

**Topic: Redox and Electrochemistry**

for chemical reactions

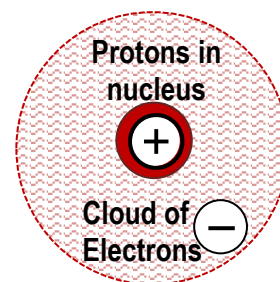
Work Book 1	<b>Electrochemistry Practical Investigation</b> provides the observations and experimental data necessary to make better sense of Redox concepts and applications.				
<b>Structure of the Observed Learning Outcomes</b>	Applying prior knowledge	<b>Part ①</b>	Displacement reactions	<b>Science as Human Endeavour using Practical tasks</b>	Page 4
	Developing one new concept		Activity series		5
	Developing multiple concepts	<b>Part ②</b>	Measuring external $e^-$ flow		6
	Relating concepts together	<b>Part ③</b>	Electrochemical reactions		12
	Extending into new situations	<b>Part ④</b>	Alkaline conditions		15
Work Book 2	<b>Redox Chemistry Notes</b> present ideas that need combining to make sense of Redox concepts and applications. Working through <b>Questions 1-to-26</b> enhances this learning.				
<b>Introduction</b> to explain why atoms shift electrons around to form chemical bonds				Pg 2,3	
<b>Review</b>	Illustrating bond graphs with Bohr model to describe chemical bonds using electronegativity differences	<b>R1</b> Identifying chemical bond types		4	
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<b>Oxidation States</b> <b>SOLO:</b> Applying prior knowledge and Developing one new concept	Oxidation States ( $\pm n$ ) defined as a mathematical product ( $\pm$ ) $\times$ ( $n$ ): • Bond <b>direction</b> ( $\pm$ ) • and Valency <b>number</b> ( $n$ )	<b>Q1</b> Assigning Bond Direction		12	
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## Why do atoms bond to each other?

In nature, all systems of matter strike up a balance between achieving the least amount of order while in a condition of having the least amount of energy.

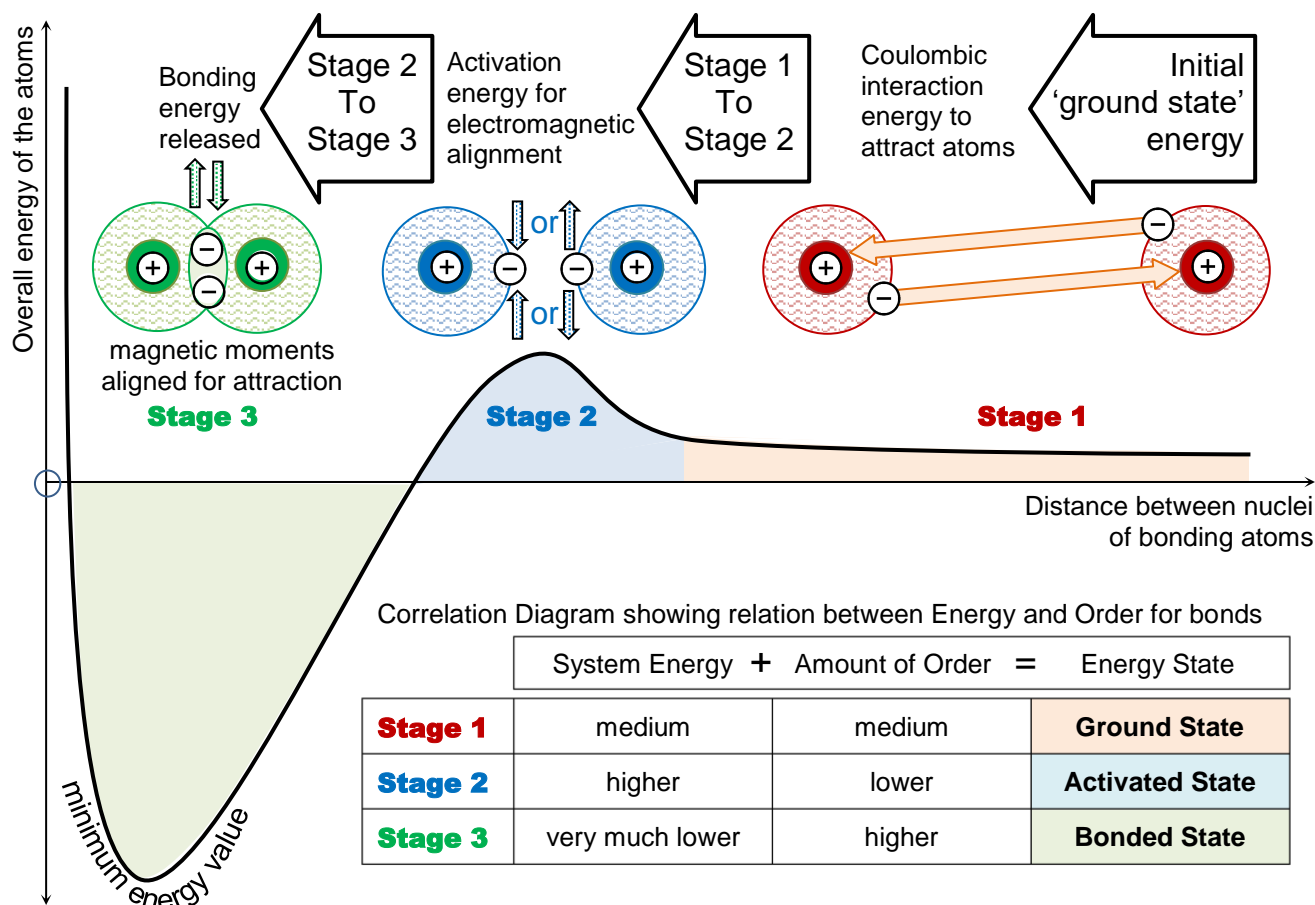
The arrangement of protons, neutrons and electrons in atoms is a good example of how this balance works. Zero charged neutrons bind with positively charged protons  $\oplus$  together in the nucleus by releasing huge amounts of energy by nuclear fusion using  $E = mc^2$ . This achieves the least amount of energy for those protons, but with lots of order as they are packed together neatly in the nucleus. The arrangement of a negatively charged cloud  $\ominus$  of dynamically mobile electrons around the nucleus produces minimised energy levels with electromagnetic interactions, but with less order in comparison to the nucleus. This is represented as the Bohr model of the atom.

### Bohr model



Balance between the least amount of order and the least amount of energy is further enhanced when atoms form chemical bonds together. Electrons moving in the electron cloud lose much energy by being shared in an orderly arrangement between the compactly placed protons and neutrons of the nuclei. This process is represented in the following correlation diagram.

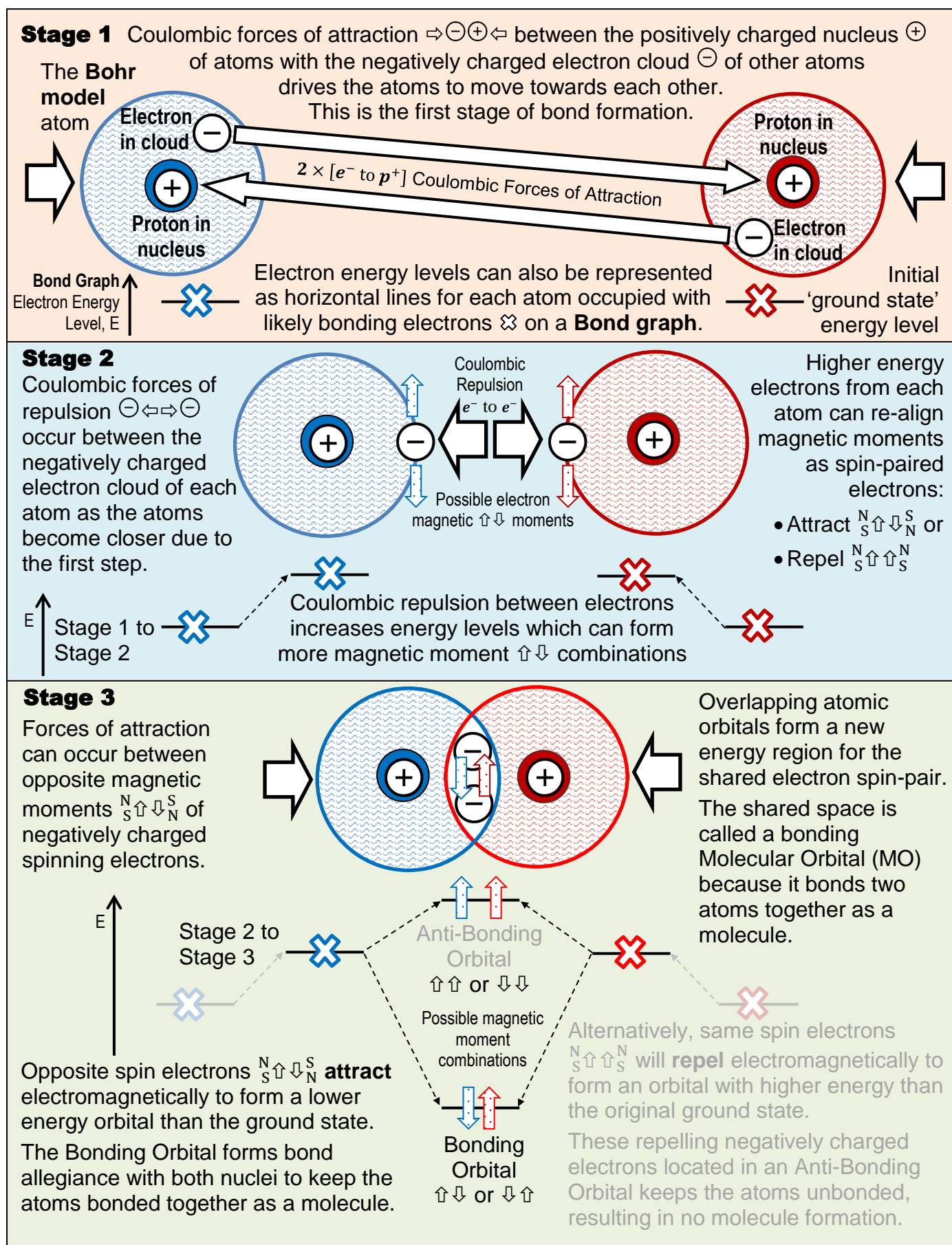
Atoms must get close together in order to form bonds. The following 'correlation' diagram represents the energy changes of this bonding in the three stages of association between atoms. The horizontal axis represents distance between the nuclei of the atoms as they get close enough to form bonds. The vertical axis represents the overall energy of the system of atoms, which includes the nuclei and electron clouds of both atoms.



The minimum energy value at Stage 3 in the correlation diagram represents the bonded condition found in molecules. When bonded, the energy balance of the system of electrons and nuclei as atoms is at its lowest. The atoms are said to be in a bonded state.

(Atoms have more energy when electrons and nuclei are in a disorderly unbonded state)

## Bohr Model with Bond Graphs<sup>1</sup> to describe Primary Bond Formation<sup>2</sup>



<sup>1</sup> Rock, P; Gerhold, G (1974) Chemistry Principles and Applications pg 94 for detailed explanation of the 3-Stage process for bond formation.

<sup>2</sup> International Union of Pure and Applied Chemistry (IUPAC) 2016 recommendation when determining chemical/primary bond oxidation states with Molecular Orbital approximation using Linear Combination of Atomic Orbitals (MO-LCAO).

The following diagrams represent the number of protons in each atom with a subscript, ex  ${}_9\text{F}$ , as a reminder of the balance between the number of protons and electrons in neutrally charged atoms. Use this representation when answering Bond graph questions with the Bohr model<sup>3</sup>.

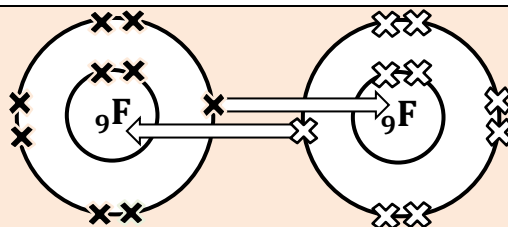
**R1** Complete the Bond graphs with Bohr models for the following bond forming situations.

- Bond formation is complete when unpaired (single) electrons form shared orbital pairs (\*\*).
- Structural diagrams represent shared electron pairs as a solid line joining atoms ( $\text{F} - \text{F}$ ).

