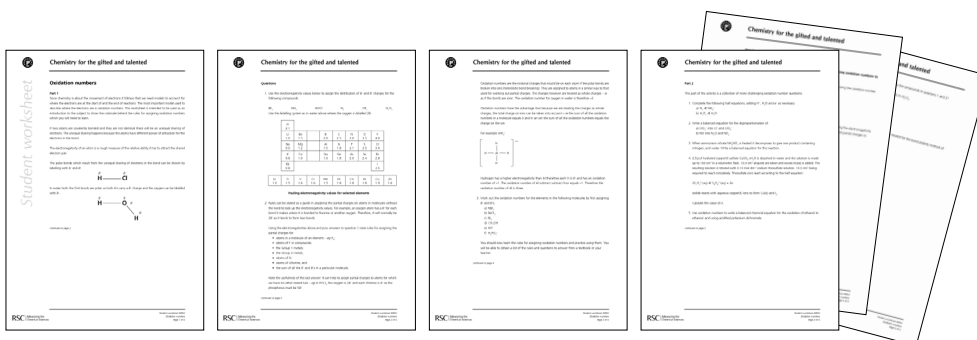
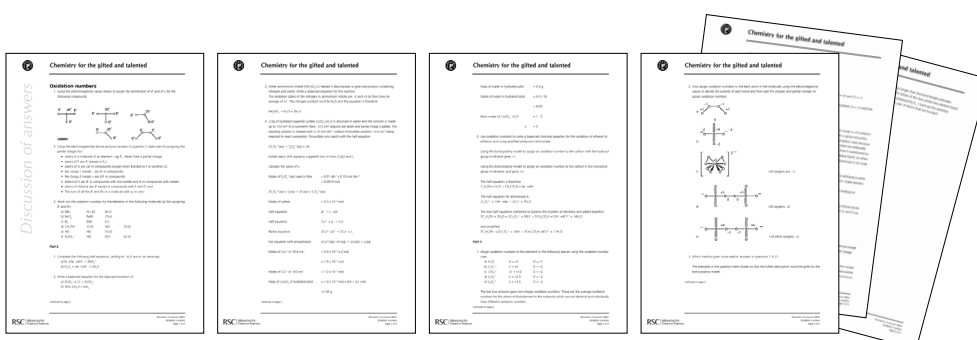


Oxidation numbers



Student worksheet: CDROM index 30SW



Discussion of answers: CDROM index 30DA

Topics

Working out oxidation numbers from electronegativity values, challenging redox questions and comparing the two methods of assigning oxidation numbers – electronegativity values and oxidation number rules.

Level

Very able post-16 students.

Prior knowledge

Polar bonds and electronegativity.

Rationale

Part 1 introduces oxidation numbers by giving a conceptual foundation for them in terms of electron accounting and polar bonds. Very able students tend to prefer this approach to starting with a set of rules.

Part 2 gives some examples of the usefulness of oxidation numbers in working out balanced equations.

Part 3 shows where the bond polarity approach gives greater insight into the oxidation numbers of atoms in particular examples. It then shows how the model used so far needs refining and asks the students to think about how this might be done.

This should lead to a greater understanding of the nature of the models that we use in chemistry as well as methods of assigning oxidation numbers. The activity shows where

non-integer oxidation numbers arise and what they mean.

Use

The activity should be done in two sections:

- Part 1 is the introduction to oxidation numbers. It is written so that students can be given this activity as a first introduction but it can also be used when they have met the oxidation number rules. It is suitable for students of all abilities.
- Parts 2 and 3 are the follow up to class work on assigning oxidation numbers using the usual rules and constructing redox equations. These parts are suitable for very able students.

Students should be given the *Discussion of answers* section to the part they have completed before moving on to the next part.



This symbol means those questions are best tackled as a discussion if a group of students is doing this activity. It is intended that written answers are not required for these questions.

The note on Al_2Cl_6 seeds the thought that not all bonds are two-electron two-centre bonds and some students may want to research that more. A brief description can be found at http://en.wikipedia.org/wiki/Three_center_bond (accessed May 2007).

Oxidation numbers

Part 1

Since chemistry is about the movement of electrons, it follows that we need models to account for where the electrons are at the start of and the end of reactions. The most important model used to describe where the electrons are is oxidation numbers. This worksheet is intended to be used as an introduction to the subject to show the rationale behind the rules for assigning oxidation numbers which you will need to learn.

