

Second Year blog on Equilibrium Constants: 4th May 2019

(This is a **revision** blog. It is merely a *summary* of some of the things that you need to know. Everything in this blog can be found in the relevant Chapters of the two books.)

Halide Ions (F⁻ / Cl⁻ / Br⁻ / I⁻ / and At⁻) as reducing agents

Let me sum it up as simply as I can.

- Halide ions (F⁻ / Cl⁻ / Br⁻ / I⁻ / At⁻) are formed when Halogen atoms take on the extra electron that they require to achieve the stability of the Noble Gas configuration.
- From OILRIG we can see that if a Halide ion were then to give up or to **lose** its extra electron it would undergo Oxidisation (**OIL**) – and anything that undergoes Oxidisation is a Reducing agent (because the species that **gains** the electron that the Halide ion lost has now gained an electron, **RIG**) which gives the Redox reaction **OILRIG**. If no changes in Oxidisation States occur, then the reaction is not a Redox reaction.
- **Please note that OIL and RIG must always happen together. One cannot happen without the other.** That is the nature of a REDOX reaction. **One species loses an electron, and another species gains that electron!**
- When talking about the reaction of Halide ions with concentrated Sulphuric Acid, we are looking at whether or not Sulphuric Acid can persuade a Halide ion to give up its extra electron, and the thing to remember is that
 - F⁻ and Cl⁻ will not do so because the extra electron is held too tightly to the nucleus for H₂SO₄ to dislodge it **therefore no redox reaction will occur** (it is a matter of how much energy is needed to dislodge the electron), but
 - the extra electron in Br⁻ / I⁻ /and At⁻ are far enough away from the nucleus for it to take less energy to dislodge the electron, therefore a redox reaction **will** occur. (NB The shorter the bond, the more energy it takes to break the bond.)

NB If you want a more detailed explanation involving the enthalpies involved in these reactions, then Jim Clark's excellent website goes into it in more detail than I wish to do.

- If a Halide ion is being Oxidised, then the question to ask is "What are the changes that are going on in the Oxidisation State of Sulphur in the redox reaction where a redox reaction takes place?", and the answer is as follows.

Oxidisation State of Sulphur in				
H₂SO₄	NaHSO₄	SO₂	S	H₂S
+6	+6	+4	0	-2

therefore

- with F⁻ and Cl⁻, Sulphur is not being reduced at all (because S still has an Ox. No. of "+6" in NaHSO₄)
- Br⁻ will reduce the S atom from +6 to +4 (where the S in SO₂ has an Ox. No of "+4")
- I⁻ will reduce the S atom from +6 all the way to -2 (where H₂S has an Ox. No. of "-2").

In essence, that sums up what is happening.

OK, now let us look at what happens and how it happens.

This topic is complicated by the fact that (i) some textbooks publish purely **Ionic** equations for the reactions involved, while others publish full **chemical** equations for the reactions and (ii) because different reactions can happen **e.g. with Iodide ions four different reactions happen one after another** before the reaction eventually finishes. However, there are a number of very good videos on this topic uploaded to *youtube* including

- i) A video by Dr Simon Orchard (the Headmaster of Our Lady of Sion School in Worthing, West Sussex) on the **simplest set of reactions** that you are expected to know at 'A' Level by all the exam boards. You can find his video at <https://www.youtube.com/watch?v=m4YPolUd2j0> . Redox reactions **do not occur** with concentrated Sulphuric Acid and Fluoride and Chloride ions, and the reactions that Dr Orchard describes are **For Bromides, first**
- $$\text{i) NaBr (s) + H}_2\text{SO}_4 \text{ (l) } \longrightarrow \text{NaHSO}_4 \text{ (s) + HBr (g)}$$
- and then**
- $$\text{ii) 2HBr (g) + H}_2\text{SO}_4 \text{ (l) } \longrightarrow \text{SO}_2 \text{ (g) + 2H}_2\text{O (l) + Br}_2 \text{ (g)}$$

NB Please keep in mind that you can get a Br⁻ ion from both NaBr and HBr, and a problem arises because Sulphuric Acid can start to attack HBr before the first reaction has finished (and the textbooks do **not** make this clear).