**Example:** Bond formation for elemental Fluorine,  $\text{F}_2$

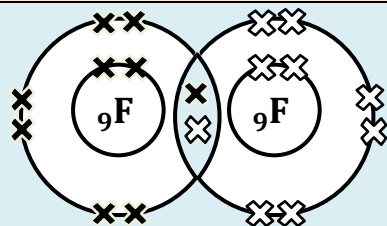
**Stage 1**

Coulombic attraction between valence electrons and nuclei

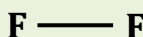


**Stage 2**

Magnetic moment alignment

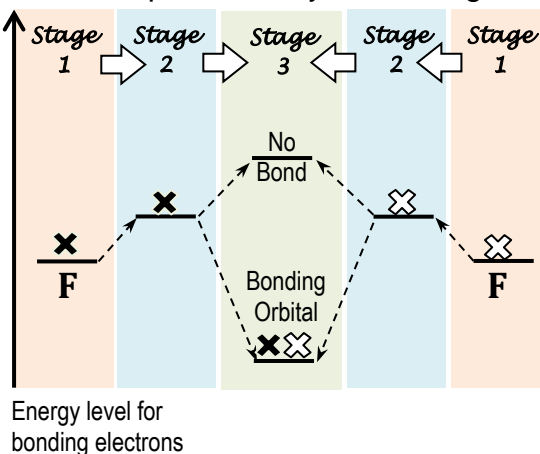


**Stage 3** Shared  $e^-$  spin-pair bond



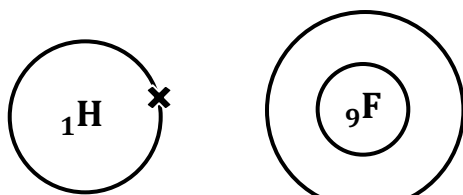
Structural formula for  $\text{F}_2$

Bond Graph summary of bonding

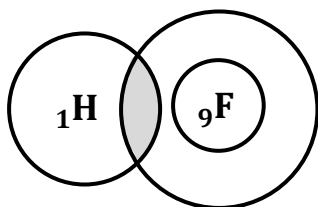


a) Bond formation for Hydrofluoric acid, HF

**Stage 1**



**Stage 2**

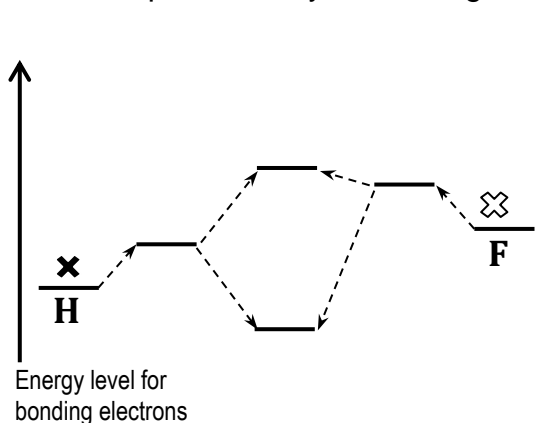


**Stage 3**



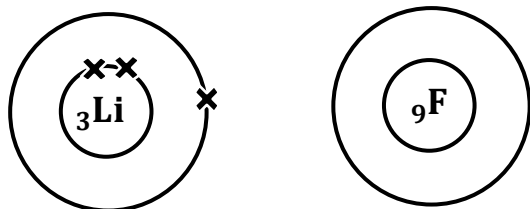
Structural formula for HF

Bond Graph summary of bonding

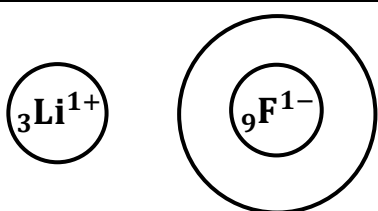


b) Bond formation for ionic salt Lithium Fluoride, LiF

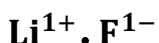
**Stage 1**



**Stage 2**

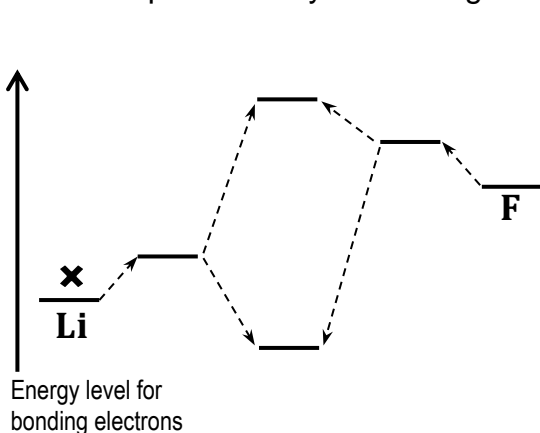


**Stage 3**



Structural formula for LiF

Bond Graph summary of bonding



<sup>3</sup> The Bohr model represents electron energy levels as circles where all electrons on the circle have similar energy levels. The four compass points on the circle represent electron energy sub-levels of identical energy known as orbitals, with a maximum of two electrons per orbital.

## Bond Type and Bond Direction using Electronegativity Differences, $\Delta\chi$

Bond graphs on the previous page describe the three-stage process for bond formation:

**Stage 1:** Coulombic ( $\pm$ ) forces attract electrons  $e^-$  to protons  $p^+$  in different atoms.

**Stage 2:** Valence electrons  $e^-$  in different atoms repel each other as atoms become closer.

**Stage 3:** Electromagnetic spin combinations with the lowest energy levels produce a bonding orbital between atoms (which join as a molecule) as an allegiance of lowest [energy + order].

**Electronegativity**  $\chi$  is the ability for an atom to attract electrons into its own valence shell.

The short-form Periodic Table of Elements opposite includes electronegativity strengths for each element expressed as 'Allen' values. There is zero expectation for students to know these values. However, students are required to know the two electronegativity trends for these values:

- $\chi$  tends to increase left-to-right horizontally
- $\chi$  tends to decrease top-to-bottom vertically
- $\chi$  differences between atoms is labelled  $\Delta\chi$
- Distance apart on Periodic Table affects  $\Delta\chi$

**$\chi$  Electronegativity Allen Values for Short Form Periodic Table**

P1	H	He							
	2.30	n/a							
P2	Li	Be	B	C	N	O	F	Ne	Non-Metals
	0.91	1.58	2.05	2.54	3.07	3.61	4.19	n/a	
P3	Na	Mg	Al	Si	P	S	Cl	Ar	
	0.87	1.29	1.61	1.92	2.25	2.59	2.87	n/a	
P4	K	Ca	Ga	Ge	As	Se	Br	Kr	
	0.73	1.03	1.76	1.99	2.21	2.42	2.67	n/a	
P5	Rb	Sr	In	Sn	Sb	Te	I	Xe	
	0.71	0.96	1.66	1.82	1.98	2.16	2.36	n/a	
P6	Cs	Ba	Tl	Pb	Bi	Po	At	Rn	
	0.66	0.88	1.79	1.85	2.01	2.19	2.39	n/a	
P7	Fr	Ra	Metals						Non-Metal
	0.67	0.89							
	G1	G2	G3	G4	G5	G6	G7	G8	

Period value is Number of  $e^-$  Energy Levels  
Group value is Number of valence electrons

**Bond Type** is predicted by Absolute value of  $\Delta\chi$  (High $\chi$ , Medium $\chi$ , Low $\chi$ ) between two atoms.

- High electronegativity attracts electrons towards the valence shell of an atom.
- Low electronegativity loses electrons from an atom to the valence shell of other atoms.

**Bond Direction** is determined by relative ( $\pm$ ) sign for  $\Delta\chi$  between two atoms.

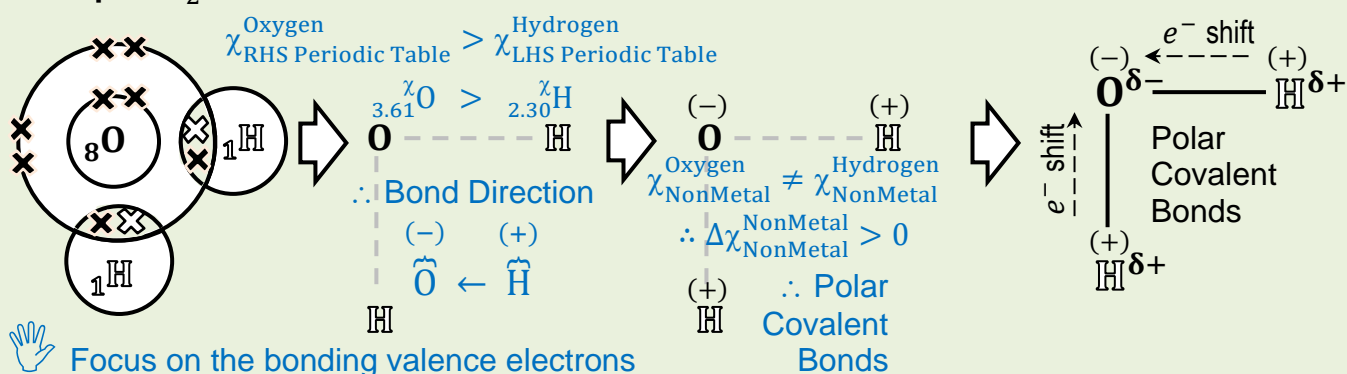
- Electron shift towards high  $\chi$  atoms is defined as having a ( $-$ ) bond direction ( $+e^- \rightarrow -$ )
- Electron shift away from low  $\chi$  atoms is defined as having a ( $+$ ) bond direction ( $-e^- \rightarrow +$ )
- There is zero overall bond direction when two atoms have the same  $\chi$  value ( ${}_A\chi - {}_A\chi = \emptyset$ )

Table 1: Comparing electronegativity values to determine bond type and bond direction

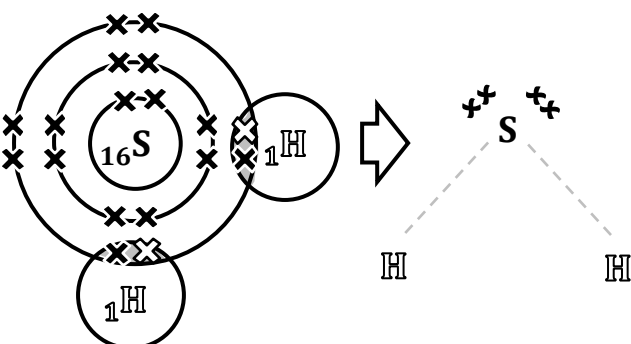
Electronegativity Difference $\Delta\chi$	Bond Type A—B	The solid line between atoms AB represents a chemical bond	Net Bond Direction (-) $\leftarrow$ (+) High $\chi$ $\leftarrow$ Low $\chi$	$e^-$ shift A $\leftarrow$ B bonding $e^-$ pair	
Large $\Delta\chi$ ${}_A\chi - {}_B\chi \gg 0$	Very High NonMetal ${}_A\chi \gg {}_B\chi$ Very Low Metal	ionic [NonMetal Metal]	(-) $\leftarrow$ (+) Highest $\chi$ $\leftarrow$ Lowest $\chi$ $e_B^-$ shifts towards A $e_A^-$ remains with A	total transfer $A^- \cdot B^+$	Localised (between AB)
Medium $\Delta\chi$ ${}_A\chi - {}_B\chi > 0$	Higher NonMetal ${}_A\chi > {}_B\chi$ Lower NonMetal	polar covalent Includes Metalloids [NonMetal NonMetal Includes Transitions]	(-) $\leftarrow$ (+) Higher $\chi$ $\leftarrow$ Lower $\chi$ $e_B^-$ partial shift from B to A $e_A^-$ partial shift towards B	partial shared $A^{\delta-} - B^{\delta+}$	
Small $\Delta\chi$ ${}_A\chi - {}_B\chi \approx 0$	Both High NonMetals ${}_A\chi \approx {}_B\chi$	non-polar covalent [NonMetal NonMetal]	(-) $\leftarrow$ (+) High $\chi$ $\leftarrow$ High $\chi$ $e_B^-$ equal shift from B to A $e_A^-$ equal shift from A to B	equal shared A—B	
	Both Low Metals ${}_A\chi \approx {}_B\chi$	metallic [Metal Metal]	(+) $\leftarrow$ (+) Low $\chi$ $\leftarrow$ Low $\chi$ $e_A^-$ equal drift from A and B $e_B^-$ equal drift from B and A	Delocalised (around all AB)	

**R2 Indicate bond direction and identify which bond types for the following bonded atoms<sup>4</sup>**

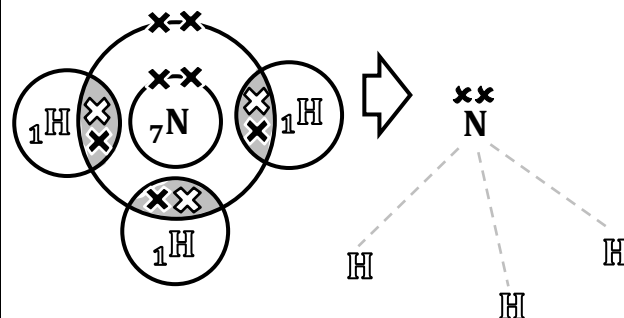
**Example: H<sub>2</sub>O water**



**a) H<sub>2</sub>S Hydrogen Sulphide (rotten egg gas)**

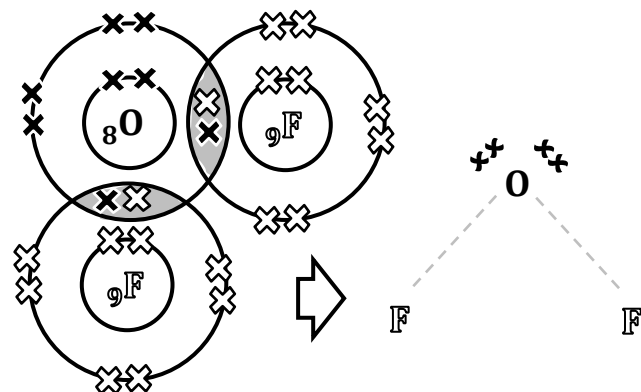


**b) NH<sub>3</sub> Ammonia**

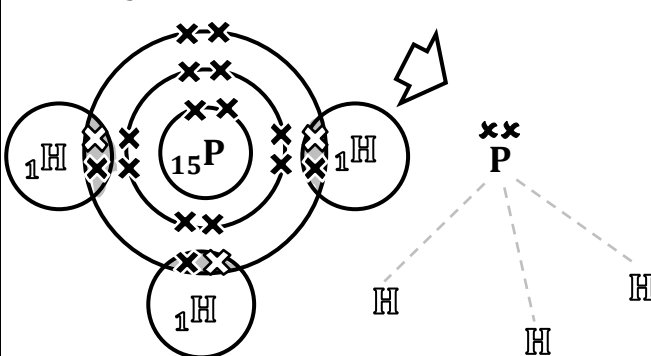


Unbonded valence electron pairs (\*\*\*) in structural diagrams are a reminder of the v-shaped (H<sub>2</sub>S, F<sub>2</sub>O & H<sub>2</sub>O) and triangular pyramid (NH<sub>3</sub> & PH<sub>3</sub>) 3D structures and are not part of the chemical bonds within the molecule.

**c) F<sub>2</sub>O Fluorine Oxide**



**d) PH<sub>3</sub> Phosphine**



**e) LiOH Lithium Hydroxide**

Unbonded valence electron pairs can be omitted from structural diagrams if they do not contribute to the 3D shape.

