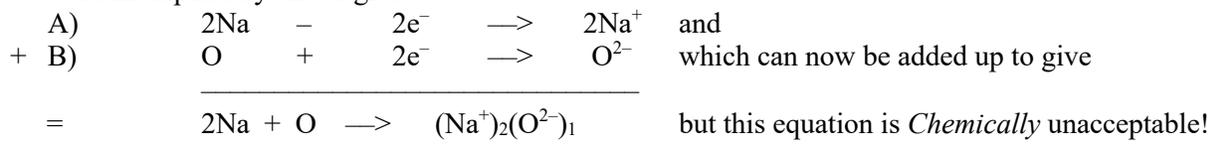


- Clearly, there are two transactions involved viz.
A) each Sodium atom loses one electron (giving, from OILRIG, an **Oxidisation** reaction)
$$\text{Na} - e^- \longrightarrow \text{Na}^+ \quad (\text{one half-equation}), \text{ and}$$

B) each Oxygen atom gains two electrons (giving a **Reduction** reaction)
$$\text{O} + 2e^- \longrightarrow \text{O}^{2-} \quad (\text{a second half-equation})$$

and each of these two statements is called a “half-equation” (because each statement represents only one half of the total transaction involved).

- However, an equation using these half-equations would not balance because each Sodium atom is giving up one electron, whereas each Oxygen atom requires two electrons to become O^{2-} ! Therefore, in order for the half-equations to give a balanced full ionic equation, the Sodium half-equation needs to be multiplied by “2” to give



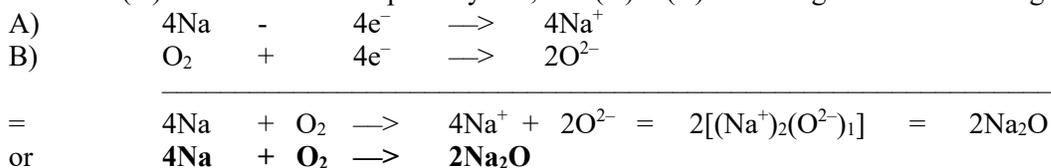
- This equation is unacceptable because Oxygen has diatomic molecules therefore the equations (A) + (B) should have read



¹ Just as ‘*aide memoire*’, could you please note that an oxidising agent will either (i) donate an “O” species to the species that is being oxidised, or (ii) it will remove an **electron** from the species that is being oxidised (OILrig), or (iii) it can accept an “H” species from the species that is being oxidised.

² Actually, I’d be a lot happier if half-equations were in fact called “part-equations” because it is possible for an ionic equation to be broken down into a lot more parts than just two ionic “half-equations”!

therefore (A) must now be multiplied by “2”, and (A) + (B) added together would now give



..... and we have now identified the *molar/stoichiometric* ratio for the reaction!

NB Getting the same number of electrons in each half-equation **IS THE KEY** to doing ionic half-equations. THAT is the essential part of the exercise because it is that which unifies the two half-equations. One half-equation must generate the same number of electrons as the other half-equation needs to complete its reaction.

- Unfortunately, even though simple reactions demonstrate clearly the principles underlying the theory of Electron transfer/Ionic half-equations/Oxidisation/Reduction/and Redox reactions, nevertheless examiners have a (not unexpected) tendency to require candidates to demonstrate a grasp of the principles involved by applying the theory to more (or very) complicated examples!
- The lovely thing about all of this however is that once the theory of the transactions has been understood, then **complicated reactions are JUST AS EASY to analyse as are simple reactions!**
- *Right, let me warn you that we are now about to get into some Chemistry that is more complicated than the stuff that we have done so far.*
- There are two very common oxidising agents in ‘A’ Level Chemistry i.e. the Dichromate (VI) ion ($\text{Cr}_2\text{O}_7^{2-}$), and the (MnO_4^-) Manganate (VII) ion³, and the most common source of the manganate ion is Potassium (VII) Permanganate (KMnO_4). The Potassium in Potassium Permanganate is a spectator ion, therefore it is only the (MnO_4^-) ion (which is written by Chemists as MnO_4^-) and not the Potassium that is acting as the oxidising agent.
- **While MnO_4^- is acting as an oxidising agent, Oxygen neither gains nor loses electrons** and its Oxidisation Number (Ox No) therefore remains at “-2”. Thus, all the time that the MnO_4^- Manganate ion, is acting as an Oxidising agent, **it is only the Mn^{7+} species in the Manganate ion that acts as the Oxidising agent – because it is the Mn^{7+} species that is gaining electrons and is thus being Reduced!**
- **I’ll say that again in a different way, because it really is VERY important!** An Mn ion is an Oxidising agent, therefore in the old-fashioned way of looking at things *it supplied Oxygen atoms to the species that it was Oxidising*. However, while MnO_4^- does have O atoms that it can release, an Mn species has no Oxygen atoms to supply, therefore in the modern way of looking at an Oxidisation reaction, using our mnemonic of OILRIG, the Oxidising agent Mn^{7+} is being reduced i.e. it is GAINING electrons from the species that is being oxidised. In this way of looking at it, *ironically Oxygen actually plays no part at all in the process of “Oxidisation”*.
- **Please remember that “oxidisation” involves the LOSS of electrons (as in OILRIG), and the very same electrons that are being lost by the species that is being “oxidised” are being gained by the Mn^{7+} species!** Let us analyse the process step by step systematically.
 $\text{MnO}_4^- = [(\text{Mn}^{7+})_1 \text{ and } (\text{O}^{2-})_4]^{1-}$, or $[\text{Mn}^{7+}(\text{O}^{2-})_4]^{1-}$ NB $[1x(+7) + 4x(-2) = -1]$.

³ “VII” indicates the Ox. No. of Manganese in the Manganate (VII) ion i.e. Mn^{7+} .