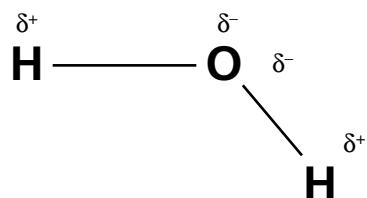
If two atoms are covalently bonded and they are not identical there will be an unequal sharing of electrons. The unequal sharing happens because the atoms have different powers of attraction for the electrons in the bond.

The electronegativity of an atom is a rough measure of the relative ability it has to attract the shared electron pair.

The polar bonds which result from the unequal sharing of electrons in the bond can be shown by labelling with δ^- and δ^+ .



In water both the O–H bonds are polar so both H's carry a δ^+ charge and the oxygen can be labelled with δ^- .



continued on page 2



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Questions

1. Use the electronegativity values below to assign the distribution of δ^- and δ^+ charges for the following compounds.



Use the labelling system as in water above, where the oxygen is labelled $2\delta^-$.

| | | | | | | | | |
|-----------|-----------|--|-----------|-----------|-----------|-----------|-----------|--|
| H 2.1 | | | | | | | | |
| Li 1.0 | Be 1.5 | | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 | |
| Na 0.9 | Mg 1.2 | | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 | |
| K 0.8 | Ca 1.0 | | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 | |
| Rb 0.8 | | | | | | | I 2.5 | |

| | | | | | | | | | |
|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Sc 1.3 | Ti 1.5 | V 1.6 | Cr 1.6 | Mn 1.5 | Fe 1.8 | Co 1.8 | Ni 1.8 | Cu 1.9 | Zn 1.6 |
|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|

Pauling electronegativity values for selected elements

2. Rules can be stated as a guide in assigning the partial charges on atoms in molecules without the need to look up the electronegativity values. For example, an oxygen atom has a δ^- for each bond it makes unless it is bonded to fluorine or another oxygen. Therefore, it will normally be $2\delta^-$ as it tends to form two bonds.

Using the electronegativities above and your answers to question 1, state rules for assigning the partial charges for:

- atoms in a molecule of an element – eg P_4 ;
- atoms of F in compounds;
- the Group 1 metals;
- the Group 2 metals;
- atoms of H;
- atoms of chlorine; and
- the sum of all the δ^- and δ^+ charges in a particular molecule.

Note the usefulness of this last answer. It can help to assign partial charges to atoms for which we have no other stated rule – eg in POCl_3 the oxygen is $2\delta^-$ and each chlorine is δ^- so the phosphorus must be $5\delta^+$.

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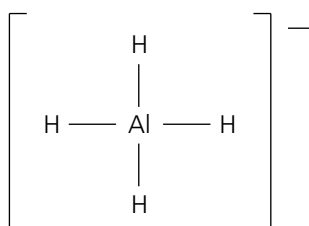


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Oxidation numbers are the notional charges that would be on each atom if the polar bonds are broken into ions (heterolytic bond breaking). They are assigned to atoms in a similar way to that used for working out partial charges. The charges, however, are treated as whole charges – *ie* as if the bonds are ionic. The oxidation number for oxygen in water is therefore -2 .

Oxidation numbers have the advantage that, because we are treating the charges as whole charges, the total charge on ions can be taken into account – *ie* the sum of all the oxidation numbers in a molecule equals 0 and in an ion the sum of all the oxidation numbers equals the charge on the ion.

For example AlH_4^-



Hydrogen has a higher electronegativity than Al, therefore each H is δ^- and has an oxidation number of -1 . The oxidation number of Al subtract four equals -1 . Therefore the oxidation number of Al is $+3$.

3. Work out the oxidation numbers for the elements in the following molecules by first assigning δ^- and δ^+ charges.
- NBr_3
 - BeCl_2
 - BI_3
 - CH_3OH
 - HO^-
 - H_2PO_4^-

You should now learn the rules for assigning oxidation numbers and practice using them. You will be able to obtain a list of the rules and questions to answer from a textbook or your teacher.

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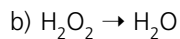
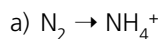


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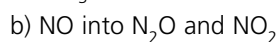
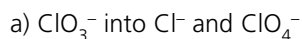
Part 2

This part of the activity is a collection of more challenging oxidation number questions.

1. Complete the following half equations, adding H^+ , H_2O and e^- as necessary.

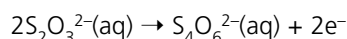


2. Write a balanced equation for the disproportionation of:



3. When ammonium nitrate, NH_4NO_3 , is heated it decomposes to give one product containing nitrogen and water. Write a balanced equation for this reaction.