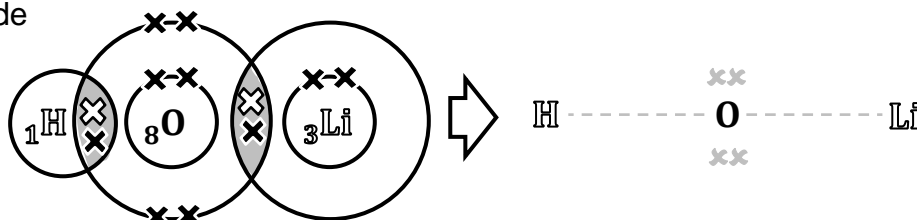
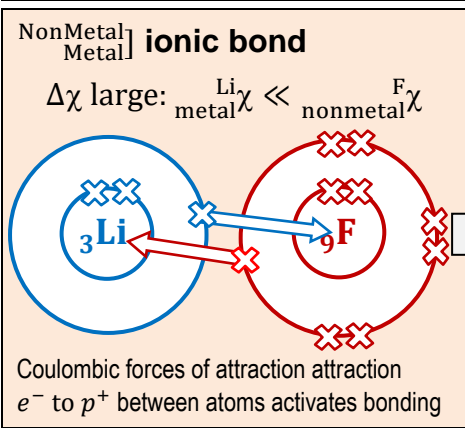
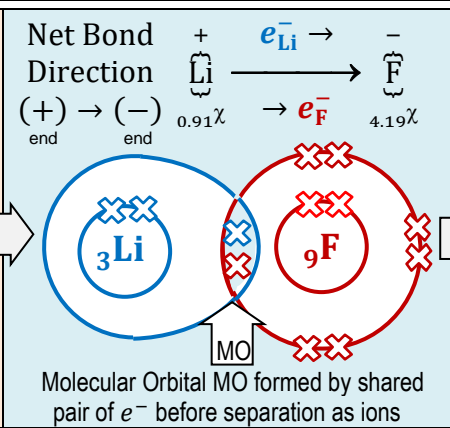
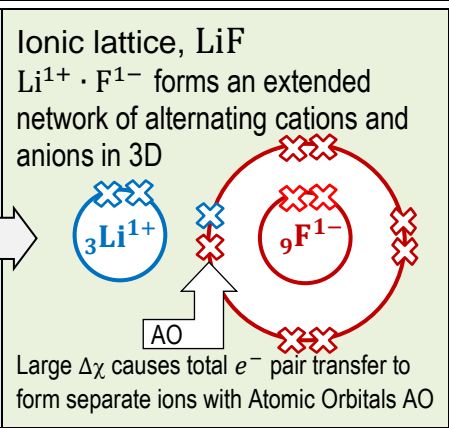
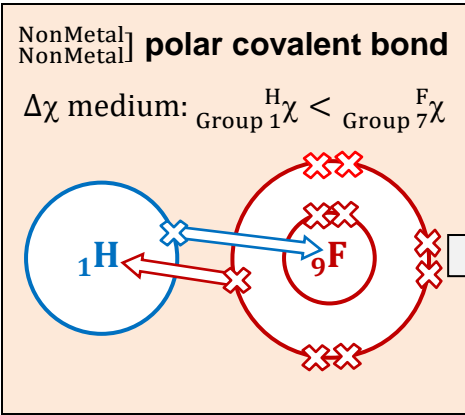
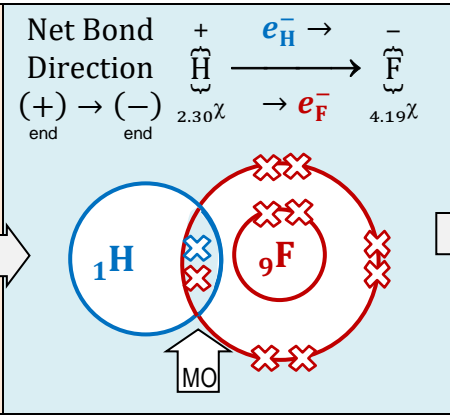
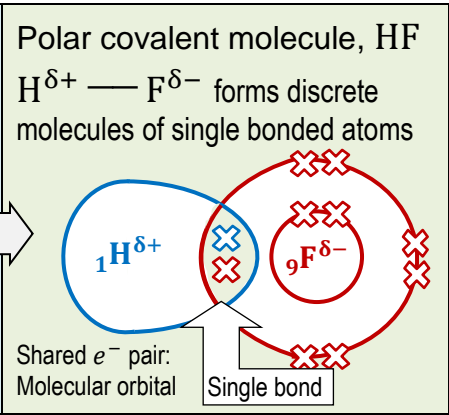
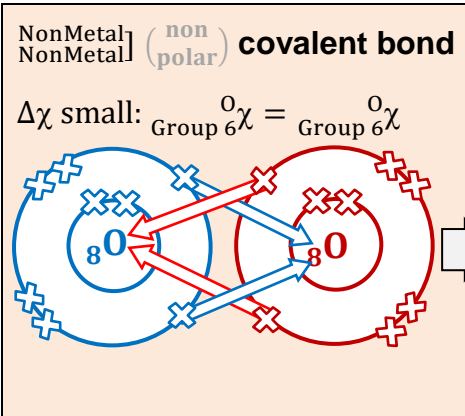
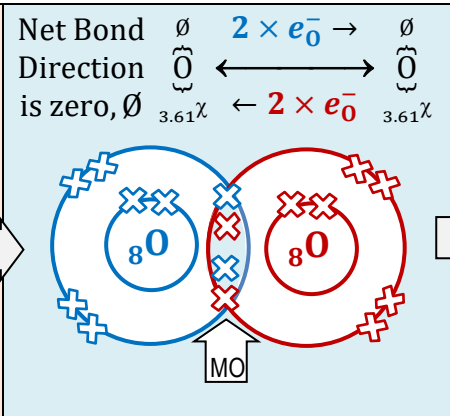
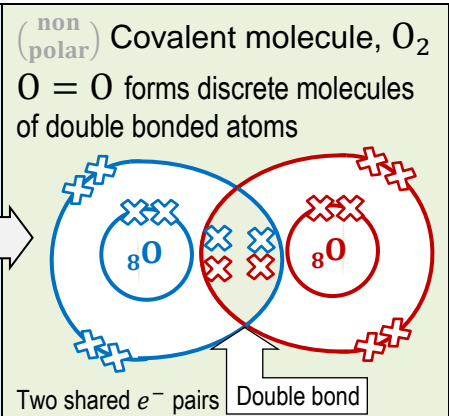
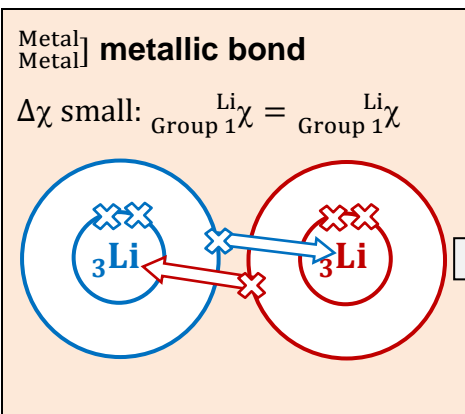
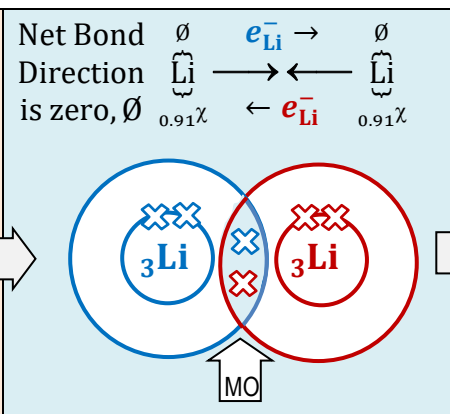
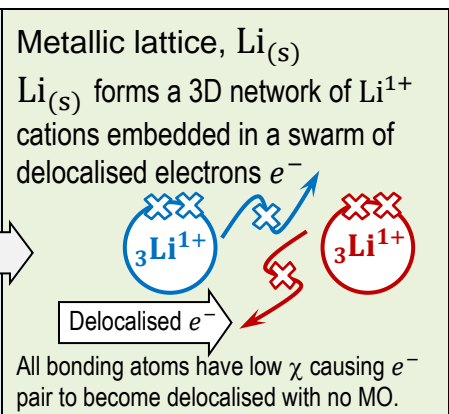


Table 2 illustrates how each bond type forms a stable configuration of valence electron orbitals.

<sup>4</sup> a) Two polar covalent bonds  $\text{S}^{\delta-} - \text{H}^{\delta+}$ ; b) Three polar covalent bonds  $\text{N}^{\delta-} - \text{H}^{\delta+}$ ; c) Two polar covalent bonds  $\text{O}^{\delta+} - \text{F}^{\delta-}$ ; d) Three covalent bonds  $\text{P}-\text{H}$  ( $2.30 \chi_{\text{H}} - 2.25 \chi_{\text{P}} = 0.05 \approx \emptyset$ ); e) One polar covalent bond  $\text{O}^{\delta-} - \text{H}^{\delta+}$  and one ionic bond  $\text{Li}^{1+} \cdot \text{OH}^{1-}$

Table 2	<b>Stage 1:</b> Negative electrons $e^-$ ( $\otimes$ ) attracted to positive protons $p^+$ in nucleus ( ${}_Z A$ )	<b>Stage 2:</b> Activated electrons align electromagnetic forces of ( $\downarrow\uparrow$ ) attraction to form spin-pair orbitals	<b>Stage 3:</b> Extent of spin-pair shift determines where the shared spin pair of electrons are re-distributed
<p>NonMetal Metal] <b>ionic bond</b></p> <p><math>\Delta\chi</math> large: <math>{}_{\text{metal}}\chi \ll {}_{\text{nonmetal}}\chi</math></p>  <p>Coulombic forces of attraction attraction <math>e^-</math> to <math>p^+</math> between atoms activates bonding</p>	<p>Net Bond Direction <math>\begin{matrix} + \\ \downarrow \\ \text{Li} \end{matrix} \xrightarrow{e_{\text{Li}}^-} \begin{matrix} - \\ \uparrow \\ \text{F} \end{matrix}</math>  <math>(+) \rightarrow (-)</math> <math>\begin{matrix} \text{end} &amp; \text{end} \\ 0.91\chi &amp; \rightarrow &amp; e_{\text{F}}^- &amp; 4.19\chi \end{matrix}</math></p>  <p>Molecular Orbital MO formed by shared pair of <math>e^-</math> before separation as ions</p>	<p>Ionic lattice, LiF</p> <p><math>\text{Li}^{1+} \cdot \text{F}^{1-}</math> forms an extended network of alternating cations and anions in 3D</p>  <p>Large <math>\Delta\chi</math> causes total <math>e^-</math> pair transfer to form separate ions with Atomic Orbitals AO</p>	
<p>NonMetal NonMetal] <b>polar covalent bond</b></p> <p><math>\Delta\chi</math> medium: <math>{}_{\text{Group 1}}\chi &lt; {}_{\text{Group 7}}\chi</math></p> 	<p>Net Bond Direction <math>\begin{matrix} + \\ \downarrow \\ \text{H} \end{matrix} \xrightarrow{e_{\text{H}}^-} \begin{matrix} - \\ \uparrow \\ \text{F} \end{matrix}</math>  <math>(+) \rightarrow (-)</math> <math>\begin{matrix} \text{end} &amp; \text{end} \\ 2.30\chi &amp; \rightarrow &amp; e_{\text{F}}^- &amp; 4.19\chi \end{matrix}</math></p> 	<p>Polar covalent molecule, HF</p> <p><math>\text{H}^{\delta+} - \text{F}^{\delta-}</math> forms discrete molecules of single bonded atoms</p>  <p>Shared <math>e^-</math> pair: Molecular orbital Single bond</p>	
<p>NonMetal NonMetal] (<b>non polar</b>) <b>covalent bond</b></p> <p><math>\Delta\chi</math> small: <math>{}_{\text{Group 6}}\chi = {}_{\text{Group 6}}\chi</math></p> 	<p>Net Bond Direction <math>\begin{matrix} \emptyset \\ \downarrow \\ \text{O} \end{matrix} \xleftrightarrow{2 \times e_{\text{O}}^-} \begin{matrix} \emptyset \\ \uparrow \\ \text{O} \end{matrix}</math>  is zero, <math>\emptyset</math> <math>\begin{matrix} \text{end} &amp; \text{end} \\ 3.61\chi &amp; \leftarrow &amp; 2 \times e_{\text{O}}^- &amp; 3.61\chi \end{matrix}</math></p> 	<p>(<b>non polar</b>) Covalent molecule, <math>\text{O}_2</math></p> <p><math>\text{O} = \text{O}</math> forms discrete molecules of double bonded atoms</p>  <p>Two shared <math>e^-</math> pairs Double bond</p>	
<p>Metal Metal] <b>metallic bond</b></p> <p><math>\Delta\chi</math> small: <math>{}_{\text{Group 1}}\chi = {}_{\text{Group 1}}\chi</math></p> 	<p>Net Bond Direction <math>\begin{matrix} \emptyset \\ \downarrow \\ \text{Li} \end{matrix} \xrightarrow{e_{\text{Li}}^-} \begin{matrix} \emptyset \\ \uparrow \\ \text{Li} \end{matrix}</math>  is zero, <math>\emptyset</math> <math>\begin{matrix} \text{end} &amp; \text{end} \\ 0.91\chi &amp; \leftarrow &amp; e_{\text{Li}}^- &amp; 0.91\chi \end{matrix}</math></p> 	<p>Metallic lattice, <math>\text{Li}_{(s)}</math></p> <p><math>\text{Li}_{(s)}</math> forms a 3D network of <math>\text{Li}^{1+}</math> cations embedded in a swarm of delocalised electrons <math>e^-</math></p>  <p>Delocalised <math>e^-</math></p> <p>All bonding atoms have low <math>\chi</math> causing <math>e^-</math> pair to become delocalised with no MO.</p>	

Combining **Bond Direction** ( $\pm$ ) with **Number of Bonds** ( $n$ ) formed produces a very useful property associated with bonded atoms known as **Oxidation State**,  $\text{OS} = (\pm) \times (n) = \pm n$ .

This forms the foundation of the next Topic: Redox and Electrochemistry.

## Determining Chemical Bond Types [Revision plus some extension]

The number of bonds formed by an atom is determined by its Group number and Period number. A stable, or expanded, octet is achieved by the loss or gain of the least number of  $e^-$  for the valence shell to produce the most spin-pair orbitals per shell  $n$  according to  $2n^2$ .