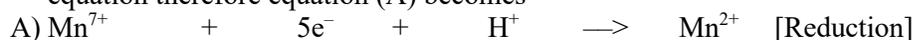
- Of the two different species inside MnO_4^- , i.e. Mn^{7+} and $(\text{O}^{2-})_4$, while the MnO_4^- ion is acting as the Oxidising agent, the four (O^{2-}) species **do not alter at all**, therefore (*in terms of electrons being lost or gained*) it is solely the Mn^{7+} species that is acting as the oxidising agent!
- OK, let's see how this works in an actual example, and the first thing that you need to know about the Manganate (VII) ion is that **when it acts as an Oxidising agent, acidified Mn^{7+} becomes an Mn^{2+} species and therefore takes on (i.e. it gains) five electrons to make the transformation.**

The Oxidisation of Fe^{2+} by the reduction of MnO_4^-

Mn^{7+} absorbs five electrons to become an Mn^{2+} species, therefore



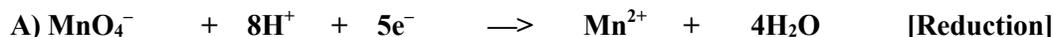
but, this happens in the presence of an acid therefore we need to add at least one " H^+ " species to the equation therefore equation (A) becomes



but, what we have not mentioned as yet is that the H^+ from the acid combines with the O from the MnO_4^- ion to form Water, therefore we need to show the Water on the RHS of the equation viz.



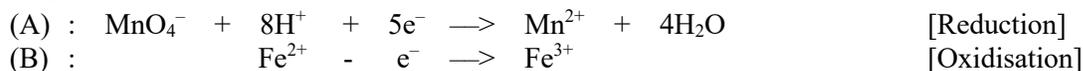
- However, we know that the MnO_4^- ion contains four O atoms, therefore we know that we will need four H_2O species on the RHS of the equation, and we will therefore need eight H^+ ions on the LHS of the equation to form the four Water molecules.
- Putting all this together we can now say that the half-equation (A) must be



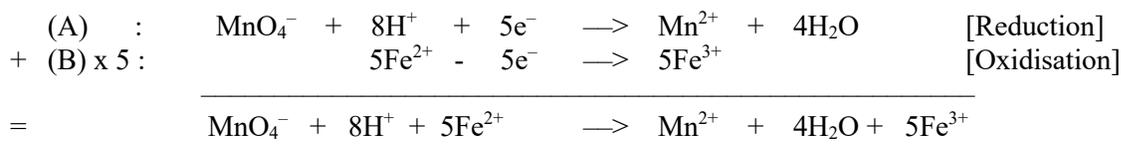
- This then is the ionic half-equation where the MnO_4^- ion acts as an Oxidising agent and is itself thereby reduced. The procedure that we have just adopted is that which is necessary **to calculate the relevant half-equation from first principles**; but, this is a fairly complicated process, and (alternatively) **the little trick to remember in your Second Year exam** is to go to the Data Sheet provided, and you will find there the relevant half-equation under the "Standard Electrode Potential Series" (which we have talked about in Chapter 10 of the Second Year Inorganic Book).
- **You will be given a data sheet in your exam therefore you will NOT need to derive it from first principles as I have done for you above!**
- There are in fact three MnO_4^- equations given in the Standard Electrode Potential Series, and you *must* be able to recognise that the equation that we have just derived is the equation that you need **with reference to the use of the MnO_4^- ion as an Oxidising agent**. You do need to know that the relevant half-equation is determined by the fact that the Manganate (VII) ion acts as an Oxidising agent *in the presence of an acid*, therefore the relevant equation (in the Data Book) is

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- OK, the (per)manganate ion in the presence of an acid acts as an oxidising agent, so how do you make use of this fact?

- Well, the context in which you are most likely to be tested on this piece of knowledge is in a “Titration” where you are given two solutions that react with each other (for example, in a Redox reaction). You will therefore start with the knowledge that one part of the reaction is an Oxidisation one, and that the other part of the reaction is a Reduction one. You start therefore by stating the two half-equations – say for example in the Oxidisation of Fe^{2+} to Fe^{3+} by MnO_4^- in the presence of an acid.



- We can now see that equation (B) must be multiplied by “5” in order to unify the two half-equations (and the electrons will then automatically cancel themselves out when the half-equations are added together).



- We have now identified the molar ratio for the reaction i.e. we now know that **1 mole** of *any* ionic **aqueous** Manganate (VII) solution (e.g. Sodium or Potassium) will react with **5 moles** of *any* ionic **aqueous** iron (II) solution (e.g. Sulphate) in the presence of **8 moles** of *any* **aqueous** acid solution, to form **1 mole** of an ionic aqueous Manganate (II) solution and **5 moles** of an ionic aqueous Iron (III) solution and **4 moles** of water – and the reactants **must** all be in aqueous form!

NB It will NOT matter whether or not there is an excess of some or of all of the reacting substances in the reaction – they will all STILL react in EXACTLY the same molar ratio as that stated in the equation above.

- If therefore you are asked to titrate a Manganate (VII) solution against an Iron (II) solution, then you would now know *exactly* what to do i.e. that you would have to add an excess of an acid, and to titrate whilst watching for the colour to change (cf. overleaf).

Reaction between MnO_4^- and $\text{S}_2\text{O}_3^{2-}$
wine into water!

- MnO_4^-
- Mn^{+4}
- Mn^{+2}
- $\text{S}_2\text{O}_3^{2-}$
- $\text{S}_4\text{O}_6^{2-}$
- Observation : Purple to colourless.
- Redox?

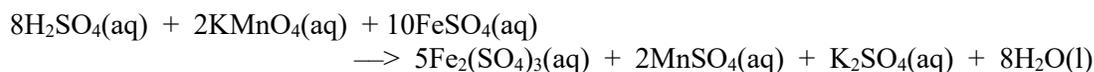
(Red) wine is coloured but Water is not. The author of the diagram is alluding to the story in the Bible of the marriage feast of Cana. If you are not familiar with the stories in the Bible, then please do not lose any sleep about the play on words.

