Chem Factsheet

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OXYACIDS

Which of the following statements are true and which are false?

Statement	True	False
Oxyacids contain the OH^- group		
Oxyacids contain oxygen		
Oxyacids are always weak acids		
Chlorine exhibits an anionic electrovalency in hyperchlorous acid		
The Group 7 elements may exhibit their ionic valency when forming an oxyacid		
Oxygen is bonded to an element of high electronegativity in an oxyacid		
On descending Group 7 the higher oxidation states become more oxidising		

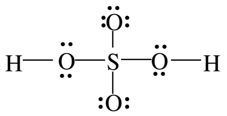
If you answered alternately false then true throughout, then you already have a good understanding of the principles involved in the formation and reactions of oxyacids. Why not try the questions at the end first?

If you found the statements problematic or had to guess, then this Factsheet aims to cure your misconceptions.

Key Fact 1

Oxyacids contain one or more O – H bonds.

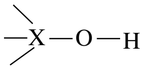
For example, H_2SO_4 contains two such bonds:



Key Fact 2

The electronegativity of the atom (X) directly attached to the OH determines whether an OH group will form an OH^- ion and so produce an alkaline solution, or lose an H^+ ion and so produce an acidic solution.

This is also true if X has other groups attached to it.



Background Understanding

It is important to understand how the atom(s) or group(s) bonded to the OH determines whether the compound behaves as an acid rather than a base.

The electronegativity of an element is a measure of its tendency to attract electrons from a covalent bond.

a) An atom of an element of low electronegativity will tend to lose electrons, so the average position of the electrons in the bond will be shifted away from the atom of that element, causing the bond to become highly polar. The element of lower electronegativity will become a centre of higher positive charge. The degree to which this occurs is dependent also on the electronegativities of the other atoms to which the atom is bonded.

b) An atom of an element of high electronegativity will tend to gain electrons, so the average position of the electrons in the bond will be shifted towards that atom, again causing the bond to become highly polar. The high electronegativity element becomes a centre of higher negative charge. Again the degree to which this occurs is dependent on the electronegativities of the other atoms to which the atom is bonded.

c) When the shift of charge is high enough, the electrons in the bond spend all of their time on one of the atoms, and ion formation results.

We can now see how this can result in the O–H group forming either OH^- ions and the compound behaving as a base, or H^+ ions and the compound behaving as an acid.

If X is a metal such as Na, K, or Ca, the low electronegativity of X results in the complete transfer of the bonding pair of electrons between X and O to the oxygen and an ionic compound involving OH^- is formed. Thus such compounds are sources of OH^- ions and behave as bases.

If X is a non-metal, the X–O bond is covalent and the compound will not readily lose an OH^- ion. These compounds will be either neutral or acidic in character.

Key Fact 3

As a general rule, the greater the electronegativity of X, the greater the acidity of the compound.

Background Understanding

The increasing acidity with increasing electronegativity of X is because:

1) The O–H bond becomes more polar as substantial drift of electrons towards the electronegative atom occurs. (The electron loving electronegative atom attracts the electrons.) This leaves the hydrogen atom with a positive charge.

For example:

$$\mathrm{Cl - O - H \quad \Leftrightarrow \quad Cl - O^- \; + \; H^+}$$

← ←

where ← represents the electron drift

K_a for HClO = 3.0×10^{-8} mol dm^{-3}

$$\mathrm{I - O - H \quad \Leftrightarrow \quad I - O^- \; + \; H^+}$$

← ←

K_a for HIO = 2.3×10^{-11} mol dm^{-3}

Chlorine is more electronegative than iodine, thus the chlorine atom will cause the electrons to move more towards itself, and the bond will become more polar. This results in HClO being a stronger acid than HIO, as reflected in the decreasing values for K_a.

[If you are not sure of the significance of K_a values and your Bronsted-Lowry Theory has not been used for a while, then Factsheet Number 25 will help you revise!]

Acid	Electronegativity of X	K_a / mol dm^{-3}
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

Key Fact 4

If oxygen atoms are attached to X, the electron withdrawing power of X is increased and thus the acidity of the oxyacids increases.

Thus the strength of the oxyacids of chlorine increases from hypochlorous or chloric(I) acid, HClO to perchloric or chloric(VII) acid, $HClO_4$. As the oxidation number of X increases as the number of oxygen atoms attached increases, this may be restated:

Key Fact 5

In a series of oxyacids the acidity increases as the oxidation number of the central atom (X) increases.

The Formation of Oxoanions and Electrovalency

The formation of oxoanions may also be considered in terms of the $E^\ominus$ values relating to the process:

$$\mathrm{Hal_2 + 2e^- \rightarrow 2Hal^-}$$

where Hal represents any halogen and Hal$^-$ corresponding halide anion

Extract from examiners report: *"A number of candidates could not distinguish between an anion and a cation" – make sure you can*

Note: Remember anions are negative and so are attracted by and go to a positive anode.

The more positive the potential for the process, the more oxidising the Hal_2 species and the less reducing the Hal$^-$ species.

	$F_2 \rightarrow 2F^-$	$Cl_2 \rightarrow 2Cl^-$	$Br_2 \rightarrow 2Br^-$	$I_2 \rightarrow 2I^-$
$E^\ominus$ in volts	+ 2.87	+ 1.36	+ 1.07	+ 0.54

[If you would like to revise Electrode Potentials and Feasibility of Reactions Factsheet Number 45 will be helpful to you.]

Remember *oxidation is loss of electrons and so an oxidising agent will have a high positive potential for gaining electrons.*

Key Fact 6

The halogens thus exhibit an anionic electrovalency. The halogens also exhibit a range of positive oxidation states, which do not correspond to the ionic valencies. Oxidation states ranging from +1 to +7 are exhibited by Cl, Br and I.