For Iodides, first

$$\text{i) NaI (s) + H}_2\text{SO}_4 \text{ (l) } \longrightarrow \text{NaHSO}_4 \text{ (e) + HI (g)}$$

and then

$$\text{ii) 8HI (g) + H}_2\text{SO}_4 \text{ (l) } \longrightarrow \text{H}_2\text{S (g) + 4I}_2 \text{ (g) + 4H}_2\text{O (l)}$$

but you get S (s) and SO₂ (g) generated along the way.

- ii) There is another *very* good video on **theory** by Dr Chris Harris of Allery Tutors in Morpeth, Northumberland, <https://www.youtube.com/watch?v=vOBqSc7dNi0> , who represents the reactions as follows.

If you watch Dr Harris' video, it will not only take you through the reactions of concentrated Sulphuric Acid and the Halide ions, but it will also be *excellent* revision for you on aquated ionic half-equations.

OXIDISATION NUMBER OF SULPHUR IN THE RELEVANT SPECIES

<u>Halide Ions</u>	<u>NaHSO₄</u>	<u>SO₂</u>	<u>S</u>	<u>H₂S</u>
Ox No.	+6	+4	0	-2
F ⁻	A			
Cl ⁻	A			
Br ⁻	A	B		
I ⁻	A	B	C	D

where A/B/C/D represent the following reaction steps

A	NaCl (s) + H ₂ SO ₄ (l) → NaHSO ₄ (s) + HCl (g)	full chemical reaction
B	Br ⁻ (s) + H ₂ SO ₄ (l) + 2H ⁺ (l) → Br ₂ (g) + SO ₂ (g) + 2H ₂ O (l)	combined ionic and chemical
C	6I ⁻ (s) + H ₂ SO ₄ (l) + 6H ⁺ (l) → 3I ₂ (g) + S (s) + 4H ₂ O (l)	combined ionic and chemical
D	8I ⁻ (s) + H ₂ SO ₄ (l) + 8H ⁺ (l) → 4I ₂ (g) + H ₂ S (g) + 4H ₂ O (l)	combined ionic and chemical

- iii) Finally, there is also a very useful video by Tine Willis at

<https://www.youtube.com/watch?v=I5O5dYEdO4>

on the mechanics of the **tests** that are involved in these reactions viz.

- **Halide ionic gases are *acidic* and they will turn blue litmus paper (or yellow litmus paper) red.**
- **Halide ionic *gases* react with Ammonia vapour and form a white cloud of an Ammonium Halide.**
- **Orange-yellow acidified Potassium Dichromate solution soaked into ordinary filter paper will be bleached colourless in the presence of Sulphur Dioxide gas, SO₂ (g), and**
- **Damp (white) Lead Acetate/Lead Ethanoate paper will turn black in the presence of Hydrogen Sulphide gas, H₂S (g). *Hydrogen Sulphide has the nasty smell of rotten eggs.***

- iv) You will also find a very detailed explanation (by the great Jim Clark) of all the theory involved at <https://www.chemguide.co.uk/inorganic/group7/halideions.html> and he introduces considerations about Enthalpy into his analysis of the reactions involved. (*I do not introduce Enthalpy into this topic. That makes a complicated topic even **more** complicated.*)

The four videos on that I have mentioned are excellent revision of a large number of topics for the exams, and are well worth the time that you will spend watching them (between one and two hours), and as you are watching them, please remember that you are doing it as revision of *different topics* for the exams!

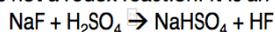
I personally think that the time you need to spend on getting to **really** understand the reactions between conc. H₂SO₄ and the Halide ions is **not** worth it. You may want to learn just the things in blue on page 1, and then spend your time in getting to grips with one of the big topics in Organic Chemistry (e.g. Carbonyl compounds) or in Inorganic (such as Electrochemistry). You could also just get to grips with Section A below (the Summary of the reactions) and ignore Section B (which goes into the *details* of the reactions involved). I hope that all is of some help, and it prevents you from wasting your time. **Remember that TIME is the most precious thing that you have.**

This is a simple summary of what I shall discuss in detail without the discussion of Enthalpy that Jim Clark goes into on his website. I show you an Enthalpy Profile Diagram from Mr Clark's website overleaf (and I really cannot sing Mr Clark's praise too highly). "scienceschool.com" puts the reactions as follows.