Interestingly, the very first chemists (short for “alchemists”) were locked in dungeons by Kings/Princes/Dukes and other such people, and expected to turn ‘base metals’ into gold!

- What we have now done (by the use of ionic half-equations and ionic full equations) is to cut out all the spectator ions and to identify the essence of the reaction that is being considered in this titration – and we have done this by

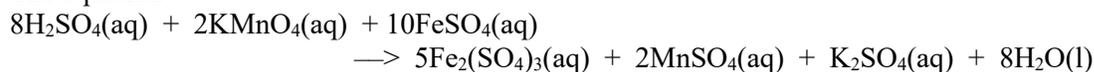
- 1) first of all formulating separately the different parts of the reaction (i.e. formulating the ionic half-equations), and then
- 2) creating a common number of electrons in each half-equation so as to allow us to unify the resulting two half-equations.

- We can easily see how this process would work in a titration, because when (for example) Sulphuric Acid is mixed with Potassium Permanganate and Iron Sulphate in the correct proportions, the following reaction will then occur



- Please could you check to see why (although I have multiplied the Ionic equation by “2”, nevertheless I have written “8 H₂SO₄(aq)”) rather than “16 H₂SO₄(aq)”? I want YOU to do this because I want YOU to question things and to think for yourself. [*Hint : count the atoms!*]

- The equation



is clearly a lot more involved than merely stating the ionic equation



and although the full equation for this titration looks complicated, it is in fact a very standard one.

- If you had been given *just* the reactants and the products involved in the titration (i.e. Sulphuric Acid, Potassium Permanganate and Iron Sulphate) with no inkling whatsoever of the molar proportions involved⁴, then before you could have made any headway with the titration, **you would first have had to balance the equation** – and I suspect that (without using ionic half-equations or a data book) you would find it extremely difficult to balance the equation! *If you could have done it – then I suspect that you probably are a Maths genius (and, for all that I know, you may well be one).*
- One of the advantages of Ionic half-equations is that they make the balancing of equations very much easier than the task would otherwise be!**
- Some titrations can be quite complicated and I promise you that if you are familiar with the manipulation of ionic half-equations, then your life will be made **much** easier, and if you are unfamiliar with the manipulation of ionic half-equations, then your life will be more difficult.
- Ionic half-equations work by
 - **breaking down an aquated ionic equation⁵ into its component parts**, and then they
 - **unify those parts by equating the number of reacting electrons in each half-equation.**
- In the ‘A’ Level written exams and in Practical exams, you may be expected to be aware of the action of the MnO₄⁻ Manganate (VII) ion as an Oxidising agent (*when in the presence of an acid*), and also of the Cr₂O₇²⁻ Dichromate (VI) ion as an Oxidising agent (*when in the presence of an acid*). There is also a third reaction that you could be expected to know viz. the reaction between a Thiosulphate ion [S₂O₃²⁻] and Iodine (*where the Iodine acts as the oxidising agent and it is thereby reduced*), so I shall now teach you how to do all three of them.

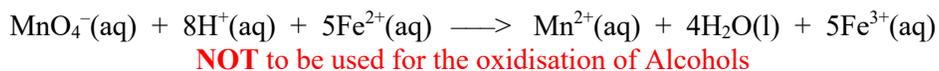
⁴ As indeed, many years ago, I was given in my Second Year Assessed Practical without being given any explanation whatsoever of what on earth was expected of me!

⁵ i.e. one in which all the spectator ions have been omitted.

- Eileen Ramsden used to give the following examples of Titration exercises in her excellent book “A Level Chemistry”.

1) Reaction between acidified Potassium Manganate (VII), KMnO_4 and $\text{Fe}^{2+}(\text{aq})$

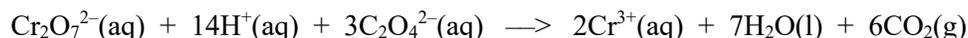
- Acidified Potassium Permanganate is a very powerful Oxidising agent. [When you get to the Oxidisation of Alcohols please remember that you must not use \$\text{KMnO}_4\$ because it is too powerful.](#) You must use acidified Potassium Dichromate (the second reaction on this page).



- At the equivalence point the purple Potassium Permanganate turns to such a pale pink that it is almost a colourless solution – and thus no indicator is needed.

2) Potassium Dichromate (VI) and Ethanedioate

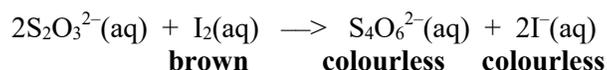
- This is the slightly gentler oxidising agent that you must use with Alcohols.



- In the Acidified⁶ Potassium Dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, the Cr^{6+} ions are reduced to Cr^{3+} ions and you get the characteristic “orange to green” colour change.

3) Iodine and Sodium Thiosulphate

- There is a lovely colour change in this titration (just as there is with Potassium Permanganate). We saw this in Chapters 7 and 7A. Just as the eventual brown colour of the Iodine starts to fade at the end of the titration, add a tiny amount of starch and the Iodine will go a bright blue (and might even go to a very dark blue black)⁷ – and at the equivalence point “bang” all the colour will disappear just like that! Iodine as a solid is purple-black but brown in aqueous solution. [There is an excellent 2 minute video of this titration on \[https://www.youtube.com/watch?v=_tZYYZ9F7fM\]\(https://www.youtube.com/watch?v=_tZYYZ9F7fM\)](#)



- We have already done an ionic half-equation using MnO_4^- , therefore let us look at an example of each of the other two in this Chapter, and then I will have given you a **very** good grounding in Ionic half-equations. Actually, you will know enough to stroll through any ‘A’ Level Titration that they ask you to do and *even enough for any entrance exam!*

⁶ The addition of a concentrated strong acid (such as concentrated Sulphuric Acid) speeds up the reaction.