Maximum electrons per shell number  $n$

$$\max_{\text{shell}} e^- \text{ per shell} = 2n^2$$

$n$	Examples from the Periodic Table
<b>Shells</b> $n < 3$	Group II Period 2 Beryllium loses two $e^-$ for a valence shell doublet (rather than gain six $e^-$ for an octet); Group V Period 2 Nitrogen gains three $e^-$ for a valence shell octet (rather than lose five $e^-$ for a doublet).
<b>Shells</b> $n \geq 3$	Group VI Period 3 Sulphur can share six $e^-$ to form six spin-pairs with $12e^- < 2 \times 3^2$ (to achieve an expanded octet); Transition Group VIIB Period 4 Manganese can share $7e^-$ to form 7 spin-pair bonds with $14e^- < 2 \times 4^2$ .


### Electronegativity Matrix for Bond Types<sup>5</sup>

Bond types between two atoms, **A** and **B**, can be determined by considering the range of electronegativity values possible (Low, Medium or High) for each atom as the columns and rows of a matrix.


- Electronegativity increases left-to-right and decreases top-to-bottom in the grid (just like in the Periodic Table).
- Assign Low $\chi$ , Medium $\chi$  or High $\chi$  value for each atom (see Periodic Table).
- Locate the intersection between the column for atom **A** and the row for atom **B** to determine Bond Type name.

$\chi_{\mathbf{A}} \leq \chi_{\mathbf{B}}$		Least $\chi$ atom; $\chi_{\mathbf{A}} \leq \chi_{\mathbf{B}}$		
		Low $\chi$	Medium $\chi$	High $\chi$
$\chi_{\mathbf{A}} \leq \chi_{\mathbf{B}}$ ; Most $\chi$ atom	High $\chi$	<b>Ionic Bond</b>	<b>Polar Covalent Bond</b>	<b>Covalent Bond</b>
	Medium $\chi$	Metallic Hydride Bond	Organo Metallic Bond	This section left blank because $\chi_{\mathbf{A}} \not\leq \chi_{\mathbf{B}}$
	Low $\chi$	<b>Metallic Bond</b>		

### Example of using the Electronegativity Matrix for $\text{NaHCO}_3$ bond types on page 12

$\chi_{\text{Na}} \ll \chi_{\text{O}}$		Least electronegative: $\chi_{\text{Na}}$		
		Low $\chi$	Med $\chi$	High $\chi$
Most electronegative: $\chi_{\text{Oxygen}}$	High $\chi$	<b>Ionic Bond</b>	Polar Covalent Bond	Covalent Bond
	Med $\chi$	 <p>Low electronegativity of <math>\chi_{\text{Na}}</math> <u>intersects</u> with High electronegativity of <math>\chi_{\text{O}}</math>, forming an <b>Ionic Bond</b></p>		
	Low $\chi$		Metallic Bond	

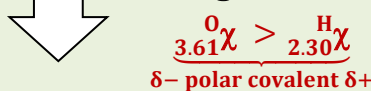
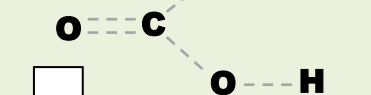
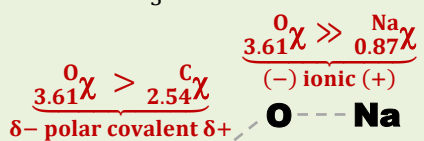
$\chi_{\text{H}} < \chi_{\text{O}}$ $\chi_{\text{C}} < \chi_{\text{O}}$		Least electronegative: $\chi_{\text{H}} \& \chi_{\text{C}}$		
		Low $\chi$	Med $\chi$	High $\chi$
Most electronegative: $\chi_{\text{Oxygen}}$	High $\chi$	Ionic Bond	<b>Polar Covalent Bond</b>	Covalent Bond
	Med $\chi$	 <p>Medium electronegativity of <math>\chi_{\text{H}}</math> and <math>\chi_{\text{C}}</math> <u>intersects</u> with High electronegativity of <math>\chi_{\text{O}}</math>, forming <b>Polar Covalent Bonds</b></p>		
	Low $\chi$	Metallic Bond		

<sup>5</sup> The two grey font bond types are not part of the SACE Chemistry curriculum. These are shown for completeness of electronegativity differences in chemical bonds. Mg atoms in chlorophyll is an example of metals forming organometallic covalent bonds with non-metals. Nickel metal Hydride (NiMH) batteries are examples of metallic hydrides.

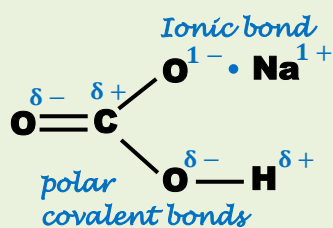


**R3** Determine and identify the **chemical bond types** present in the following compounds, as described above.

**Ex:** Sodium hydrogen carbonate



Replace the bond line for the ionic bond with a non-directional dot.

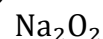


Use solid lines for all covalent bonds and dots between ions for ionic bonds

a) Sodium hypochlorite

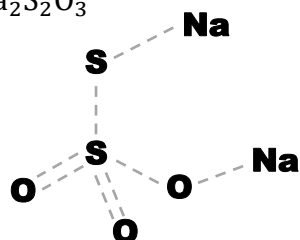
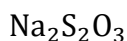


b) Sodium peroxide

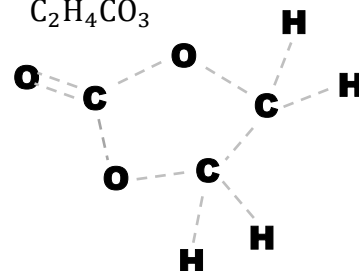
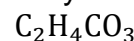


Ionic charge represents the surplus, or deficit, of electrons transferred completely between atoms or molecules when forming ionic bonds.

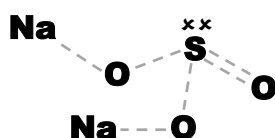
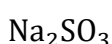
c) Sodium thiosulphate



d) Ethylene Carbonate

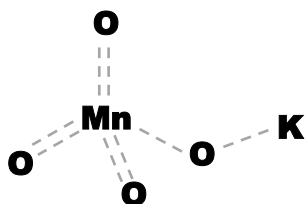
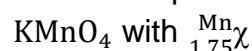


e) Sodium sulphite



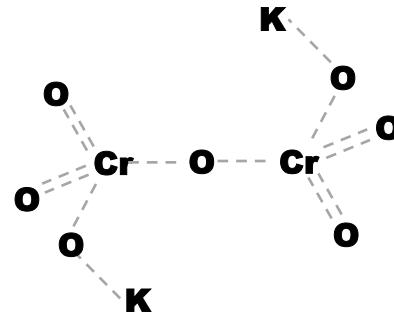
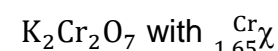
Unbonded  $e^-$  pairs  $\times\times$  affecting the shape of the molecule are included in structural formula diagrams.

f) Potassium permanganate

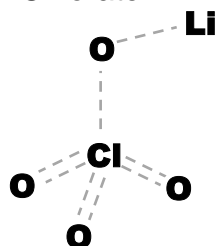


Transition element metals expand the octet in many compounds due to d-orbitals.

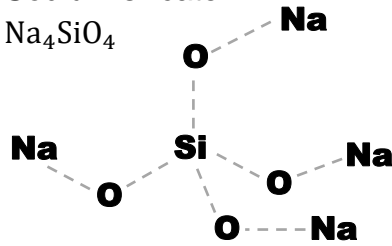
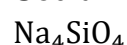
g) Potassium dichromate



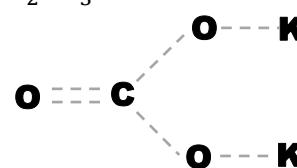
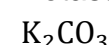
h) Lithium Chlorate



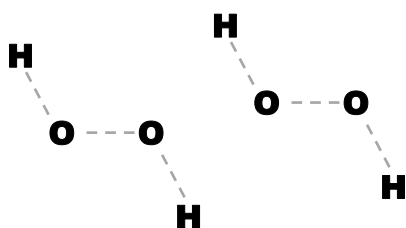
i) Sodium silicate



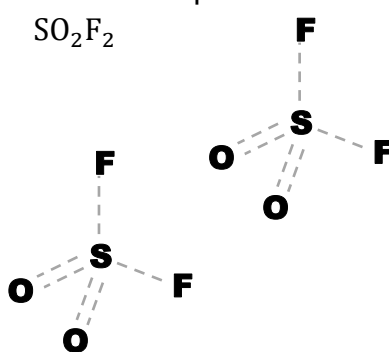
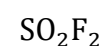
j) Potassium carbonate



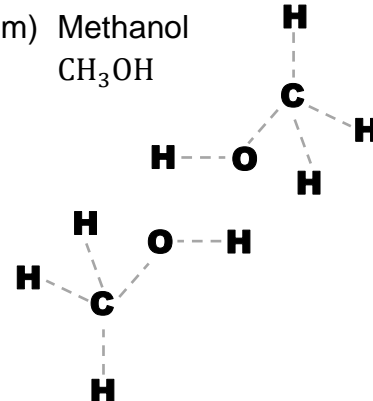
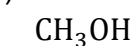
k) Hydrogen peroxide



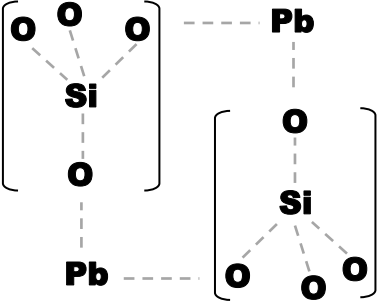
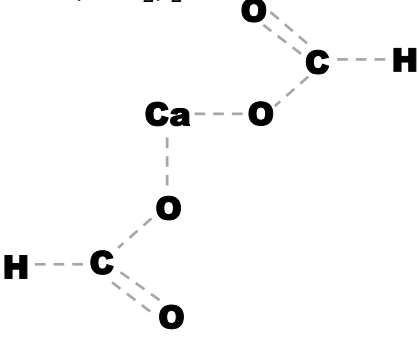
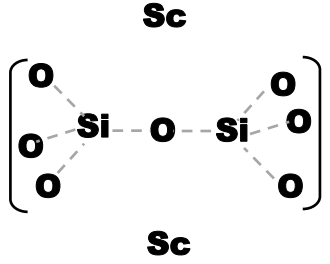
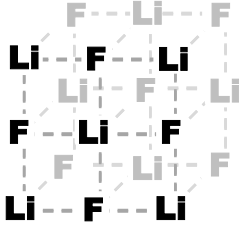
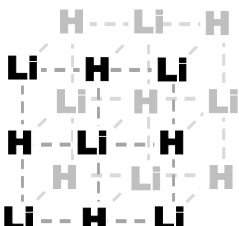
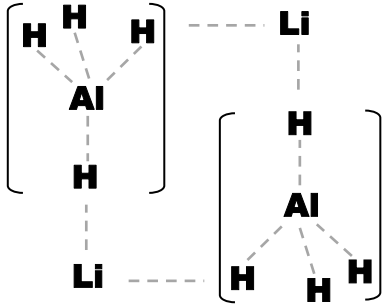
l) Difluoro sulphur dioxide



m) Methanol



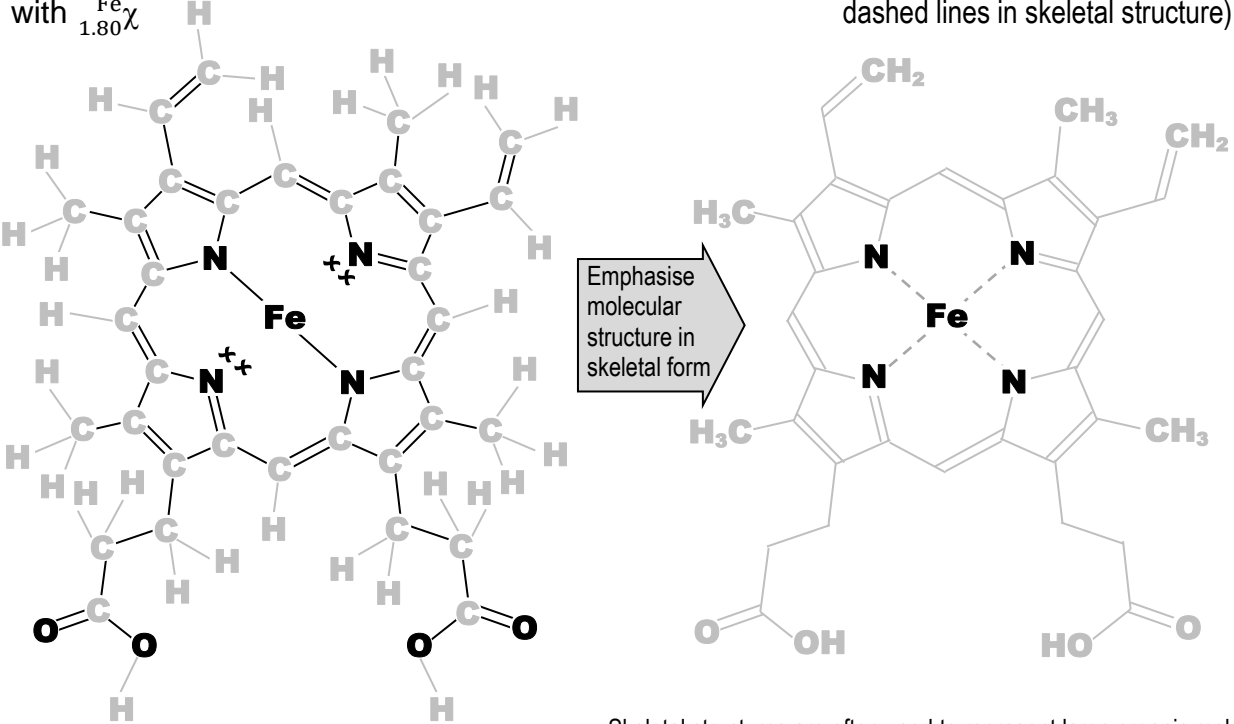
Secondary forces of attraction represented as prominent dashed lines between molecules

<p>n) Lead (IV) silicate <math>\text{PbSiO}_4</math></p> 	<p>o) Calcium ethanoate <math>\text{Ca}(\text{HCO}_2)_2</math></p> 	<p>p) Scandium (III) disilicate <math>\text{Sc}_2\text{Si}_2\text{O}_7</math> (Thortveitite)</p> 
<p>q) Lithium Fluoride <math>\text{LiF}</math></p> 	<p>r) Lithium Hydride <math>\text{LiH}</math></p> 	<p>s) Lithium aluminium hydride <math>\text{LiAlH}_4</math> as an ionic lattice</p> 
<p>An extended network of alternating (+) with (-) ions forms a 3D ionic lattice</p>		

t) Haemoglobin  
 $\text{C}_{34}\text{H}_{32}\text{O}_4\text{N}_4\text{Fe}$   
with  $\frac{\text{Fe}_x}{1.80\lambda}$

All atoms and bonds shown  
(including co-ordinate  $e^-$  pairs  $\times\times$ )

Skeletal structural formula  
(co-ordinate  $e^-$  pairs shown as with dashed lines in skeletal structure)



Emphasise molecular structure in skeletal form

Skeletal structures are often used to represent large organic molecules. Removal of most carbon and hydrogen atoms draws attention to 'active' reaction sites.