The oxoanions formed by oxyacids are examples where Cl, Br and I have these oxidation states. The following examples should be remembered specifically

Chlorine has the oxidation state +1 in OCl^- [chlorate(I)]
the oxidation state +5 in ClO_3^- [chlorate(V)]
the oxidation state +7 in ClO_4^- [chlorate(VII)]

Iodine has the oxidation state +7 in IO_4^- [iodate(VII)]

Key Fact 7

Although they are behaving as anions and form salts with the alkali metals of Group I, the bonds between the halogen and oxygen(s) are covalent, due to the comparability of the electronegativity values of oxygen and the halogens.

Key Fact 8

The higher oxidation states are highly oxidising

e.g. chlorate (V), ClO_3^- and chlorate (VII), ClO_4^-, tend to be reduced to Cl^-.

However, as Group 7 is descended and the electronegativity of the halogen decreases, the higher oxidation states become more stable and less strongly oxidising.

e.g. the tendency of IO_3^- to become I^- is less than the tendency for ClO_3^- to become Cl^-.

Formation of the oxoanion ClO^-

ClO^- is formed by the redox disproportionation reaction between chlorine gas and cold, dilute sodium hydroxide solution:-

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

Oxidation state of chlorine 0 -1 +1

If chlorine is passed into hot concentrated sodium hydroxide solution, the following reaction occurs:-

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + H_2O$$

Oxidation state of chlorine 0 -1 +5

Disproportionation of the oxoanion ClO^-

Warming of a solution containing ClO^- results in the following disproportionation:

$$3ClO^- \rightarrow 2Cl^- + ClO_3^-$$

Oxidation state of chlorine +1 -1 +5

Oxidising Properties of ClO^-

The chlorate anion behaves in a similar way to chlorine, having substantial oxidising power and displaying bleaching and bactericidal action.

This type of oxidation reaction results in chlorine (+1) in ClO^- being reduced to chlorine (-I) in Cl^-.

Key Fact 9

The decrease in electronegativity as one goes down Group 7 results in the elements becoming less oxidising and thus the higher oxidation states are more stable.

For example iodate (V) IO_3^- is less oxidising than chlorate (V), ClO_3^-, and thus more stable.

Reactions of sodium halides when heated with concentrated sulphuric acid

At first, the sodium halides react to form the corresponding hydrogen halides:

$$NaHal + H_2SO_4 \rightarrow NaHSO_4 + HHal$$

where Hal = F, Cl, Br or I

These are *not* redox reactions.

Question1:
What is the change in oxidation number for a) the halogen b) sulphur in the reaction above?

However, **HBr and HI are then oxidised** by the oxyacid H_2SO_4 to form the free halogen.

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

Extract from examiners' report: *Many candidates recognised the brown gas as bromine, but failed to state that bromine was* ***an oxidation product***

Question2:
What is the change in oxidation number for a) bromine b) sulphur in the reaction above?

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$$

$$6HI + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$$

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$$

The reducing power of the hydrogen halide becomes greater as one goes further down Group 7. This is to be expected as the $E^?$ values for $Hal_2 \rightarrow 2Hal^-$ become less positive, thus reflecting the decreasing oxidising power of the free halogen and increasing reducing power of the hydrogen halides.

Question3:
What is the change in oxidation number for a) iodine b) sulphur in each of the reactions above?

Practice Questions

1. Arrange the following compounds in order of increasing acid strength: H_2SeO_3, H_2SeO_4, H_2O
2. Which of the following pairs of oxyacids will be the stronger?
   a) HNO_2 HNO_3 b) H_2SO_3 H_2SeO_3
   c) HIO HBrO d) $HClO_3$ $HClO_2$
3. Give the oxidation state of:
   a) Iodine in IO_3^- b) Bromine in BrO_2^- c) Chlorine in ClO^-
4. Name the gas produced when solid sodium chloride is reacted with concentrated sulphuric acid.
5. Name the two gases produced when solid sodium bromide reacts with concentrated sulphuric acid and give their appearance.
6. Give the equation for the reaction of chlorine with dilute aqueous sodium hydroxide at room temperature. Explain, using oxidation numbers why this may be regarded as a disproportionation reaction.

Answers to Questions from Text

Q1 a) 0 (-1 → -1) b) 0 (+6 → +6)]
Q2 a) +1 (-1 → 0) b) -2 (+6 → +4)]
Q3 a) +1 (-1 → 0) in all reactions
b) -2 (+6 → +4); -6 (+6 → 0); -8(+6 → -2).]

Answers

1. *The correct order is* H_2O (*weakest*) - H_2SeO_3 - H_2SeO_4 (*strongest*)
Explanation: *Selenium is a non-metal (similar to sulphur) and thus is an element of higher electronegativity than hydrogen and forms a stronger acid . The acidity of oxyacids increases as the number of oxygen atoms bonded to the central atom increases. This means that* H_2SeO_4 *will be a stronger acid than* H_2SeO_3.
2. a) $\mathbf{HNO_3}$ as the number of oxygen atoms bonded to the nitrogen is greater.
   b) $\mathbf{H_2SO_3}$ as the electronegativity of sulphur is greater than that of selenium (sulphur is higher up group six).
   c) **HBrO** as bromine is more electronegative than iodine.
   d) $\mathbf{HClO_3}$ as the number of oxygen atoms bonded to chlorine atom is greater.
3. a) +5 b) +3 c) +1
4. **Hydrogen chloride** gas
5. **Bromine** gas – brown ; **sulphur dioxide** gas - colourless
6. $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$
   Disproportionation because the chlorine is simultaneously oxidised and reduced from oxidation state 0 to -1 and +1

Acknowledgements: *This Factsheet was researched and written by* **Christine Collier**.
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