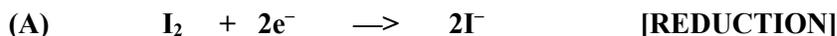
⁷ You might want to go to <https://www.youtube.com/watch?v=KWJpKNQfXWo> to see Prof Sir Martyn Poliakoff’s (Nottingham University’s) “Iodine clock” video. However, there is a huge number of ‘Iodine clock’ reactions on youtube that you can watch. (*NB The noun ‘number’ is in the singular.*) The Iodine clock reaction is one of the most videoed chemical reactions available on the internet.

- Let us start with the reaction between a Thiosulphate ion and Iodine first of all, because this is the one that you are most likely to encounter in Titration – and when we get to the topic “Trends and Patterns” you will be expected to know this reaction off by heart! I’ll do it in great detail first, and then I’ll show you how to “cheat” and use your Data Book in the exams. Actually, it is more about being intelligent than about “cheating”, but we will come to that in good time).

1) Iodine will oxidise a Thiosulphate ion (S₂O₃²⁻) into a Tetrathionate ion (S₄O₆²⁻)

(where Iodine is the Oxidising agent and the Iodine is thereby reduced I → I⁻)

- As you already know, a Sulphate ion (SO₄²⁻) is the salt of Sulphuric Acid (H₂SO₄), and **when one of the O atoms in a Sulphate ion is replaced by a Sulphur atom, then a thiosulphate ion (S₂O₃²⁻) is created.** [A tetrathionate ion (S₄O₆²⁻) is the salt of tetrathionic acid, i.e. H₂S₄O₆.]
- Iodine** is a Group VII element therefore it needs to gain one electron for it to have 8 electrons in its outermost shell, and since electrons are being gained, (then from oil**RIG**) we can see that the process is a Reductive one. We know that Iodine has a diatomic molecule (and indeed all the Halogens have diatomic molecules), therefore we are now in a position to write out the first half-equation that we need i.e.

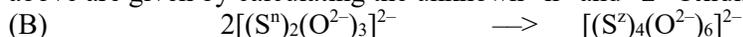


- A thiosulphate ion when not in the presence of an acid becomes a tetrathionate ion⁸**, therefore what we want here is



and please note that, because there are four S species on the RHS of the equation, you need *two* lots of the thiosulphate on the LHS of the equation.

- For ‘A’ Level purposes, other than in Hydrogen Peroxide or when in a reaction with Fluorine, Oxygen always has an Oxidisation Number of “-2”, therefore the Oxidisation Numbers of the Sulphur species above are given by calculating the unknown “n” and “z” Oxidisation Numbers in the equation below.



Start by solving for the Oxidisation Number “n” (cf. footnote⁹)

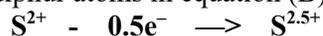
On the LHS of the equation the “2” in front of the brackets affects the *whole* of the Oxidisation Number calculation, and the calculation thus becomes

$$[(2.n.2) + \{2.(-2).3\} = 2.(-2)], \text{ therefore } 4n - 12 = -4, \text{ therefore } 4n = -4 + 12 = +8, \text{ therefore } n = 2.$$

and then on the RHS of the equation solve for the Oxidisation Number “z”

$$[z.4 + (-2).6 = -2] \text{ therefore } 4z - 12 = -2, \text{ therefore } 4z = -2 + 12 = +10, \text{ and } z = 2.5.$$

Therefore if we deduct half an electron from S²⁺ we will obtain the *ionic half-equation* for the oxidation of the Sulphur atoms in equation (B) above viz.



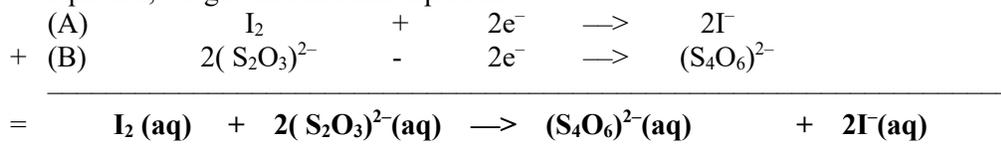
⁸ A thiosulphate ion reacting not with Iodine but with an ACID would give Sulphur, Sulphur Dioxide and Water – but that is NOT the reaction that we are considering in this instance.

⁹ In order to avoid confusing “x” as an unknown with “x” as the symbol for multiplication, I shall now use the convention of a “.” for the symbol for multiplication.

- However, there is no such thing as half an electron; and, **since there are in fact four Sulphur atoms on each side of equation (B)**, then if we multiply $[S^{2+} - 0.5e^{-} \rightarrow S^{2.5+}]$ by 4, we will get $[4S^{2+} - 2e^{-} \rightarrow 4S^{2.5+}]$ and we now have the correct numbers of S atoms, therefore if we put these two electrons and the values for “n” and “z” into equation (B) we will get the ionic half-equation
 (B) = $2[(S^{2+})_2(O^{2-})_3]^{2-} - 2e^{-} \rightarrow [(S^{2.5+})_4(O^{2-})_6]^{2-}$

- The numbers shown as indices against each element are Oxidisation Numbers (or Oxidisation States) therefore we can write the half-equation (B) as
 (B) $2(S_2O_3)^{2-} - 2e^{-} \rightarrow (S_4O_6)^{2-}$

and if we now add the two equations (A) and (B) together and cancel out the two electrons in each equation, we get the full ionic equation



NB You may at some stage be given an aqueous Iodine solution of an unknown concentration, and asked to find out *its concentration* by titrating it against a known solution of (say Sodium) Thiosulphate. Iodine dissolved in water has a brown colour and you will know the exact point at which one substance has neutralised the other by the fact that the brown liquid will suddenly turn colourless (but see Appendix B)! *It is a lovely experiment, and you will love it when you do it in your lab. Please see page 15 for further details.* I certainly love it. You will find a 2 minute video of the experiment at <https://www.youtube.com/watch?v=tZYYZ9F7fM>.