(i) each vertex is a tetra-valent carbon atom, unless otherwise indicated for O, N, Fe.  
(ii) terminal groups identified with functional groups  $-\text{CH}_n$ ,  $-\text{OH}$  and  $\text{O}$ .  
(lii) carbon atoms showing less than four bonds include bonded hydrogen atoms.

## Part 1 Defining Oxidation States

Knowledge of the bond direction **and** the number of chemical bonds between atoms (valency) in a molecule or extended network lattice enables us to determine oxidation states for atoms.

**Bond Direction** due to electronegativity  $\chi$  forces of attraction shifting  $e^-$  between atoms:

- Increasing  $e^-$  control makes an atom more negatively charged:  $\therefore +e^- \rightarrow (-)$  **direction**.
- Decreasing  $e^-$  control makes an atom less negatively charged:  $\therefore -e^- \rightarrow (+)$  **direction**.

**Valency** is the **number** ( $n$ ) of chemical bonds formed by shifting  $e^-$  to form stable valence spin-pair orbitals:

- Stable doublet for LHS Period 1 and 2.
- Stable octet for RHS Period 2 and higher.
- Expanded octet for Period 3 and higher.

Bond **direction** ( $\pm$ ) **WITH** Valency **number** ( $n$ ) is **Oxidation State** ( $\pm n$ ) <sup>[aka OS]</sup>.

- **Reduction** is shifting  $e^-$  towards a reactant: **Gain** (+)  $e^- \times n = (-n)$  **decreased OS**
  - **Oxidation** is shifting  $e^-$  away from a reactant: **Lose** (-)  $e^- \times n = (+n)$  **increased OS**.
- Reduction and Oxidation** occur simultaneously during chemical reactions as **Redox**.

**Oxidation State** ( $\pm n$ ) is the product between bond **direction** ( $\pm$ ) with the **number** ( $n$ ) of bonding-electrons shifting between atoms for chemical bond formation, ( $\pm n$ ) = ( $\pm$ )  $\times$  ( $n$ ):

- ( $\pm$ ) The **direction** of electrons shifting between atoms due to **differences** in electronegativity  $\Delta\chi$ ;
- ( $n$ ) The **number** of chemical bonds an atom makes with **different** elements.

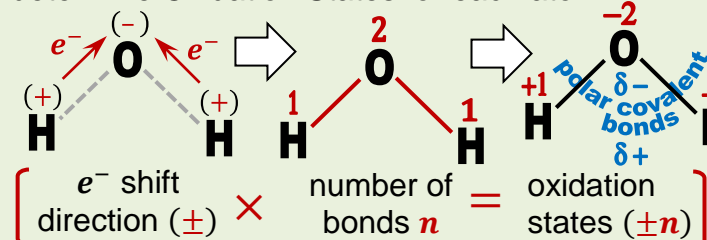
- Non-zero Oxidation State may be assigned when there is a chemical bond between two, or more, atoms.
- Differences in  $\chi$  ( $\Delta\chi$ ) between atoms produce different bond types.
- Zero electronegativity difference produces a zero-oxidation state.

Electronegativity $\chi$		Bond Type	$e^-$ Shift	
$\Delta\chi$	Type			
Zero to low	Both Low	metallic [Metal Metal]	delocalised	
	Both High	(Non Polar) covalent [Non Metal Non Metal]	shared	Localised
medium	Medium with High	polar covalent [Non Metal Non Metal]	partial	
high	One Low One High	ionic [Metal Non Metal]	complete	

**What directional sign for Oxidation State, in Compounds?** (-) or (+) or (zero)

- Structural formulae represent shared valence  $e^-$  pairs as a line between two bonded atoms.
- High  $\chi$  atoms have  $e^-$  shift towards them, producing a (-) **OS** sign for atoms with high  $\chi$ .
- Low  $\chi$  atoms have  $e^-$  shift away from them, producing a (+) **OS** sign for atoms with low  $\chi$ .
- Equal  $\chi$  atoms have  $e^-$  shift equally between them, giving a (zero) **OS** sign for each atom.

**Example:** Use the 'short form' Periodic Table to consider which atoms in a  $H_2O$  molecule have the highest and which the lowest electronegativity to determine Oxidation States for each atom.



**Short Form Periodic Table**

H								He	P1
Li	Be	B	C	N	O	F	Ne	P2	
Na	Mg	Al	Si	P	S	Cl	Ar	P3	
K	Ca	Ga	Ge	As	Se	Br	Kr	P4	
Rb	Sr	In	Sn	Sb	Te	I	Xe	P5	
Cs	Ba	Tl	Pb	Bi	Po	At	Rn	P6	
Fr	Ra	Transition Rare							P7
G1	G2	G3	G4	G5	G6	G7	G8		
+1	+2	+3	+4	-3	-2	-1	n/a		

- **Electronegativity**  $\overset{(+)}{H} < \overset{(-)}{O}$
  - **Valency**  $H = 1; O = 2$
- H<sub>2</sub>O**

## Assigning Bond Direction ( $\pm$ ) Using Periodic Table Electronegativity Trends

**Oxidation States** represent electron movement between bonding atoms along chemical bonds. Distribution of bonding electrons between atoms is caused by electronegativity differences,  $\Delta\chi$ .

- Equal sharing of electrons between atoms produces (Non Polar) covalent bonds for two atoms both with high electronegativity, or metallic bonds for atoms all having low electronegativity.
- Partial sharing of electrons between atoms produces polar-covalent bonds.
- Complete transfer of electrons atom-to-atom produces separate ions were each ionic charge represents one **ionic bond**. **Ex:**  $\text{Li}^{1+}$  forms one ionic bond;  $\text{P}^{3-}$  forms three ionic bonds.

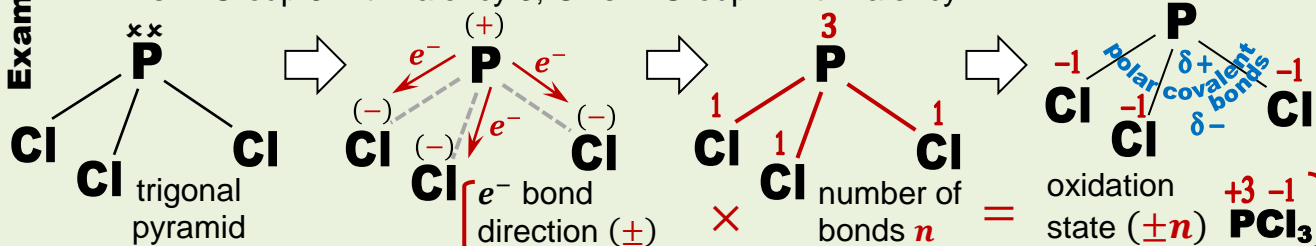
**Q1** Write **oxidation state** ( $\pm n$ ) above each atom in these structural **and** molecular formulae.

- Derive bond **direction** ( $\pm$ ) using **electronegativity** differences from Short Form Table;
- Obtain **valency** ( $n$ ) by counting the number of bonds shown in the structural formulae.

**Example #1**

Phosphorous trichloride **PCl<sub>3</sub>** is a non-metal / non-metal polar covalent molecule.

- P is slightly left of Cl on the Periodic Table in same Period; **electronegativity P < Cl**
- P is in Group 5 with valency 3; Cl is in Group 7 with valency 1

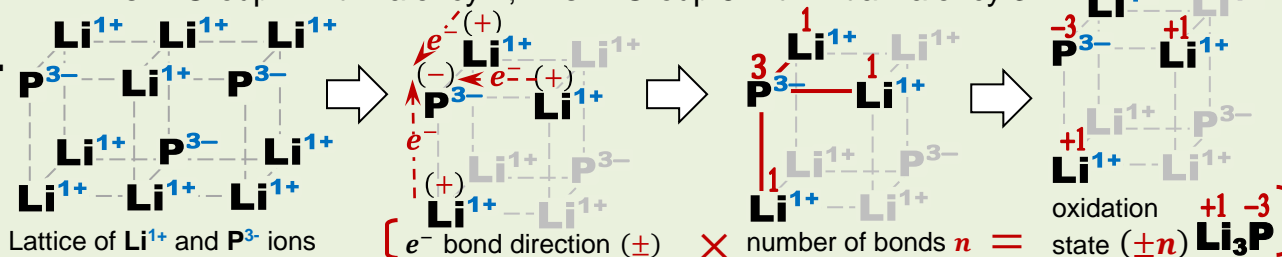


a) <b>NH<sub>3</sub></b> Ammonia		b) <b>Br<sub>2</sub></b> Bromine		c) <b>CO<sub>2</sub></b> Carbon Dioxide	
d) <b>SiF<sub>4</sub></b> Silicon Fluoride		e) <b>CaO</b> Calcium Oxide		f) <b>Na<sub>2</sub>O<sub>2</sub></b> Sodium Peroxide	
g) <b>HClO</b> Hypochlorous Acid		h) <b>CH<sub>4</sub></b> Methane		i) <b>CF<sub>4</sub></b> Tetra Fluoro Methane	

**Example #2**

Lithium phosphide is a metal / non-metal ionic lattice of  $3 \times \text{Li}^{1+} + \text{P}^{3-} \rightarrow \text{Li}_3\text{P}$ .

- Li is very much to the left of P on the Periodic Table; **electronegativity Li  $\ll$  P**
- Li is in Group 1 with valency 1; P is in Group 5 with initial valency 3



## Summing Up ( $\Sigma$ ) Oxidation State Bond Orders

**Oxidation state** values within each type of chemical species are the arithmetic sum ( $\Sigma$ ) of the overall ionic (electrical charge) value of the species when considered as structural formula. This outcome is the result of accounting for the distribution of electrically charged bonding electrons.

- The generalised name for any type of chemical is 'species'; this includes combinations of structural type (molecule/lattice) with formula (element/compound) and charge (neutral/ion):
  - Solid ammonium nitrate is an ionic lattice of molecular ions:  $\text{NH}_4\text{NO}_3 \rightarrow (\text{NH}_4)^{1+} + (\text{NO}_3)^{1-}$
  - Aqueous sodium bicarbonate contains dissociated ions:  $\text{NaHCO}_3(\text{s}) \xrightarrow{(\text{aq})} \text{Na}_{(\text{aq})}^{1+} + (\text{HCO}_3)_{(\text{aq})}^{1-}$
  - Glucose is a discontinuous lattice of polar molecules:  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \xrightarrow{(\text{aq})} \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$

**Q2** Write **oxidation state** ( $\pm n$ ) above each atom in these structural and molecular formulae.

- Oxidation state values add up to the overall ionic charge for molecules (including zero)

**Example: Sodium bicarbonate  $\text{NaHCO}_3$**

Sodium bicarbonate  $\text{NaHCO}_3$  dissociates into bicarbonate anion  $\text{HCO}_3^{1-}$  when dissolved in water<sub>(aq)</sub>:

$$\text{NaHCO}_3 \xrightarrow{(\text{aq})} \text{Na}^{1+} + \text{HCO}_3^{1-}$$

Ionic sodium bicarbonate  $\xrightarrow{\text{aqueous dissociation}}$  Molecular bicarbonate ion  $\text{HCO}_3^{1-}$  + Dissociated ions  $\text{Na}^{1+}$  Monatomic sodium ion

**Electronegativity**  $\text{Na} \ll \text{H} < \text{C} < \text{O}$       $\text{Na} \ll \text{O}$       $\text{H} \ll \text{O}$       $\text{C} < \text{O}$

**Valency**  $\text{Na} = 1; \text{H} = 1; \text{C} = 4; \text{O} = 2$      metal non metal     non metal non metal     strongly polar covalent non metal     mildly polar covalent non metal

$\left[ e^- \text{ bond direction } (\pm) \times \text{ number of bonds } n = \text{ oxidation state } (\pm n) \right]$

The **arithmetic** sum  $\Sigma$  of all **oxidation state** values for each atom must equal **ionic charge** of that species.

$$\left[ \begin{matrix} +1 \\ \text{Na} \\ +1 \end{matrix} \right] \left[ \begin{matrix} +1 & +4 & -2 \\ \text{H} & \text{C} & \text{O}_3 \\ +1 & +4 & -6 \end{matrix} \right] \left[ \begin{matrix} 1+ \\ 1+ & 4- & 2- \\ 1+ & 4- & -6 \end{matrix} \right] \Sigma (1 \times +1) + (1 \times +4) + (3 \times -2) = 1^-$$

The **only** situation when oxidation state value is equivalent to ionic bond charge is for monatomic ions  $\text{Na}^{1+}$

<p>a) Lithium carbonate <math>\text{Li}^{1+}</math> <math>\text{Li}^{1+}</math> ionic bond sites <math>\left\{ \begin{matrix} 1- \\ \text{O} \\ \text{C}=\text{O} \\ \text{O} \\ 1- \end{matrix} \right\}</math></p> $\text{Li}_2\text{CO}_3 \xrightarrow{(\text{aq})} 2\text{Li}^{1+} + \text{CO}_3^{2-}$	<p>b) Calcium sulphate <math>\text{Ca}^{2+}</math> ionic bond sites <math>\left\{ \begin{matrix} \text{O} \\ \text{S} \\ \text{O} \\ \text{O} \\ 1- \end{matrix} \right\}</math></p> $\text{CaSO}_4 \xrightarrow{(\text{aq})} \text{Ca}^{2+} + \text{SO}_4^{2-}$
<p>c) Sodium chlorate <math>\text{Na}^{1+}</math> ionic bond site <math>\left\{ \begin{matrix} \text{O} \\ \text{Cl} \\ \text{O} \\ \text{O} \end{matrix} \right\}</math></p> $\text{NaClO}_3 \xrightarrow{(\text{aq})} \text{Na}^{1+} + \text{ClO}_3^{1-}$	<p>d) Copper (I) thiocyanate <math>\text{Cu}^{1+}</math> ionic bond site <math>\text{S}^{1-}-\text{C}\equiv\text{N}</math></p> $\text{CuSCN} \xrightarrow{(\text{aq})} \text{Cu}^{1+} + \text{SCN}^{1-}$
<p>g) Potassium phosphate <math>\text{K}^{1+}</math> <math>\text{K}^{1+}</math> ionic bond sites <math>\left\{ \begin{matrix} \text{O} \\ \text{P} \\ \text{O} \\ \text{O} \\ \text{O} \end{matrix} \right\}</math></p> $\text{K}_3\text{PO}_4 \xrightarrow{(\text{aq})} 3\text{K}^{1+} + \text{PO}_4^{3-}$	<p>h) Sodium hydroxide <math>\text{Na}^{1+}</math> ionic bond site <math>\text{O}^{1-}-\text{H}</math></p> $\text{NaOH} \xrightarrow{(\text{aq})} \text{Na}^{1+} + \text{OH}^{1-}$

## Averaging Oxidation States

Individual atoms can gain and lose electrons when surrounded by atoms with different electronegativity values. The resultant competing bond directions requires structural analysis.