REACTIONS OF HALIDE IONS WITH SULPHURIC ACID

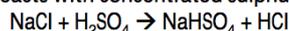
Fluoride ions and sulphuric acid

A fluoride ion is a very weak reducing agent. This is not surprising as fluorine is very reactive, and so gains electrons very easily to make fluoride ions. To reverse this reaction would be difficult. The reaction of fluoride ions, in solid sodium fluoride, with concentrated sulphuric acid is not a redox reaction. It is an acid-base reaction:



Chloride ions and sulphuric acid

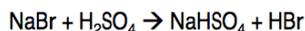
A chloride ion is also a very weak reducing agent, so it reacts in a similar way to fluoride ions. Solid sodium chloride reacts with concentrated sulphuric acid like this:



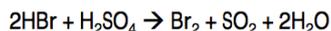
In this reaction, and the fluoride ion reaction above, a hydrogen ion (H⁺) has been lost from the sulphuric acid and joined with the halide ion. The sodium ion is just a spectator to the reaction.

Bromide ions with sulphuric acid: A redox reaction

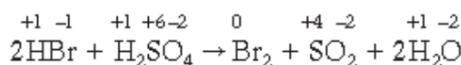
Bromide ions start off reacting in a similar way to chloride ions, so some misty HBr fumes may be seen:



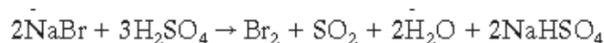
Bromide ions in the hydrogen bromide are quite strong reducing agents, so they reduce the sulphuric acid and are oxidized to red-brown bromine:



This is a redox reaction as there is a change in oxidation states:



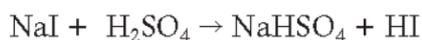
Here is an equation for the reaction in one step;



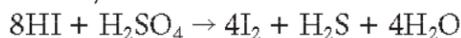
The iodide ion: an even stronger reducing agent

An iodide ion is so large that it loses an electron easily, so it is an electron donor, a strong reducing agent. It is so strong that it reduces sulphuric acid to hydrogen sulphide:

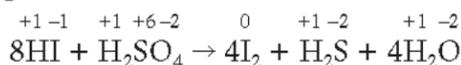
1 HI is made:



2 Then the HI is oxidized, and so reduces the sulfuric acid:

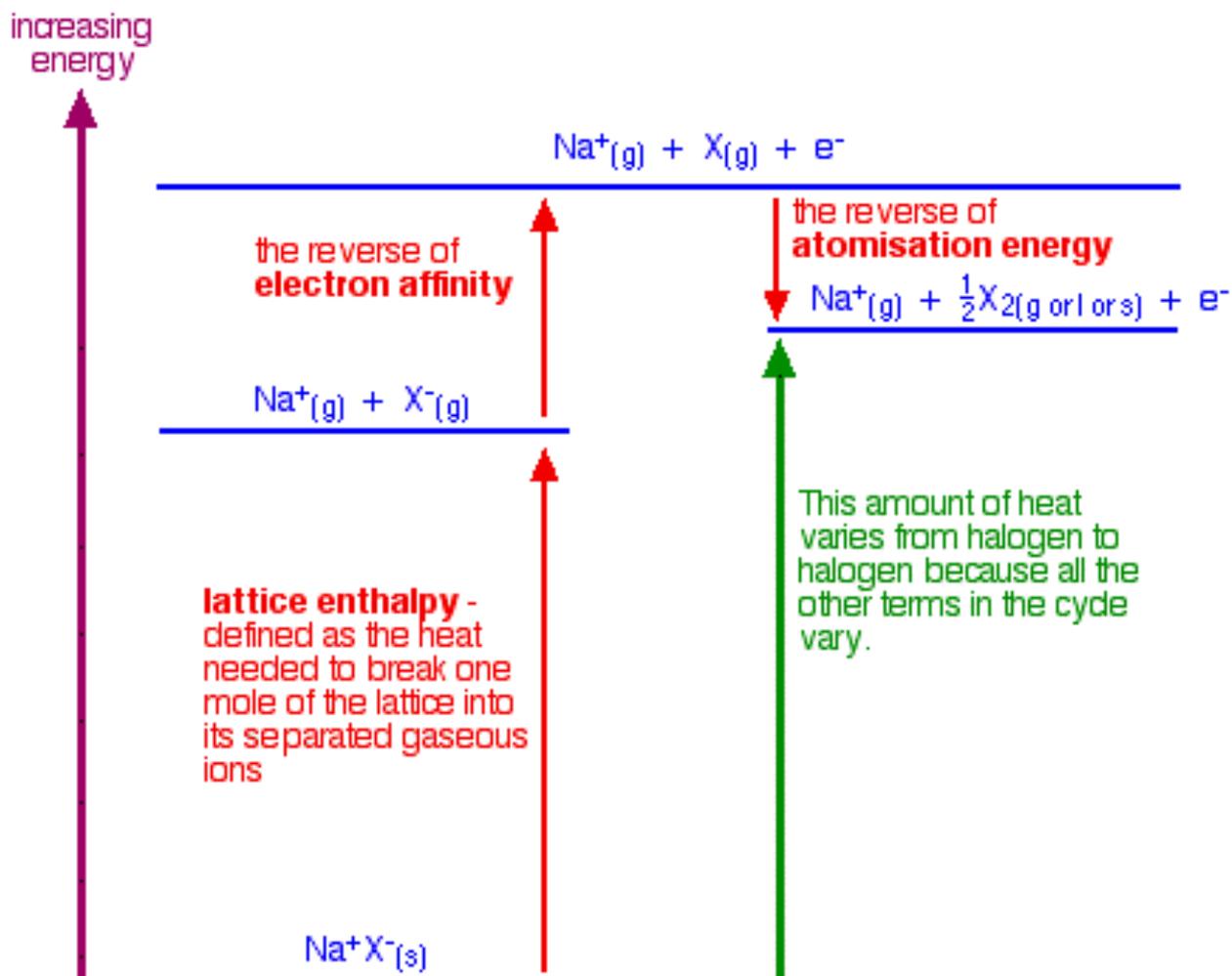


This time the change in oxidation states is this:



Should you want to read about the Enthalpy involved in these reactions, you can read Jim Clark's article on the reaction of Sulphuric Acid and the Halides, and you will find it on

<https://www.chemguide.co.uk/inorganic/group7/halideions.html> .



OK, this is now a detailed explanation of the reactions of concentrated H₂SO₄ and the Halide ions

These reactions are exothermic ones, therefore some of the substances generated turn into **gases** in these reactions.

CAUTION It is one thing to talk about HF(g) or HCl(g) being generated in a reaction but quite another thing to deal with the highly acidic substances that are *actually* generated. **You really do NOT want to inhale the fumes of dangerous Halide Acid gases. They can damage your lungs.**

PLEASE DO NOT PERFORM THIS REACTION OTHER THAN IN THE TINIEST OF QUANTITIES IN A TEST TUBE AND IN A FUME CUPBOARD, and then please wash the test tube out very carefully thereafter. Better still, just watch someone else doing the reactions on *youtube*! (I show my students videos of other people doing *dangerous* experiments. Nearly all of my students do **not** want to read Chemistry for their Degree. They just want an A or an A* in Chemistry so that they can gain admittance to the University of their choice – and I quite understand such an objective.)

A bit about Sulphuric Acid

- Sulphuric Acid is a **strong protonating** agent. (I deal with this elsewhere.)
- Sulphuric Acid is a **moderate oxidising** agent (**OILRIG**).
- Sulphuric Acid is a **dehydrating** agent¹ (**NB Dehydration is a chemical process. “Drying” is a physical process as in drying the clothes on a washing line or drying up the washing after a meal.**) Sulphuric Acid can be used to remove a molecule of water **chemically** from organic compounds. (I talk about ‘dehydration’ in Organic Chemistry e.g. as in the conversion of Alcohols into Alkenes on pages 12/13 of Chapter 6 of the First Year book on Organic Chemistry.

When you get down to the *details* of this reaction the process becomes quite complicated, but **most UK Exam Boards do NOT require you to understand the minute details of the reaction of Halide ions with Sulphuric Acid.**

It would be **monstrously** unfair if the examiners were to ask you anything but the most cursory of questions about the reactions of concentrated Sulphuric Acid and Halide ions. In my opinion, all that you should be required to know is that if you are using say Sodium Halides then if the reactions are allowed to go right to the end

- concentrated Sulphuric Acid will form double-displacement reactions with Fluoride and Chloride ions, but that
- with Bromide ions, **Br₂ (g)** and **SO₂ (g)** [and **Na₂SO₄ (s)** and **H₂O (l)**] will be produced, and
- with Iodide ions, **I₂ (g)** and **H₂S (g)** [and **Na₂SO₄ (s)** and **H₂O (l)**] will be produced.