The reaction between Iodine and a Thiosulphate ion is the normal basis for the Iodine Clock Reaction (as in Chapter 7A in my Second Year Inorganic Book).

Doing the titration by “Cheating” i.e. by using a Data Book¹⁰

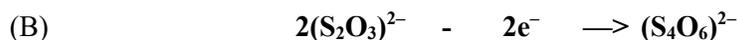
- In Chemistry, there are many standard Oxidising agents, and at University you will be expected to know their workings fairly intimately! At ‘A’ Level, if you are not aware of the workings of a particular Oxidising agent (i.e. you cannot remember what the Oxidising agent changes into when it acts as an Oxidising agent), then in most cases you can “cheat” by looking up the relevant half-equation in the Standard Electrode Potential Series in a Data Book. *Actually it is not really “cheating” at all – and it could in fact instead be construed as a display of your superior understanding of the connection between Standard Electrode Potentials and the unification of ionic half-equations (which in fact it clearly is)!*
- I really would prefer you to know how to do ionic half-equations right from first principles (because it is intellectually **so** much more satisfying to understand what you are doing, than to do something without understanding what you are doing), but **you will NOT have the time to do ionic half-equations from first principles in an exam**, therefore I will show you how to do them by using the Standard Electrode (or Redox) Potential Series (SEP) table in a Data Book (so that in an exam you can just whip through the Maths involved in literally just a few seconds).

¹⁰ By the way, in your data book you may see these equations written with an “=” sign between the two sides; but, this is clearly incorrect because the species on the LHS of the equations are not mathematically **equal** to those on the RHS. However, Chemists are not as robust Mathematicians as they ought to be, but sadly, that’s life!

- If you want to know the reaction between Iodine and a Thiosulphate ion, then go to the SEP table in your Data Book and you will see there the relevant half-equation viz.



- There is only one *Thiosulphate* half-equation given in your data book, but it is given back to front (so to speak) because the convention is always to write Redox equations so that the electrons in the equation have a positive sign in front of them. It is shown as $\frac{1}{2} (\text{S}_4\text{O}_6)^{2-} + \text{e}^- \longrightarrow (\text{S}_2\text{O}_3)^{2-}$ and the way that the equation is written is influenced by the electrostatic relationship that Sulphur has to Hydrogen (or, cf. Chapter 10) by the potential difference between a Sulphur half-cell and a Hydrogen half-cell).
- All that you really need to know is that **this is a reversible reaction** therefore it is perfectly legitimate for us to multiply it by “2” and write the equation as $(\text{S}_4\text{O}_6)^{2-} + 2\text{e}^- \rightleftharpoons 2(\text{S}_2\text{O}_3)^{2-}$ or



- We now have exactly the same two half-equations that we previously derived from first principles on page 2, and “cheating” (*but it is not really “cheating”*) is a lot quicker than doing it from first principles! The remainder of the exercise (i.e. in creating the full aqueous *ionic* equation) is exactly the same as before.
- I **do** want you to be able to do the exercise both ways i.e. I want you to be able to work out the half-equations from first principles, AND I want you to be able to use your brains and short circuit the work involved by using the SEP table in your Data Book.
- In the next exercise we shall examine the fact that a Dichromate (VI) ion acts as an Oxidising agent when in the presence of an acid – and **this is precisely the relationship that we exploit** in Organic Chemistry/“Chains & Rings” when we oxidise Alcohols into different sorts of Carbon molecules (such as Aldehydes/Ketones/and Carboxylic Acids).

2) A $\text{Cr}_2\text{O}_7^{2-}$ Dichromate (VI) ion acting as an Oxidising agent in an acid solution

[A $\text{Cr}_2\text{O}_7^{2-}$ Dichromate (VI) ion is a less aggressive oxidising agent than an MnO_4^- Manganate (VII) ion, and this fact is rather important in Organic Chemistry.]

- Let us start by considering from first principles what happens in this operation viz.
 Dichromate (VI) ion + An acid \longrightarrow Chromate (III) ion + Water
 $[(\text{Cr}^{6+})_2 (\text{O}^{2-})_7]^{2-} + \text{H}^+ \longrightarrow \text{Cr}^{3+} + \text{H}_2\text{O}$
Orange colour *Blue colour*¹¹
- There are two “ Cr^{6+} ” species on the LHS of the equation, therefore we need “ 2Cr^{3+} ” species on the RHS of the equation, and the 7 O atoms on the LHS of the equation need 14 H atoms to form 7 molecules of Water, therefore we get



¹¹ When something that is blue is mixed with something that is orange, then the resulting mixture appears green – and it is precisely the colour change from orange to green when the blue Cr^{3+} ion mixes with the orange Cr^{6+} ion to give a green coloured mixture that tells us that this reaction is taking place.

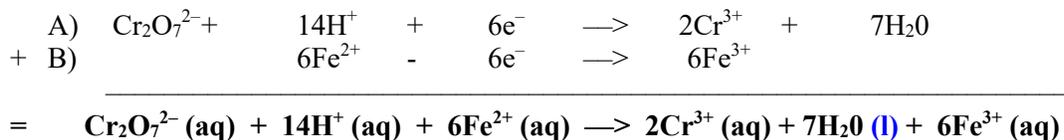
- We now need to balance **the charges** because on the LHS of the equation the positive and negative charges add up to “12” [i.e. “-2” on the Chromate ion plus “+14” on the Hydrogen atom which gives “+12”], whereas on the RHS of the equation they add up to “+6” [i.e. “2 x (+3)”].
- There are therefore 6 too many positive charges on the LHS of the equation, and if we were to **ADD 6 (negative) electrons** to the LHS of the equation, then this would REDUCE the positive charge on the LHS of the equation by “6” because each electron has a single negative charge! We would therefore get
 “(-2) + (+14) + (-6) = 12 - 6 = 6 = 2 x (+3)”, and this gives us our first half-equation



and, if we wanted to use the SEP table in the Data Book, there is only one equation given for $\text{Cr}_2\text{O}_7^{2-}$, and having multiplied it by “2” we would get exactly the equation as that which we have derived above!