- Organic molecules often have the same carbon atom taking electrons from hydrogen while losing electrons to oxygen (or halogens) within the same structure.
- Carbon-to-carbon bonds contribute a zero-oxidation state (atoms of the same element).
- The competing bond directions can be averaged for each element in a species.

**Q3** Write **oxidation state** ( $\pm n$ ) above each atom in these structural and molecular formulae.

- Average the oxidation state for elements with competing bond directions.
- Assign fractional oxidation states as a value averaged over a molecule as appropriate.

**Example #1: CH<sub>2</sub>O Methanal**

Electrons move from the central Carbon atom towards Oxygen

Electrons move from Hydrogen towards the same Carbon atom

Bond direction?  $\overset{+}{\text{C}} < \overset{-}{\text{O}}$   
How many bonds between atoms?  $\overset{2}{\text{C}} : \overset{2}{\text{O}}$   
**Oxidation State**  $\overset{+2}{\text{C}} \overset{-2}{\text{O}}$

Bond direction?  $\overset{+}{\text{H}} < \overset{-}{\text{C}}$   
How many bonds between atoms?  $\overset{1}{\text{H}} : \overset{2}{\text{C}}$   
**Oxidation State**  $\overset{+1}{\text{H}} \overset{-2}{\text{C}}$

Average =  $\frac{(+2 + -2)}{1 \text{ Carbon}}$

Carbon has competing bond directions +2 and -2

**CH<sub>2</sub>O** denotes zero net electron movement for bonded Carbon

a) <b>CH<sub>3</sub>F</b> Fluoro methane (compare to CH <sub>4</sub> Q1h)		b) <b>CH<sub>2</sub>F<sub>2</sub></b> Di-fluoro methane		c) <b>CHF<sub>3</sub></b> Tri-fluoro methane (compare to CF <sub>4</sub> Q1i)	
d) <b>CH<sub>2</sub>O<sub>3</sub></b> Carbonic acid		e) <b>CH<sub>2</sub>O<sub>2</sub></b> Methanoic acid		f) <b>CH<sub>2</sub>O</b> Methanal (reprise Q3 example #1)	
g) <b>C<sub>3</sub>H<sub>6</sub>O</b> Propanone		h) <b>C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N</b> Glycine		i) <b>C<sub>2</sub>H<sub>3</sub>F<sub>3</sub></b> 1,1,2 tri-fluoro Ethane	
j) <b>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>1-</sup></b> Ethanoate anion		k) <b>C<sub>2</sub>H<sub>3</sub>Cl</b> Vinyl chloride		l) <b>CH<sub>4</sub>ON<sub>2</sub></b> Urea	

**Example #2: C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> propanoic acid**

Bond direction first

Number of bonds with different elements

**C** atoms averaged as:  $\frac{(-3 - 2 + 3)}{3 \text{ Carbons}} = \frac{-2}{3} \rightarrow$  **Oxidation State**  $\Sigma(-2 + 6 - 4) = 0$

**C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>**

## Using Structural Formulae

**Oxidation states (OS)** can be determined using the definition<sup>6</sup> in Part 1 with structural formulae.

Sulphur can only have three types of **valency**:

- $n = 2$  to achieve a 'stable octet' for **Group 6**;
- $n = 4$  or  $6$  as **Period 3** can 'expand the octet'.

Each valency type can then combine with many different elements to produce a large range of **electronegativity** differences as  $\pm n$  OS:

- **Zero difference** between two sulphur atoms;
- **OS = -2 or -1** with elements having lower electronegativity values than Sulphur;
- **OS = +1, +2, +4 or +6** with higher values.

**Electronegativity Allen Values for Short Form Periodic Table**

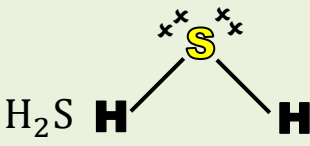
P1	<b>H</b> 2.30									He n/a
P2	Li 0.91	Be 1.58	B 2.05	<b>C</b> 2.54	<b>N</b> 3.07	<b>O</b> 3.61	F 4.19			Ne n/a
P3	<b>Na</b> 0.87	Mg 1.29	Al 1.61	Si 1.92	<b>P</b> 2.25	<b>S</b> 2.59	<b>Cl</b> 2.87			Ar n/a
P4	K 0.73	Ca 1.03	Transition/Rare	Ga 1.76	Ge 1.99	As 2.21	Se 2.42	Br 2.67	Kr n/a	Non-Metals
P5	Rb 0.71	Sr 0.96		In 1.66	Sn 1.82	Sb 1.98	Te 2.16	I 2.36	Xe n/a	
P6	Cs 0.66	Ba 0.88		Tl 1.79	Pb 1.85	Bi 2.01	Po 2.19	At 2.39	Rn n/a	Non-Metals
P7	Fr 0.67	Ra 0.89								
	G1	G2		G3	G4	G5	G6	G7	G8	
	Metals			Metalloids		Non-Metals				

Electronegativity increases from bottom-left to top-right and decreases from top-left to bottom-right.

**Q4** Write **oxidation state** ( $\pm n$ ) above each atom in these structural and molecular formulae.

- Obtain **valency** ( $n$ ) by counting the number of bonds shown in the structural formulae;
- Derive **bond direction** ( $\pm$ ) using electronegativity differences from Short Form Table<sup>7</sup>.

**Example**

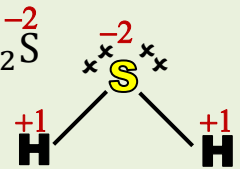
$\text{H}_2\text{S}$   Hydrogen sulphide

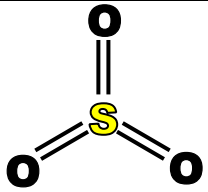
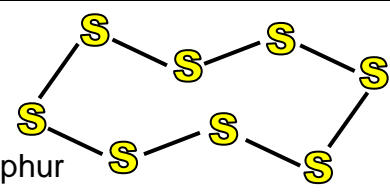
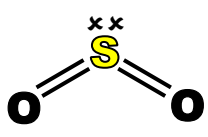
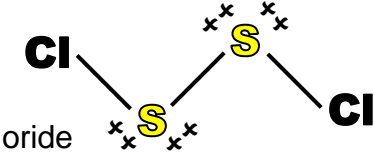
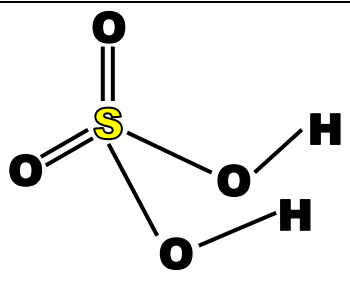
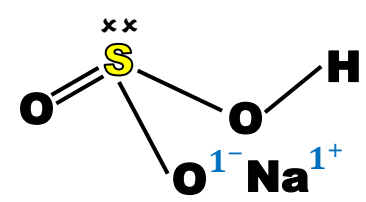
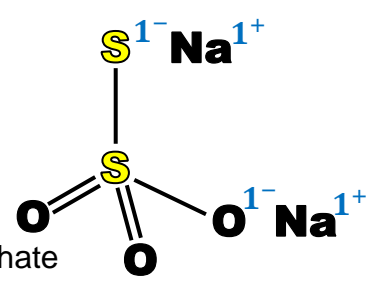
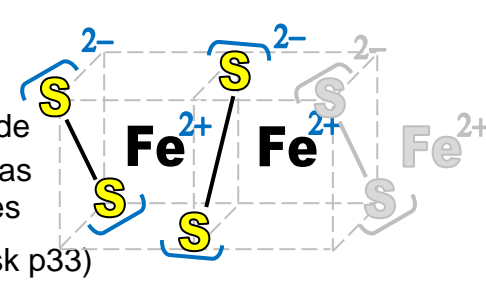
• **Valency:** H = 1, S = 2

• **Electronegativity:** H < S

$\left. \begin{array}{l} \text{H} \\ \times 2 \end{array} \right\} \begin{array}{l} +1 \\ -2 \end{array}$  written as  $\overset{+1}{\text{H}}\overset{-2}{\text{S}}$

No  $\text{H}^{1+}$  or  $\text{S}^{2-}$  ions in the  $\text{H}_2\text{S}$  molecule, although  $\text{H}_2\text{S}_{(\text{aq})} \rightleftharpoons \text{H}_{(\text{aq})}^{1+} + \text{HS}_{(\text{aq})}^{1-}$ .



a) $\text{SO}_3$ Sulphur trioxide		b) $\text{S}_8$ Elemental sulphur	
c) $\text{SO}_2$ Sulphur dioxide		d) $\text{S}_2\text{Cl}_2$ Disulphur dichloride	
e) $\text{H}_2\text{SO}_4$ Sulphuric acid		f) $\text{NaHSO}_3$ Sodium bisulphite	
g) $\text{Na}_2\text{S}_2\text{O}_3$ Sodium thiosulphate		h) $\text{FeS}_2$ Iron (II) persulphide is known as iron pyrites (SHE Task p33)	
			

<sup>6</sup> IUPAC is currently reviewing the use of pre-determined rules to be the definition for Oxidation States due to the inherent circularity.

<sup>7</sup> IUPAC preferred electronegativity scale; see <https://www.degruyter.com/view/j/pac.2016.88.issue-8/pac-2015-1204/pac-2015-1204.xml>

### Three Rules arising from the Oxidation State Definition

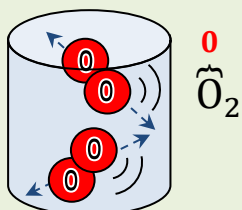
Non-zero **Oxidation states** ( $\pm n \neq 0$ ) represent the number of chemical bonds an atom makes with **different** types of atoms (elements) in a chemical compound (two, or more, different elements).

#### ① Elements as neutrally charged atoms have oxidation state of zero

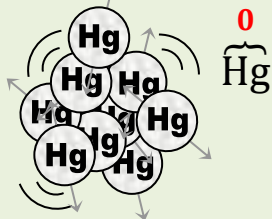
- Identical atoms have  $\Delta\chi = 0$ , and therefore zero overall bond direction.
- Hence, **oxidation state** of any (charge neutral) element is **zero**, regardless of  $n$   $OS = \pm n = 0 \times n = 0$

Solid, liquid or gas; monatomic, molecule or 3D lattice; elemental **atoms** have an **OS of zero**

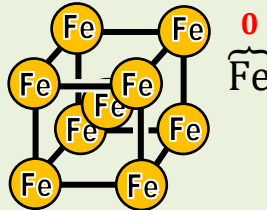
Gaseous oxygen  $O_2$  is a diatomic molecular element



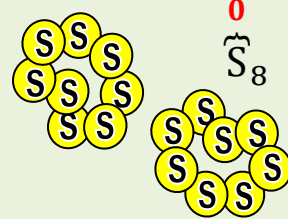
Liquid mercury Hg is a monatomic element



Solid iron Fe is a 3D crystalline lattice element



Amorphous sulphur  $S_8$  is a cyclic molecular element



#### ② Oxygen forms compounds with oxidation state -2 (but not with itself or Fluorine)

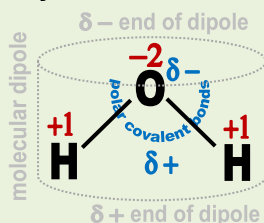
- The very rare element Fluorine has the highest Allen's electronegativity value of 4.2
- The very common element oxygen has the second highest Allen's electronegativity value of 3.6
- Oxygen is the most electronegative **common** element: All the other elements  $\chi < \text{Oxygen } 3.6\chi < \text{Fluorine } 4.2\chi$

Group VI oxygen has a Valency of **2** to achieve a stable octet and a very high electronegativity for **OS -2**.

Paradigm example for oxygen (-2)

**Water Molecule**  $H_2O$

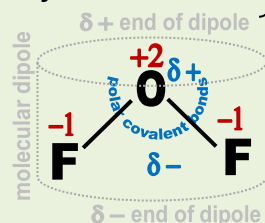
Electronegativity  $H < O$  }  $\begin{matrix} +1 & -2 \\ \overline{H} & \overline{O} \\ \times 2 & \times 1 \end{matrix}$   
Valency  $O = 2; H = 1$



Two variations (+2 and -1) on oxidation state for oxygen (-2).