On the whole, the examiners just want you to have a superficial understanding of the reactions. Let us therefore

- A) look at a summary of the reactions,**
- and for those very few of you who may actually want to know about the details of the reactions involved
- B) we will look at the details of the reactions.**

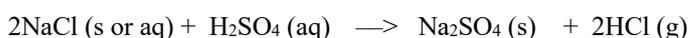
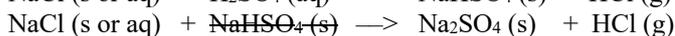
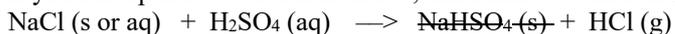
¹ “Dehydrating” is not the same as “drying”. Concentrated Sulphuric Acid will react with the substance and remove not wet water (as in the wringing out of a face-flannel) but **molecules** of water from the very chemical composition of the substance.

Section A: A summary of the simple reactions

- With a Fluoride or a Chloride ion, concentrated Sulphuric Acid will first dissociate one of its protons e.g. if we look at NaCl and H₂SO₄ we get
NaCl (s or aq) + H₂SO₄ (aq) → NaHSO₄ (s) + HCl (g) [effervescence as HCl(g) is generated]
and then the NaHSO₄ will dissociate the *second proton*
NaCl (s or aq) + NaHSO₄ (s) → Na₂SO₄ (s) + HCl (g)

NB Please note that there are NO changes in Oxidisation States in these reactions. Check it for yourself and see. These are not REDOX reactions. If there is no change in the Oxidisation Numbers that are involved, then it CANNOT be a Redox reaction. These are just double-displacement reactions.

- If you add up the two reactions above, and cancel out the NaHSO₄ on each side and you get



NB You need a temperature higher than RTP for the second proton to be disassociated. Therefore please just *learn* this 2-stage reaction for Fluoride and Chloride reactions with Sulphuric Acid. These are not redox reactions. They are just simple double-displacement reactions.

However, Bromide and Iodide ions do undergo REDOX reactions with concentrated Sulphuric Acid.

Different reactions take place (at different temperatures), but I am going to explain just one set of reactions for Bromide and Iodide ions with concentrated Sulphuric Acid (the one that I think is the most plausible one given all the facts as I know them).

In contrast to F⁻ and Cl⁻, the electrons that have been gained by the Br⁻ and I⁻ ions **are further away from**, and thus are not as tightly held to the nuclei of the Bromide and Iodide atoms², and thus they *can* be more easily prised away and taken by the concentrated Sulphuric Acid. (This is all about Ionisation energy. It takes less energy to prise the electrons away from Bromide and Iodide than from Fluoride and Chloride ions.) The Bromide and Iodide ions are losing electrons (they are being oxidised) and they are thus **reducing agents** i.e. they reduce the concentrated Sulphuric Acid.

Sulphuric Acid is an OXIDISING Agent, and Halide ions are REDUCING Agents.

As Group VII is descended, the Halide ions become stronger and stronger reducing agents.

Reactions with Halides

Different reactions can take place when a Halide ion comes into contact with concentrated Sulphuric Acid. From OILRIG, for concentrated Sulphuric Acid to oxidise a Halide ion,

- the Halide ion must **lose** one or more electrons, and
- the Sulphuric Acid must **gain** electrons (i.e. it must be reduced).

The electrons in a **FLUORIDE** ion and in a **CHLORIDE** ion are held so closely to their nuclei that they will **not** let go of their electrons and thus they **do not act as reducing agents with regard to concentrated Sulphuric Acid**. This is clearly also a function of the inability of concentrated Sulphuric Acid to pull the electrons off Fluoride and Chloride ions. In other words, once Fluorine and Chlorine have reached the stability of the Noble Gas Configuration (i.e. they have become Fluoride or Chloride ions with the electron configuration of Neon and Argon respectively), **then concentrated Sulphuric Acid cannot disrupt that stability**. All that happens with concentrated Sulphuric Acid and a Fluoride or a Chloride is that an ordinary *double-displacement reaction* occurs – **and the Fluoride and Chloride ions still remain as Fluoride and Chloride ions.** (*Their oxidation states do NOT alter.*)

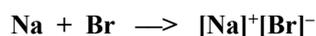
We could say that because both Fluoride and Chloride ions lie above concentrated Sulphuric Acid in the Reactivity series, then Sulphuric Acid cannot pull electrons off them.