- Therefore what we have is a reaction in which the $\text{Cr}_2\text{O}_7^{2-}$ Dichromate (VI) ion is absorbing (or gaining) six electrons (*and from OilRIG it is being reduced*) in the presence of an acid, therefore it is an Oxidising agent (Oxidisation involves the loss of electrons)!
- We could for example use it to oxidise Fe^{2+} to Fe^{3+} (remember **OILRIG**), therefore the second half-equation that we would need would be
 B) $\text{Fe}^{2+} - \text{e}^- \longrightarrow \text{Fe}^{3+}$ [because (+2) - (-1) = (+3)]

and all that we would then need to do would be to equate the electrons [by multiplying equation (A) by “6”] to unify the half-equations, and we would then get the aqueous ionic equation

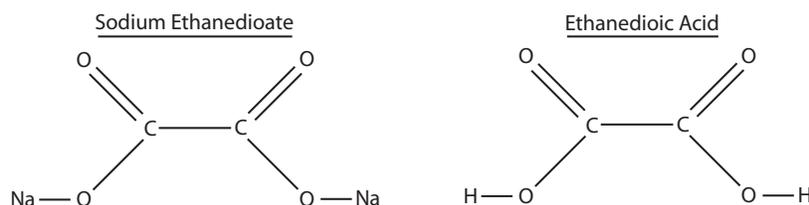


NB We do of course (in the final stage) have to put in the states or phases of each substance in order to give us an **AQUATED IONIC EQUATION**, and in Appendix A you can see an example of a full ionic equation where a Dichromate (VI) ion has been used as an oxidising agent (and please do remember that an *OXIDISING* agent will be *REDUCED* as it performs its oxidising function).

- I shall do one more example for you
 - because ionic half-equations are so important
 - because they are quite difficult to do (until you get the hang of them), and
 - because you will quite often encounter the next ion in “Chains & Rings”.
- The ion that I shall use is called the “dioate” ion, and it comes from the carboxylic acid “Ethanedioic Acid” or “Oxalic Acid”. [If you think about the “-COOH” bit of a Carboxylic Acid, and then imagine two of these bits joined together back-to-back, then that is exactly what “Ethanedioic Acid” looks like (cf. the diagram below).]

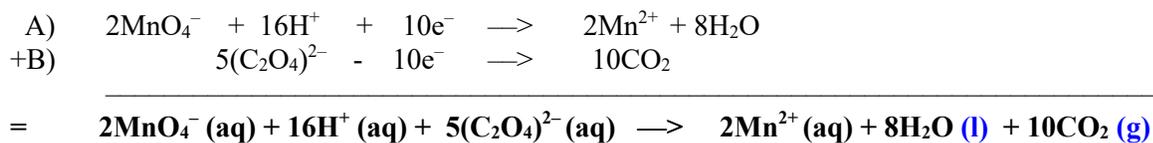
3) The analysis of the reaction between an Oxidising agent (MnO₄⁻) and a Dioate ion

- The ion that will here be oxidised into Carbon Dioxide is called the “Ethane-dioate ion” (or “Ethanedioate ion”) and it is written (C₂O₄)²⁻, and it can be found for example in Sodium Ethanedioate Na₂C₂O₄, and in Ethanedioic acid H₂C₂O₄. In the example that I am about to do, I have chosen to use the MnO₄⁻ Permanganate (VII) ion as the oxidising agent. You do need to know that when a dioate ion is oxidised, it forms Carbon Dioxide. *[In fact, on Oxidisation, ALL Carbon compounds form either Carbon Monoxide and this is called “incomplete oxidisation”, or they form Carbon Dioxide and this is called “complete oxidisation”.]*
- Just in case you are starting to forget how to draw bond line diagrams, I shall draw both Sodium Ethanedioate Na₂C₂O₄, and Ethanedioic acid H₂C₂O₄ for you (*and please do remember that we are talking about a “Dioate” and a “Dioic Acid” – and in Greek “di” means “two”*).



- You should by now be able to recognise the MnO₄⁻ Manganate (VII) half-equation that you require!
 (A): $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [Reduction]
 (B): $(\text{C}_2\text{O}_4)^{2-} - 2\text{e}^- \longrightarrow 2\text{CO}_2$ [Oxidisation]
 and it is obvious that equation (A) has to be multiplied by “2” and equation (B) by “5” in order to equate the two half-equations.

- If we do this and then add equations (A) and (B) together we get



- As you can now see, Ionic half-equations are actually not that difficult to do once you get the hang of them. They just look difficult at first – and if you don’t have to do them from first principles (and you can, when possible, use the SEP table in a Data Book), then **they really are not difficult at all!**
- In order to knock off these complicated reactions within seconds, it is vital to MEMORISE the changes that take place with the common Oxidising agents – and the changes that take place to the above-mentioned Oxidising agents are

- Mn⁷⁺ becomes Mn²⁺ [the positive charge has been **Reduced**]
- Cr⁶⁺ becomes Cr³⁺ [the positive charge has been **Reduced**]
- I₂ becomes 2I⁻ [the zero charge has been **Reduced**]
- Fe³⁺ becomes Fe²⁺ [the positive charge has been **Reduced**]

- There is no substitute for knowing these changes – and unless these changes are known, the only other way is by having access to a Data Book.**

- Clearly if an oxidising agent is being **REDUCED**, then the other substance in the reaction is being **OXIDISED** – and we can see that by looking at what is happening in the reactions that we have discussed in this Chapter viz.