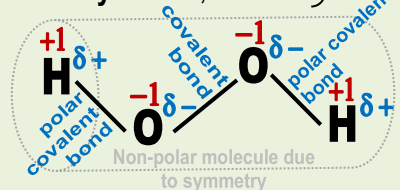
**Oxygen Di-fluoride**  $F_2O$

Electronegativity  $O < F$  }  $\begin{matrix} +2 & -1 \\ \overline{O} & \overline{F} \\ \times 1 & \times 2 \end{matrix}$   
Valency  $O = 2; F = 1$



**Hydrogen Peroxide**  $H_2O_2$

Electronegativity  $H < O$  }  $\begin{matrix} +1 & -1 \\ \overline{H} & \overline{O} \\ \times 2 & \times 2 \end{matrix}$   
 $O = 0$   
Valency  $O = 2; H = 1$



Lavoisier suggested that **Oxidation State**<sup>9</sup> was the measure of how much oxygen had combined with an element.

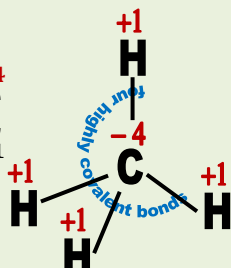
#### ③ Hydrogen forms compounds with oxidation state +1 (but not with metals)

Hydrogen OS **+1** with Non-Metals as  $H_{2,3}\chi < \text{Non-Metals}\chi$

**Methane**  $CH_4$

Electronegativity  $H < C$  }  $\begin{matrix} +1 & -4 \\ \overline{H} & \overline{C} \\ \times 4 & \times 1 \end{matrix}$   
Valency  $H = 1; C = 4$

There are **no** hydrogen cations  $H^{1+}$  in the methane molecule.

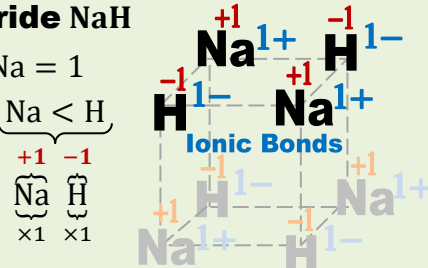


Hydrogen OS **-1** with Metals as  $H_{2,3}\chi > \text{Metals and Metalloids}\chi$

**Sodium Hydride**  $NaH$

Valency  $H = 1; Na = 1$   
Electronegativity  $\{Na < H\}$

There are hydride anions  $H^{1-}$  in the 3D lattice.



<sup>8</sup> Only 1 in 10 million ( $10^7$ ) water molecules self-ionise  $H_2O \xrightarrow{(aq)} H_{(aq)}^{1+} + OH_{(aq)}^{1-}$  to form ions external to any water  $H_2O$  molecules

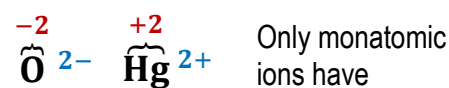
<sup>9</sup> <https://www.chemheritage.org/historical-profile/antoine-laurent-lavoisier>



## The Arithmetic Link Between Oxidation State and overall Ionic Charge

Ionic charge is the surplus, or deficit, of electrons in an atom or molecule due to complete electron transfer between atoms or molecules with high electronegativity differences.

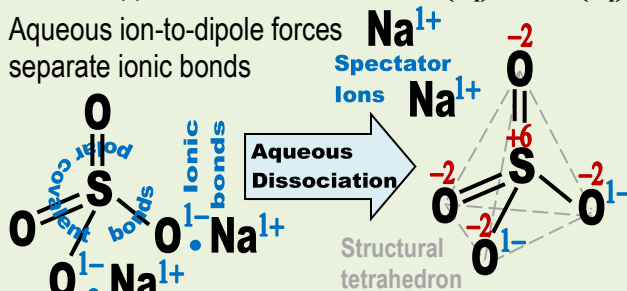
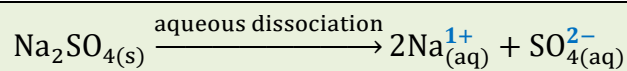
Single atoms that gain, or lose, electrons become monatomic ions with ionic charges equivalent to their oxidation state values.



Molecules that gain, or lose, electrons become polyatomic ions with an algebraic connection between the total sum of oxidation states within the molecule and its overall ionic charge.



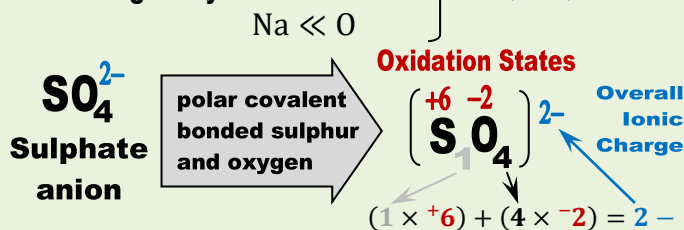
**Sodium sulphate**  $\text{Na}_2\text{SO}_4$  is an ionic salt that contains a variety of non-ionic primary bond types:



The polar-covalent bonds between oxygen and sulphur remain within the sulphate anion  $\text{SO}_4^{2-}$ :

**Valency:** Na = 1; S = 6; O = 2

**Electronegativity:** Na < S < O



Multiply the subscripted proportionality value ( $S_1$  and  $O_4$ ) for each element with its matching oxidation state;

- $S_1$  for sulphur with  $\overset{+6}{\text{S}}$  to obtain  $1 \times +6 = +6$
- $O_4$  for oxygen with  $\overset{-2}{\text{O}}$  to obtain  $4 \times -2 = -8$
- These arithmetic products are then summed together to obtain the overall ionic charge as  $+6 + -8 = 2-$ ;

$$\sum \text{SO}_4^{2-} = \left[ \overset{+6}{\text{S}}_1 + \overset{-2}{\text{O}}_4 \right] = (1 \times +6) + (4 \times -2) = (+6) + (-8) = 2-$$

Overall Ionic Charge

The correct **oxidation state** value for all elements can be calculated by applying the 'three rules' every time:

- OS between **elements** is **zero**;
- OS for **oxygen** is usually **-2**;
- OS for **hydrogen** is **+1 with non-metals**
- All other elements need to adjust their oxidation state arithmetically to correspond with these three rules.

Alternatively, structural diagrams do reveal the number of bonds being made, but they can become very complex.

**Q5** Assign oxidation state values to the underlined elements in the following compounds.

(a) Elements in Period 3, and higher, can 'Expand the Octet'			(b) Transition elements and Metalloids	
Phosphorous	Chlorine	Sulphur	Transition	Metalloids
$\underline{\text{P}}\text{H}_3$	$\text{H}\underline{\text{Cl}}$	$\underline{\text{S}}\text{F}_6$	$\underline{\text{V}}\text{O}$	$\underline{\text{Po}}\text{Br}_2$
$\underline{\text{P}}\text{F}_3$	$\text{Na}\underline{\text{ClO}}$	$\text{H}_2\underline{\text{S}}\text{O}_4$	$\underline{\text{V}}\text{O}_2$	$\underline{\text{Po}}\text{O}_2$
$\underline{\text{P}}_4\text{O}_{10}$	$\underline{\text{Cl}}\text{O}_2$	$\text{H}_2\underline{\text{S}}\text{O}_3$	$\underline{\text{V}}_2\text{O}_3$	$\underline{\text{Sb}}\text{H}_3$
$\text{Na}_4\underline{\text{P}}_2\text{O}_7$	$\text{Na}\underline{\text{ClO}}_3$	$\underline{\text{S}}\text{O}_2\text{F}_2$	$\underline{\text{V}}_2\text{O}_5$	$\underline{\text{Te}}\text{O}_2$
$\text{H}_2\underline{\text{P}}\text{O}_4^{1-}$	$\underline{\text{Cl}}\text{O}_4^{1-}$	$\underline{\text{S}}_2\text{O}_4^{2-}$	$\text{H}_2\underline{\text{V}}\text{O}_4^{1-}$	$\text{H}_4\underline{\text{Te}}\text{O}_6^{2-}$

**Q6** Write **oxidation states** above the atoms in the following formulae **and** structural diagrams as in these examples.

**Example**

Sodium Hydroxide  $\overset{+1}{\text{Na}}\overset{-2}{\text{O}}\overset{+1}{\text{H}}$  (3D ionic lattice)

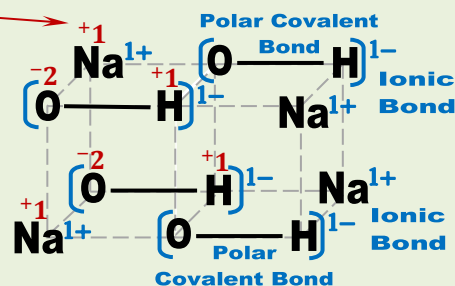
**Valency** Na = 1; H = 1; O = 2

**Electronegativity** Na  $\ll$  H  $\ll$  O

Na  $\ll$  O } **ionic bond** ; H  $\ll$  O } **strongly polar covalent bond**  
 metal non metal } ; metalloid non metal }

The  $\text{Na}^{1+}$  cations and  $\text{OH}^{1-}$  anions are arranged in a 3D repeating pattern extending in all directions.

There are **no**  $\text{O}^{2-}$  or  $\text{H}^{1+}$  ions in the extended lattice.



a) Ammonia  $\text{NH}_3$

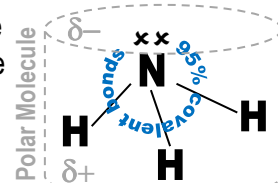
**Valency** N = 3; H = 1

**Electronegativity**

H < N } **polar covalent bond**  
 metalloid non metal }

Non-symmetric distribution of the three polar covalent bonds cause  $\text{NH}_3$  to be a polar molecule.

There are distinct  $\delta^-$  and  $\delta^+$  ends for the overall molecule.



b) Methane  $\text{CH}_4$

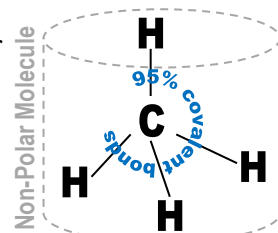
**Valency** C = 4; H = 1

**Electronegativity**

H  $\approx$  C } **slightly polar covalent bond**  
 metalloid non metal }

Symmetric distribution of the four polar covalent bonds cause  $\text{CH}_4$  to be a non-polar molecule.

There are no  $\delta^-$  or  $\delta^+$  ends for the overall molecule.



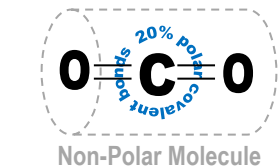
c) Carbon Dioxide  $\text{CO}_2$

**Valency** C = 4; O = 2

**Electronegativity**

C < O } **mildly polar covalent bond**  
 non metal non metal }

Symmetric distribution of the two sets of polar covalent bonds cause  $\text{CO}_2$  to be a non-polar molecule.



d) Silica  $\text{SiO}_2$   
(3D continuous Lattice)

**Valency** Si = 4; O = 2

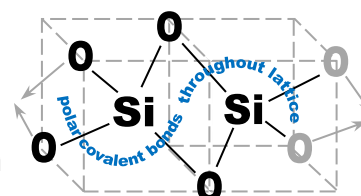
**Electronegativity**

Si < O } **polar covalent bond**  
 metalloid non metal }

Each **Si** has four **O** as its nearest neighbours.

Each **O** has two **Si** as its nearest neighbours.

These lattice coordination values average to  $\text{SiO}_2$ .



e) Peridot  $\text{Mg}_2\text{SiO}_4$  (gem-stone quality olivine)

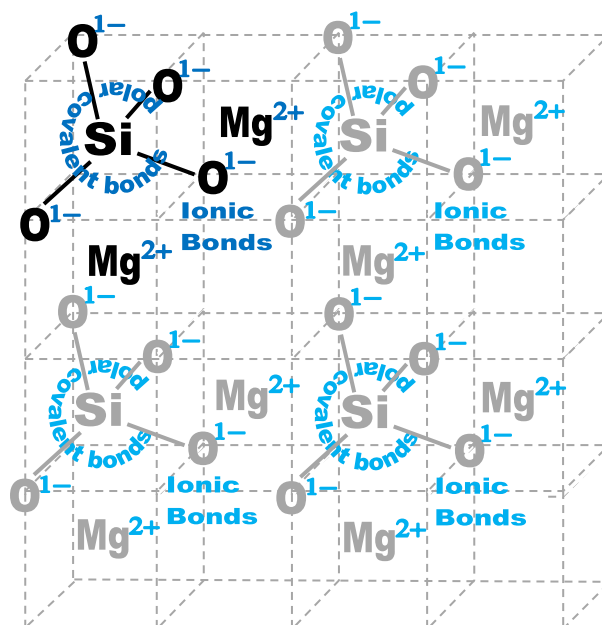
Orthosilicates contain independent  $\text{SiO}_4^{4-}$  anions.

**Valency** Mg = 2; Si = 4; O = 2

**Electronegativity** Mg < Si < O

Mg  $\ll$  O } **ionic bond** ; Si < O } **polar covalent bond**  
 metal non metal } ; metalloid non metal }

The cubic framework for the 3D lattices in Part d) Silica and Part e) Peridot show four oxygen atoms at diagonally opposite corners of the cubes, with one silicon atom at the centre. This arrangement represents the tetrahedral  $\text{SiO}_4$  structural unit usually found in silicates. Sometimes the tetrahedra are independent anions, sometimes interlocking crystals.

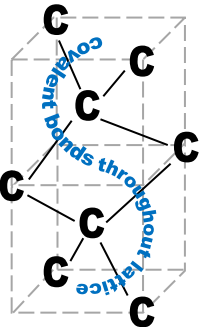
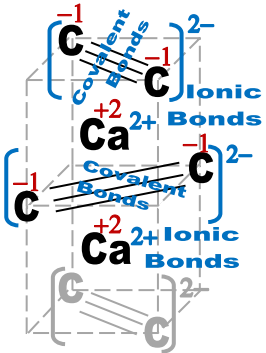


## Identifying Oxidation States with Carbon

Carbon has a range of **oxidation states** from  $-4$  in methane  $\text{CH}_4$  to  $+4$  in carbon dioxide  $\text{CO}_2$ .

- The oxidation state of carbon will be either negative ( $-$ ) or positive ( $+$ ) depending on the electronegativity difference with the other element with which it is bonding.
  - When carbon bonds with hydrogen, carbon contributes a negative oxidation state value.
  - When carbon bonds with oxygen, carbon contributes a positive oxidation state value.
- When carbon bonds with itself, there is zero electronegativity difference between the bonding atoms. Therefore, each carbon-to-carbon bond contributes zero oxidation state value.