4. 2.5g of hydrated copper(II) sulfate, $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, is dissolved in water and the solution is made up to 100 cm^3 in a volumetric flask. 10.0 cm^3 aliquots are taken and excess $\text{KI}(\text{aq})$ is added. The resulting solution is titrated with 0.10 mol dm^{-3} sodium thiosulfate solution, 10.0 cm^3 being required to react completely. Thiosulfate ions react according to the half equation:



Iodide reacts with aqueous copper(II) ions to form $\text{CuI}(\text{s})$ and I_2 .

Calculate the value of x .

5. Use oxidation numbers to write a balanced chemical equation for the oxidation of ethanol to ethanoic acid using acidified potassium dichromate.

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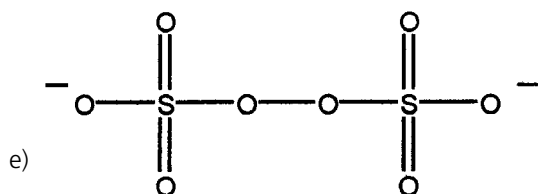
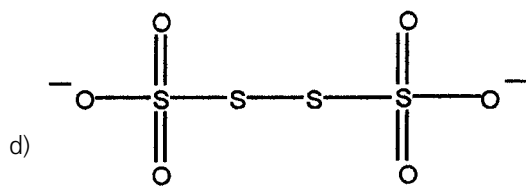
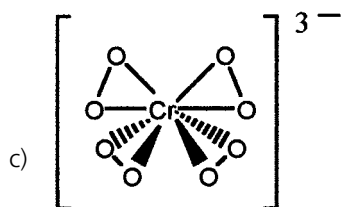
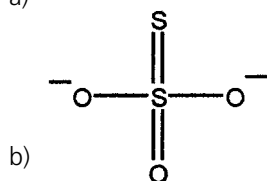
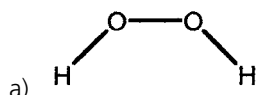
Part 3

Before you start this activity you need to be proficient at assigning oxidation numbers to elements in compounds using the oxidation number rules.

1. Assign oxidation numbers to the elements in the following species using the oxidation number rules.

- a) H_2O_2
- b) $\text{S}_2\text{O}_3^{2-}$
- c) CrO_8^{3-}
- d) $\text{S}_4\text{O}_6^{2-}$
- e) $\text{S}_2\text{O}_8^{2-}$

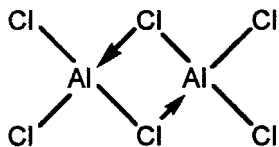
2. Now assign oxidation numbers to each atom in the molecules. Use the electronegativity values to decide the polarity of each bond and then add the charges and partial charges to assign oxidation numbers.



continued on page 6

3. Which method gives more realistic answers to the compounds in questions 1 and 2?

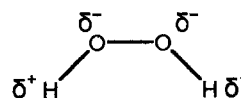
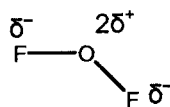
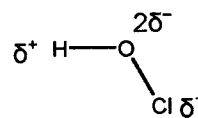
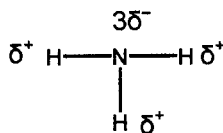
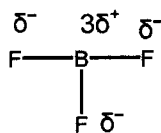
4. Use both methods to assign oxidation numbers in Al_2Cl_6 .



- Are both sets of answers reasonable?
- How would you suggest dative bonds are treated for the bond polarity method of assigning oxidation numbers?

Oxidation numbers

1. Use the electronegativity values below to assign the distribution of δ^- and δ^+ charges for the following compounds.



2. Using the electronegativities above and your answers to question 1, state rules for assigning the partial charges for:

- atoms in a molecule of an element – eg P_4 – never have a partial charge;
- atoms of F are δ^- (except in F_2);
- atoms of O are $2\delta^-$ in compounds (except when bonded to F or another O);
- the Group 1 metals are δ^+ in compounds;
- the Group 2 metals are $2\delta^+$ in compounds;
- atoms of H are δ^+ in compounds with non-metals and δ^- in compounds with metals;
- atoms of chlorine are δ^- except in compounds with F and O; and
- the sum of all the δ^- and δ^+ charges in a molecule add up to zero.