Ethanedioate ($\text{C}_2\text{O}_4^{2-}$) becomes CO_2 therefore C^{3+} becomes C^{4+} ,
and an increase in positive charge = **Oxidisation** or, a loss of electrons = **Oxidisation**

- and a Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) ion reacting with Iodine becomes ($\text{S}_4\text{O}_6^{2-}$)
therefore S^{2+} becomes $\text{S}^{2.5+}$,
and an increase in positive charge = **Oxidisation** or, a loss of electrons = **Oxidisation**

NB A Thiosulphate reacting not with Iodine but with an ACID would give Sulphur, Sulphur Dioxide and Water.

- I have talked about the Manganate/the Thiosulphate/and the Dichromate ions as oxidising agents, but anything that will allow another species to lose electrons (i.e. to oxidise) is an oxidising agent. An oxidising agent oxidises another species by taking on/gaining the electrons that the species that is being oxidised is losing (and vice versa). Purdue University¹² says

OXIDISING AGENTS

“Atoms, ions, and molecules that have an unusually large affinity for electrons tend to be good oxidizing agents. Elemental fluorine, for example, is the strongest common oxidizing agent. **F₂ is such a good oxidizing agent that metals, quartz, asbestos, and even water burst into flames in its presence.** Other good oxidizing agents include O₂, O₃, and Cl₂.

Another place to look for good oxidizing agents is among compounds with unusually large oxidation states, such as the permanganate (VII) ion (MnO_4^-), the chromate (VI) ion (CrO_4^{2-}), and the dichromate (VI) ion ($\text{Cr}_2\text{O}_7^{2-}$), and also nitric acid (HN^{5+}O_3), perchloric acid ($\text{HCl}^{7+}\text{O}_4$), and sulfuric acid ($\text{H}_2\text{S}^{6+}\text{O}_4$). These compounds are strong oxidizing agents because **elements become more electronegative as the oxidation states of their atoms increase.**

REDUCING AGENTS

Good reducing agents include the active metals, such as sodium, magnesium, aluminium, and zinc, which have relatively small ionization energies and low electro-negativities. Metal hydrides, such as NaH, NaBH₄, CaH₂, and LiAlH₄, which formally contain the **H⁻** ion, are also good reducing agents.

Some compounds can act as either oxidizing agents or reducing agents. One example is hydrogen gas, **which acts as an oxidizing agent when it combines with metals and as a reducing agent when it reacts with non-metals.**

¹² Where the spelling is theirs and not mine.

Common Oxidising agents

Non-metals love to gain electrons

- O₂
- O₃ (Ozone)
- Cl₂
- MnO₄⁻ (the Manganate ion)
- CrO₄²⁻ (the Chromate ion)
- Cr₂O₇²⁻ (the Dichromate ion)
- HNO₃
- HClO₄ (Perchloric Acid)
- H₂SO₄
- Chlorine/Bromine/Iodine
- H₂O₂ (Hydrogen Peroxide)

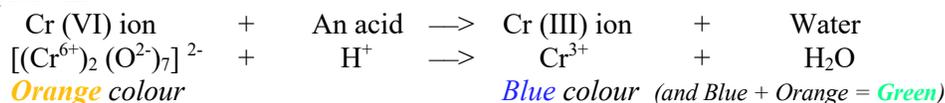
Common Reducing Agents

Metals love to give up electrons

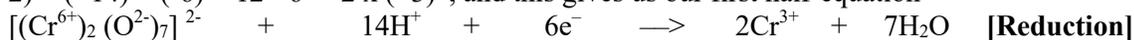
Sodium
Magnesium
Aluminium
Zinc
Iron (II) ions (Fe²⁺)
Iodide ions
Sulphite ions (SO₃²⁻)
NaH
CaH₂
NaBH₄
LiAlH₄

Appendix A

- An Alcohol can be oxidised into an Aldehyde/a Carboxylic Acid/or a Ketone depending on what sort of Alcohol it is and what the reaction conditions are. Whatever happens, an oxidising agent in conjunction with concentrated sulphuric acid **must** be used – and *the Sulphuric Acid is here NOT acting just as a catalyst (because during the oxidisation reaction the Sulphuric Acid will here be converted into both Sodium and Chromium sulphates)*. The $\text{Cr}_2\text{O}_7^{2-}$ Chromium (VI) Dichromate ion is normally used and it can come from either Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Let us, for the purposes of this exercise, use Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), concentrated Sulphuric Acid (H_2SO_4) and Ethanol $\text{CH}_3\text{CH}_2\text{OH}$), and let us start by considering the operation from first principles viz.



- There are two “ Cr^{6+} ” species on the LHS of the equation, therefore we need “ 2Cr^{3+} ” species on the RHS of the equation. The 7 O atoms on the LHS of the equation will form 7 molecules of water therefore we need 14 protons from the acid to form the 7 molecules of Water, and we get
- $$[(\text{Cr}^{6+})_2 (\text{O}^{2-})_7]^{2-} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$
- We now need to balance **the charges** in the equation because on the LHS of the equation they add up to “12” [ie “(-2) + (+14) = 12”], whereas on the RHS of the equation they add up to “6” [i.e. “2 x (+3)”].
 - There are therefore 6 too many positive charges on the LHS of the equation, and if we were to **ADD 6 (negative) electrons** to the LHS of the equation, then this would REDUCE the positive charge on the LHS of the equation by “6” because each electron has a single negative charge! We therefore get “(-2) + (+14) + (-6) = 12 - 6 = 2 x (+3)”, and this gives us our first half-equation



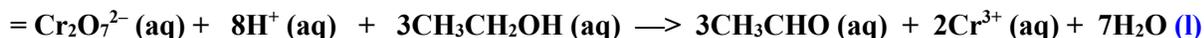
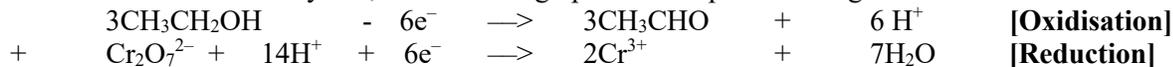
- When a Primary Alcohol is converted into an Aldehyde two H^+ species are ejected, and since there must be an Oxidisation reaction to balance the Reduction reaction, the Alcohol has to lose at least one electron therefore we now get the basis of our second equation viz.