² Please remember that the factors that govern how tightly electrons are held to the nucleus of an atom are (i) distance (ii) the number of protons (iii) shielding, and (iv) mutual repulsion.

Section B: The details of the reactions

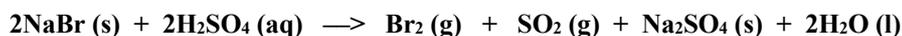
Bromide ions

At this stage, a question that you might want to ask yourself is “The Sulphur ion in H_2SO_4 (aq) can be considered to be in a state where it has *used* six electrons³ i.e. it is in an Oxidisation State of S^{6+} , therefore it may well be considered to be anxious to regain some or all of those electrons, and thus it may well be very happy to go from S^{6+} to say S^{4+} or even S^0 ; but, a Bromine atom (in Group VII) took on an electron to achieve the stability of the noble gas configuration of the Krypton atom



therefore why on earth would it want to give up this newly-found stability to give electrons to S^{6+} ? It was desperate to get hold of those electrons, so why would it then give them up? There are therefore three questions that need answering viz. what / how / and why? I am not going to address the question of “why” because I would then have to talk about the Reactivity series – and I do not want to do that here. However, I will now address the questions of “what” and “how”.

Let me start by telling you what happens, and then I will explain how it happens. Sodium Bromide is a white soluble solid salt (just like Sodium Chloride), and the overall reaction equation (if you let it go right to the end) is



First of all, two Bromide ions give up two electrons to become two Bromine atoms (or one Bromine molecule)



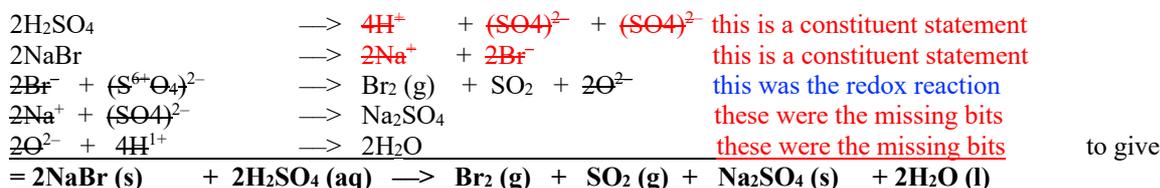
Then one Sulphate (SO_4)²⁻ anion from one unit of H_2SO_4 (i.e. $\text{H}_2\text{S}^{6+}\text{O}_4$) accepts the two electrons that have been released to become SO_2 (S^{4+}O_2) $\text{S}^{6+} + 2\text{e}^- \longrightarrow \text{S}^{4+}$
and if you add up the two equations you get



or $2\text{NaBr} (\text{s}) + \text{H}_2\text{SO}_4 (\text{aq}) \longrightarrow \text{Br}_2 (\text{g}) + \text{SO}_2 (\text{g})$ (and other stuff still to be accounted for).

If you go back and look at the overall reaction equation, that leaves two Na^+ ions and one (SO_4)²⁻ ion and 2O^{2-} ions and 4H^+ ions unaccounted for, and it is they that form the $\text{Na}_2\text{SO}_4 (\text{s}) + 2\text{H}_2\text{O} (\text{l})$.

For the overall reaction we can now add everything up and cancel out things that are the same on each side of the equation and get



I admit that this looks a bit complicated, and textbooks tend *not* to explain clearly what is going on, but you can *now* see exactly what is happening when concentrated Sulphuric Acid reacts with Bromide ions.⁴

³ It does not actually lose 6 electrons. In nature, nothing can actually pull 6 electrons off something else. “6+” is merely the oxidation state/oxidation number of Sulphur in H_2SO_4 . ‘Oxidation numbers’ are purely theoretical constructs.

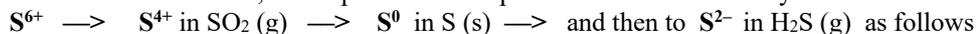
⁴ Some sources say that NaHSO_4 is formed in the reaction (just as it is with NaF and NaCl). It certainly is formed, but only as an intermediate species.