3. Work out the oxidation numbers for the elements in the following molecules by first assigning δ^- and δ^+ charges.

| | | | |
|------------------------------|----------|--------|--------|
| a) NBr_3 | N (-III) | Br (I) | |
| b) BeCl_2 | Be(II) | Cl(-I) | |
| c) BI_3 | B(III) | I(-I) | |
| d) CH_3OH | C(-II) | H(I) | O(-II) |
| e) HO^- | H(I) | O(-II) | |
| f) H_2PO_4^- | H(I) | P(V) | O(-II) |

Part 2

1. Complete the following half equations, adding H^+ , H_2O and e^- as necessary.

- $\text{N}_2 + 6\text{e}^- + 8\text{H}^+ \rightarrow 2\text{NH}_4^+$
- $\text{H}_2\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}$

2. Write a balanced equation for the disproportionation of:

- $4\text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{ClO}_4^-$
- $3\text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2$

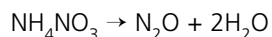
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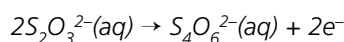
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3. When ammonium nitrate, NH_4NO_3 , is heated it decomposes to give one product containing nitrogen and water. Write a balanced equation for this reaction.

The oxidation states of the nitrogen in ammonium nitrate are -3 and $+5$, so they have an average of $+1$. The nitrogen product must be N_2O and the equation is therefore:



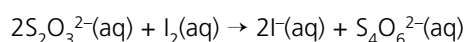
4. 2.5g of hydrated copper(II) sulfate $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ is dissolved in water and the solution is made up to 100 cm^3 in a volumetric flask. 10.0 cm^3 aliquots are taken and excess $\text{KI}(\text{aq})$ is added. The resulting solution is titrated with 0.10 mol dm^{-3} sodium thiosulfate solution, 10.0 cm^3 being required to react completely. Thiosulfate ions reacts with the half equation:



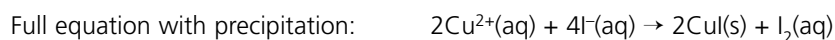
Iodide reacts with aqueous copper(II) ions to form $\text{CuI}(\text{s})$ and I_2 .

Calculate the value of x .

$$\begin{aligned} \text{Moles of } \text{S}_2\text{O}_3^{2-}(\text{aq}) \text{ used in titre} &= 0.01 \text{ dm}^3 \times 0.10 \text{ mol dm}^{-3} \\ &= 0.0010 \text{ mol} \end{aligned}$$



$$\text{Moles of iodine} = 5.0 \times 10^{-4} \text{ mol}$$



$$\text{Moles of } \text{Cu}^{2+} \text{ in } 10.0 \text{ cm}^3 = 5.0 \times 10^{-4} \times 2 \text{ mol}$$

$$= 1.0 \times 10^{-3} \text{ mol}$$

$$\text{Moles of } \text{Cu}^{2+} \text{ in } 100 \text{ cm}^3 = 1.0 \times 10^{-2} \text{ mol}$$

$$\text{Mass of } \text{CuSO}_4 \text{ in hydrated solid} = 1.0 \times 10^{-2} \text{ mol} \times (64 + 32 + 64)$$

$$= 1.60 \text{ g}$$

continued on page 3



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$$\text{Mass of water in hydrated solid} = 0.9 \text{ g}$$

$$\text{Moles of water in hydrated solid} = 0.9 / 18$$

$$= 0.05$$

$$\text{Ratio moles of CuSO}_4 : \text{H}_2\text{O} = 1 : 5$$

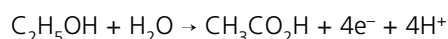
$$x = 5$$

5. Use oxidation numbers to write a balanced chemical equation for the oxidation of ethanol to ethanoic acid using acidified potassium dichromate.

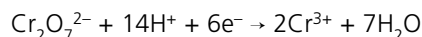
Using the bond polarity model to assign an oxidation number to the carbon with the hydroxyl group in ethanol gives -1 .

Using the bond polarity model to assign an oxidation number to the carbon in the functional group in ethanoic acid gives $+3$.

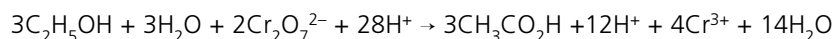
The half equation is therefore



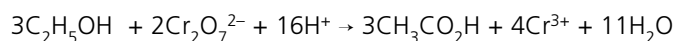
The half equation for dichromate is:



The two half equations combined to balance the number of electrons and added together:



and simplified:



Part 3

1. Assign oxidation numbers to the elements in the following species using the oxidation number rules.

$$\text{a) H}_2\text{O}_2 \quad \text{H} = +1 \quad \text{O} = -1$$

$$\text{b) S}_2\text{O}_3^{2-} \quad \text{S} = +2 \quad \text{O} = -2$$

$$\text{c) CrO}_8^{3-} \quad \text{Cr} = +13 \quad \text{O} = -2$$

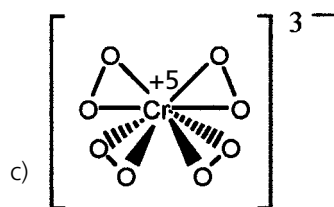
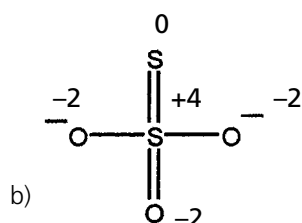
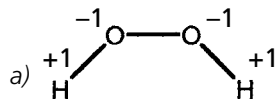
$$\text{d) S}_4\text{O}_6^{2-} \quad \text{S} = +2.5 \quad \text{O} = -2$$

$$\text{e) S}_2\text{O}_8^{2-} \quad \text{S} = +7 \quad \text{O} = -2$$

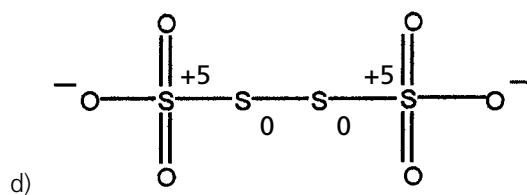
The last two answers are worthy of discussion, as they do not give an accurate representation of the actual oxidation numbers. Instead, these are the average oxidation numbers for the atoms of that element in the molecule which are not identical and individually have different oxidation numbers.

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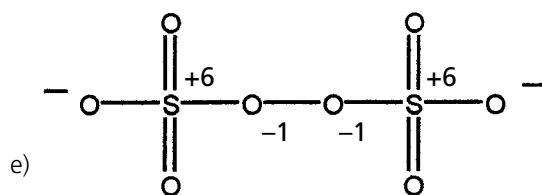
2. Now assign oxidation numbers to each atom in the molecules. Use the electronegativity values to decide the polarity of each bond and then add the charges and partial charges to assign oxidation numbers.



(All oxygens are -1)



(All oxygens are -2)



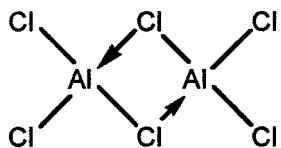
(All other oxygens are -2)

3. Which method gives more realistic answers in questions 1 & 2?

The examples in the question were chosen so that the fullest description would be given by the bond polarity model.

continued on page 5

4. Use both methods to assign oxidation numbers in Al_2Cl_6



Using the oxidation number rules we get oxidation numbers for Al = +3 and Cl = -1

Using the partial charges method it is tempting to assign oxidation numbers Al = +4 and the bridging chlorines = -2

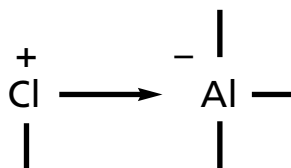
a) Are both sets of answers reasonable?

No. Here the bond polarity model lets us down. It is unreasonable to assign a +4 oxidation number to the aluminium. The reason that +4 is the wrong answer is quite instructive. The partial charge δ^+ on a hydrogen atom in HCl is assigned a +1 oxidation state because the hydrogen atom contributed an electron to the bond and then, when we notionally break up the bond into ions, the hydrogen atom loses the electron that it contributed to the bond. The aluminium does not contribute any electrons to the dative bond, so when we notionally break the bond, the electrons are given back to chlorine, so aluminium is no more oxidised than it is in $AlCl_3$.

When $AlCl_3$ dimerises and the dative bonds are formed, the aluminium is acting as a Lewis base and the chlorine as a Lewis acid, so this could be classed as an acid – base reaction.

b) How would you suggest dative bonds are treated for the bond polarity method of assigning oxidation numbers?

There are several strategies that would work. We could simply ignore any dative bonds (including ligand bonds). Dative bonds are sometimes drawn with charges in and if we take these into account the oxidation numbers should work out.



Accounting for electrons in molecules with dative bonds is addressed in the formal charge model of electron accounting. There is an accompanying activity called *Formal charge*.

continued on page 6



A note about Al_2Cl_6

The purpose of the question about Al_2Cl_6 is to show what we need to do when the model we are using starts to break down. Our model of bonds as always two-electron two-centre (between two atoms) bonds starts to fail with Al_2Cl_6 . The bond lengths for the aluminium to the bridging chlorines are considerably longer than the bond lengths between aluminium and the terminal chlorines. The failure of the two-electron two-centre bond model is better illustrated by the similar compound B_2H_6 . Count up the electrons required if there are two in between each pair of atoms that are bonded!