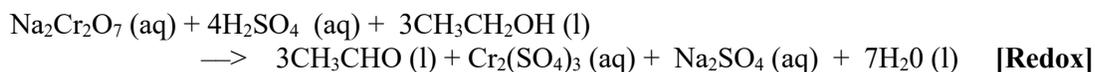
but we now need to put 2e^- into the equation to balance the electrostatic charges



- Lastly, in order to balance the number of electrons in the two Redox equations we must multiply the Oxidisation reaction by “3”, and on adding up the two equations we get



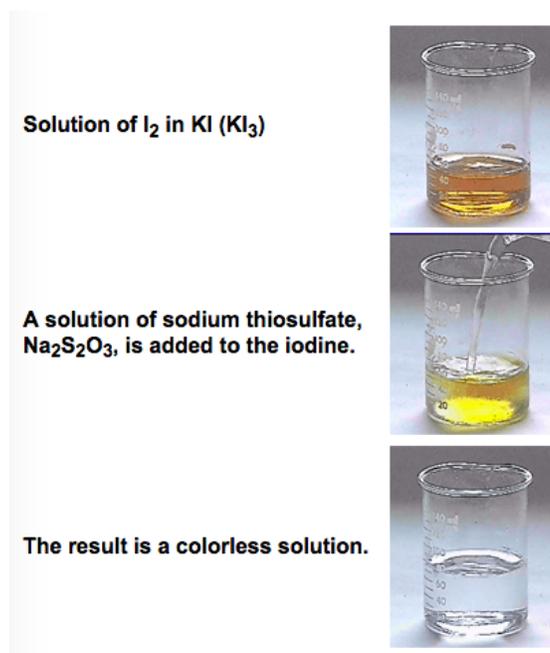
and when we insert the spectator ions (where 4H_2 is the equivalent of 8H) we get



APPENDIX B

The Iodine-Thiosulphate reaction in practice (where the Iodine is reduced, and the Thiosulphate is oxidised)

- In practice it is not easy to work with Iodine.* It is only sparingly soluble in water and it can easily be lost from the solution because of its volatility. Iodide ions such as I_3^- are much more soluble than Iodine, and therefore, in practice, for this titration Iodine can be dissolved in Potassium Iodide where $KI(aq) + I_2(s) \rightarrow KI_3(aq)$. As you can see from the pictures below, the addition of Sodium Thiosulphate then renders the Iodide solution colourless.



- In this experiment, Iodine is generated in a conical flask by reacting a standard (0.02 mol dm^{-3}) solution of potassium iodate (KIO_3) for each titration with excess potassium iodide. **Iodine is thus liberated** from the iodate and iodide according to the equation:



The Iodine solution, which is a golden-brown colour (cf. above) can be titrated against a sodium thiosulfate solution. The sodium thiosulfate solution is placed in a burette and, as it is added to the conical flask, it reacts with the Iodine and the colour of the solution fades. When it reaches a very pale yellow colour, a few drops of a freshly prepared starch solution are added. The solution becomes *bluey-black*, and the titration is continued until it goes colourless. The titration reaction may be represented by the equation:



- To avoid forming too much starch-Iodine complex, starch indicator is added only when it is **close to the equivalence point**.
- There is an excellent 8 minute video on youtube on doing the calculations in this experiment at <https://www.youtube.com/watch?v=w4tpyDLK5vA> .

APPENDIX C

- I am putting this table here so that you can relate the things that we have talked about in this Chapter (Redox / Titration) with the things that we talked about elsewhere (Voltaic cells where electrons flow from the half-cell with the smaller E° to the half-cell with the larger E°). From OILRIG you know that the half-cell that is losing the electrons is being oxidised and the half-cell gaining the electrons is being reduced. If you now look at the SEPs/SRPs below you will see that the values for the MnO_4^- half-cell is given as 1.51 and that for the Iodine half-cell is 0.54. The Iodine half-cell is the smaller half-cell on the Standard Electrode Potential number line and is being oxidised (OIL), and it is thus a reducing agent.

Standard Reduction Potentials at 25°C (298K)

<u>Half-Reaction</u>	<u>$E^\circ(\text{V})$</u>
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.81
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.78
$\text{PbO}_2(\text{s}) + \text{HSO}_4^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au}$	+1.69
$\text{Pb}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq})$	+1.67
$2\text{HClO}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+1.63
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$2\text{HBrO}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Br}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+1.60
$\text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$	+1.52
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Mn}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq})$	+1.51
$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Cl}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	+1.47
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.40
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{O}_2 + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{ClO}_4^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{I}_2(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	+1.20
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.09
$\text{HNO}_2(\text{aq}) + \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	+0.89
$\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{BrO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Br}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	+0.76
$\text{MnO}_4^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.60
$\text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.56
$\text{MnO}_4^{2-}(\text{aq}) + \text{e}^- \rightarrow \text{MnO}_4^{2-}(\text{aq})$	+0.56
$\text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.56
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.54
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.52
$\text{H}_2\text{SO}_3(\text{aq}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow \text{S}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	+0.45
$\text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq})$	+0.45
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{ClO}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	+0.36
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	+0.22

Increasing Strength of Oxidizing Agent

Increasing Strength of Reducing Agent