Iodide ions

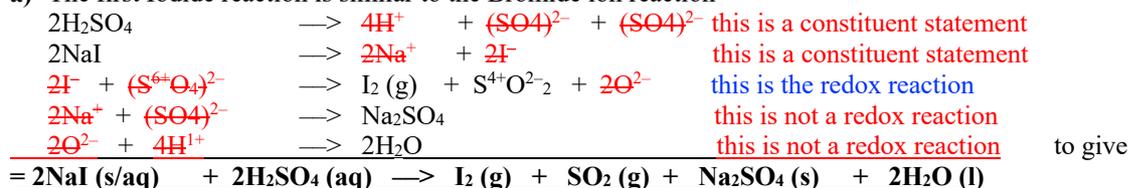
Let us start with the overall reaction that I intend to explain



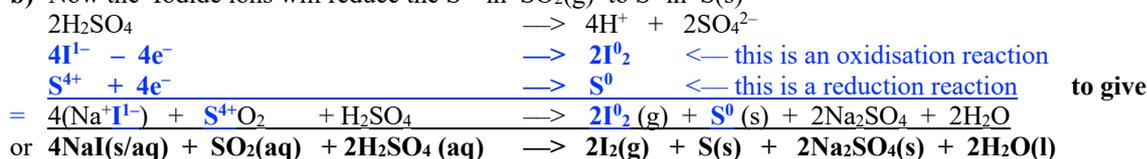
In the earlier reaction with the Bromide ions, S^{6+} was reduced to S^{4+} , but in the reaction of concentrated Sulphuric Acid with Iodide ions, the sulphur in the Sulphuric Acid is successively reduced to



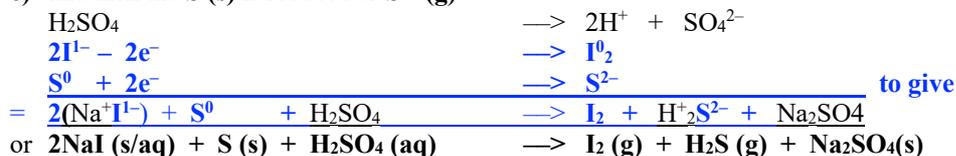
a) The first Iodide reaction is similar to the Bromide ion reaction



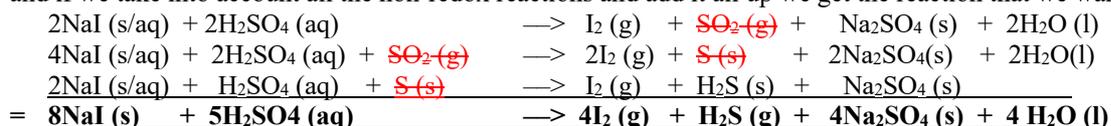
b) Now the Iodide ions will reduce the S^{4+} in SO_2 (g) to S^0 in S (s)



c) and then the S (s) is reduced to $\text{S}^{2-} \text{ (g)}$



and if we take into account all the non-redox reactions and add it all up we get the reaction that we want



but along the way you would have had some S(s) and some $\text{SO}_2\text{(g)}$ given off.

NB H_2S is toxic and flammable and smells awful and for all I know it may even be toxic! (Please just watch all this on youtube. I am not going to do it for you. I do not want accidentally to cause you any harm.) The reaction is exothermic, therefore Iodine might be seen as a dark vapour or it could be deposited as a dark solid.

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- concentrated Sulphuric Acid will form double-displacement reactions with Fluoride and Chloride ions and that
- with Bromide ions, $\text{Br}_2 \text{ (g)}$ and $\text{SO}_2 \text{ (g)}$ [and $\text{Na}_2\text{SO}_4 \text{ (s)}$ and $\text{H}_2\text{O (l)}$] will be produced, and
- with Iodide ions, $\text{I}_2 \text{ (g)}$ and $\text{H}_2\text{S (g)}$ [and $\text{Na}_2\text{SO}_4 \text{ (s)}$ and $\text{H}_2\text{O (l)}$] will be produced, but along the way you would also have had some S(s) and some $\text{SO}_2\text{(g)}$ given off.