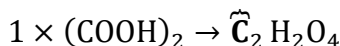
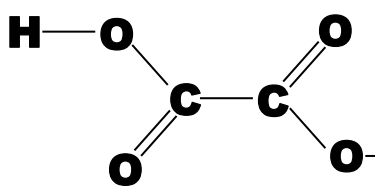
The overall oxidation state for carbon is an arithmetic average of these contributions.

Crystal Lattice Examples for Carbon	<p><b>Diamond</b> consists of carbon atoms covalently bonded in a three-dimensional 3D tetrahedral lattice.</p> <p>The lattice extends in all directions.</p>	 <p>In diamond there are no bonds between <u>different</u> types of atoms.</p> <p><b>Oxidation State of Carbon in diamond</b></p> <ul style="list-style-type: none"> <li>Valency C = 4 (tetravalent);</li> <li>Electronegativity difference 0;</li> </ul> <p><b>Oxidation state</b> <math>\pm n = 0 \times 4 = 0</math></p> <p style="text-align: center;"><b>0</b> C</p> <p>All atoms in their elemental form have oxidation state zero due to this type of zero-value electronegativity difference.</p>
	<p><b>Calcium carbide</b> consists of:</p> <p><math>\text{CaC}_2 \rightarrow \text{Ca}^{2+} + \text{C}_2^{2-}</math></p> <p>Each carbon atom in carbide <math>\text{C}_2^{2-}</math> is triple bonded to another. One site remains available for an ionic bond.</p>	 <p><b>Oxidation States</b></p> <p><math>\text{Ca}^{2+} \cdot [\text{C} \equiv \text{C}]^{2-}</math></p> <p><math>\text{Ca}^{2+} \cdot [\overset{-1}{\text{C}} \equiv \overset{-1}{\text{C}}]^{2-}</math></p> <p><math>(1 \times +2) + (2 \times -1) = 0</math></p>
Organic Molecule	<p><b>Ethanal <math>\text{CH}_3\text{CHO}</math></b> has two tetravalent carbon atoms with a variety of <b>oxidation state</b> contributions:</p> <p>(+) with Oxygen; (0) with Carbon; (-) with Hydrogen</p> <p>Electronegativity: H &lt; C three Hydrogen bonds <math>-3</math> one Carbon bond <math>0</math></p> <p>Electronegativity: C &lt; O H &lt; C two Oxygen bonds <math>+2</math> one Hydrogen bond <math>-1</math> one Carbon bond <math>0</math></p> <p>The average oxidation state for carbon in ethanal <math>\text{C}_2\text{H}_4\text{O}</math> is <math>-1</math></p> <p><math>\frac{(-3) + (+1)}{2} = -1</math></p> <p>Ethanal <math>\text{CH}_3\text{CHO}</math></p> <p><math>\begin{matrix} x &amp; +1 &amp; -2 \\ \text{C}_2 &amp; \text{H}_4 &amp; \text{O} \\ \times 2 &amp; \times 4 &amp; \times 1 \end{matrix}</math></p> <p>Overall Charge</p> <p><math>2x + 4 - 2 = 0</math></p> <p><math>\text{C}_2\text{H}_4\text{O}_1 \rightarrow \overset{-1}{\text{C}}_2\text{H}_4\text{O}</math> as <math>\text{CH}_3\text{CHO}</math></p>	

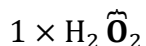
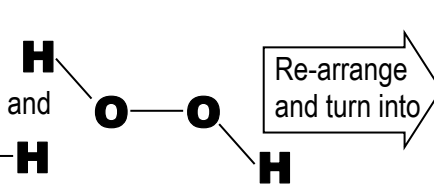
**Q7** Determine and write **oxidation states** in the following formulae and structural diagrams

that represent the reaction equation  $(\overset{\sim}{\text{C}}\text{OOH})_2 + \text{H}_2\overset{\sim}{\text{O}}_2 \xrightarrow{\text{change into}} 2\overset{\sim}{\text{C}}\text{O}_2 + 2\text{H}_2\overset{\sim}{\text{O}}$

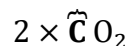
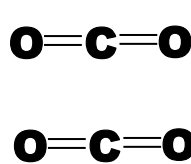
a) Oxalic Acid (in Rhubarb)



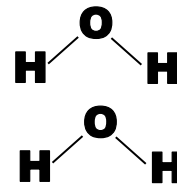
b) Hydrogen Peroxide



c) Carbon Dioxide

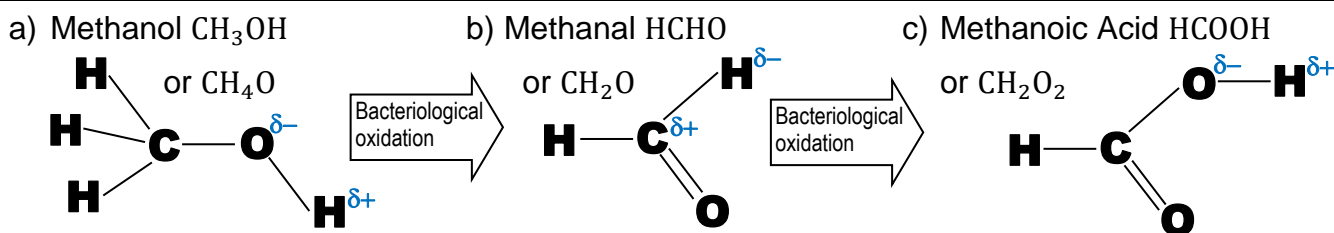


d) Water



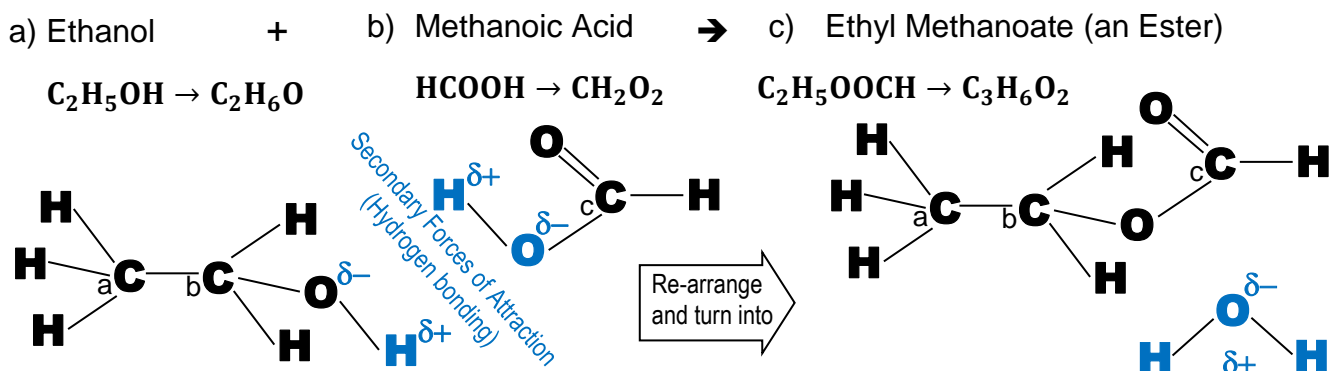
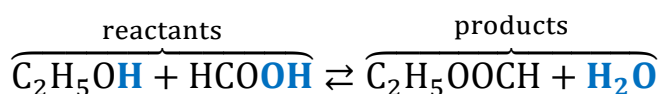
Many organic and biological reactions are redox as indicated by the changing **oxidation states** of carbon as electrons are shifted within molecules for the process of Reactant  $\rightarrow$  Product.

**Q8** Determine and write **oxidation states** above the atoms in the following formulae and structural diagrams



Application of the three rules of Redox provide a reasonable approximation for determining the extent to which oxidation states change during more complex organic reactions. Much more detailed calculations using molecular orbital combinations would be needed for more precise oxidation state values than the fractions suggested in the next question.

**Q9** Determine **oxidation states** for the carbon atoms in this reaction joining two smaller molecules into one larger molecule.



d) State valency of each carbon atom in the organic molecules.

Reactants	Product
a <b>C</b>	a <b>C</b>
b <b>C</b>	b <b>C</b>
c <b>C</b>	c <b>C</b>

e) State **oxidation state** of each carbon atom in the organic molecules.

Reactants	Product
a <b>C</b>	a <b>C</b>
b <b>C</b>	b <b>C</b>
c <b>C</b>	c <b>C</b>

f) State **oxidation state** for Carbon as an element in each organic molecule.

Ethyl Methanoate	$\tilde{\text{C}}_3 \text{H}_6\text{O}_2$
Methanoic Acid	$\tilde{\text{C}}_1 \text{H}_2\text{O}_2$
Ethanol	$\tilde{\text{C}}_2 \text{H}_6\text{O}$

g) State the **changes** in **oxidation state** for Carbon as an element:

$\tilde{\text{C}}$ (Ethanol) $\rightarrow$ $\tilde{\text{C}}$ (Ester)
$\tilde{\text{C}}$ (Acid) $\rightarrow$ $\tilde{\text{C}}$ (Ester)

• Ethanol  $\rightarrow$  Ester **increases OS** for two carbon atoms  
 $-2 \xrightarrow{\text{up to}} -\frac{2}{3}$  which is a  $+1\frac{1}{3} \times 2 = +2\frac{2}{3}$  **oxidation**.

h)

• Acid  $\rightarrow$  Ester **decreases OS** for one carbon atom  
 $+2 \xrightarrow{\text{down to}} -\frac{2}{3}$  which is a  $-2\frac{2}{3} \times 1$  **reduction**.

Why do these redox changes suggest that electrons can become partially delocalised<sup>10</sup> from their covalent bonds and have movement across the central atoms of the molecule<sup>11</sup>?

<sup>10</sup> Moore, Physical Chemistry 5<sup>th</sup> Edition; Non-localised Molecular Orbitals pp 718 – 722; Longman 1972

<sup>11</sup> Rock & Gerhold, Chemistry Principles and Applications; (Extended) Molecular-Orbital Methods pp 122 – 126; W.B. Saunders Co., 1974

## When Oxidation States Differ from Group Numbers

The Periodic Table of Elements shown below is a 'Short Form' version. It does not show the Transition Elements or the Rare Earths. This highlights the diagonal trends in the Period Table.

- The **metals** with low electronegativity values form positive (+) oxidation states with fixed (*n*).
- The **metalloids (and Transition Elements)** with intermediate electronegativity values form (+) oxidation states with multiple possible values (*n*) for elements in Period 3 and greater.
- The **non-metals** with high electronegativity values form negative (-) oxidation states. They also form multiple values (*n*) for Period 3 and greater, known as 'Expanding the Octet'.

'Short Form' Periodic Table of the Elements **Oxidation State Summary**

Oxidation State values tend to correspond with Group number	P1	$\pm 1$ <b>H</b>		Hydrogen has chemical properties of both Group 1 and Group 7					Most Electronegative	n/a He
	P2	+1 <b>Li</b>	+2 <b>Be</b>		+3 <b>B</b>	$\pm 4$ <b>C</b>	-3, -5 <b>N</b>	-2 <b>O</b>	-1 <b>F</b>	n/a Ne
	P3	+1 <b>Na</b>	+2 <b>Mg</b>		+3 <b>Al</b>	+4 <b>Si</b>	$\pm 3, \pm 5$ <b>P</b>	$\pm 2, \pm 4$ <b>S</b>	-1 <b>Cl</b>	n/a Ar
	P4	+1 <b>K</b>	+2 <b>Ca</b>	Transition and Rare Earths	+3 <b>Ga</b>	+4 <b>Ge</b>	+3, +5 <b>As</b>	+2 <b>Se</b>	-1 <b>Br</b>	n/a Kr
	P5	+1 <b>Rb</b>	+2 <b>Sr</b>		+3 <b>In</b>	+2, +4 <b>Sn</b>	+3, +5 <b>Sb</b>	+2 <b>Te</b>	-1 <b>I</b>	n/a Xe
	P6	+1 <b>Cs</b>	+2 <b>Ba</b>		+3 <b>Tl</b>	+2, +4 <b>Pb</b>	+3 <b>Bi</b>	+2 <b>Po</b>	+1 <b>At</b>	n/a Rn
	P7	+1 <b>Fr</b>	+2 <b>Ra</b>							
				<b>Metals</b>			<b>Metalloids</b>		<b>Non</b>	
Least Electro Negative	<b>G1</b> lose $1 \times e^-$	<b>G2</b> lose $2 \times e^-$	Variable $\pm n$	<b>G3</b> lose $3 \times e^-$	<b>G4</b> lose $4 \times e^-$ or gain	<b>G5</b> gain $3 \times e^-$ or lose	<b>G6</b> gain $2 \times e^-$ or lose	<b>G7</b> gain $1 \times e^-$ or lose	<b>G8</b> n/a	

**Oxidation State** is applied for bonds. The  $\pm n$  values shown are for the formation of the four possible bond types:

- Ionic
- Polar Covalent
- Covalent
- Metallic

**Metals**  $\pm n$  only equals ionic charge for mono-atomic ions in salts.

**Q10** Refer to the Short Form Periodic Table above to determine the **oxidation state** of the underlined elements.

**Example** Arsenic Acid  $\text{H}_3\text{AsO}_4$   $\rightarrow$   $\overset{+1}{\text{H}}_3 \overset{x}{\text{As}} \overset{-2}{\text{O}}_4 \rightarrow \text{H}_3 \overset{+3}{\text{As}} \overset{-2}{\text{O}}_4$  Overall Charge = 0

If  $(+3) + x + (-8) = 0$  then  $x = +5$  for the single As

a) <u>Metalloids</u>	<u>As</u> <sub>2</sub> O <sub>3</sub>	<u>Sb</u> <sub>2</sub> S <sub>3</sub>	<u>Po</u> Cl <sub>4</sub>	<u>Si</u> <sub>4</sub> O <sub>11</sub> <sup>6-</sup>
b) <u>Group III and IV metals</u>	<u>Tl</u> <sub>2</sub> S	<u>Ga</u> <sub>2</sub> O <sub>3</sub>	<u>Sn</u> Cl <sub>2</sub>	<u>Pb</u> SO <sub>4</sub> <sup>2-</sup>
c) <u>Nitrogen and its many variations</u>	<u>N</u> H <sub>3</sub>	<u>N</u> <sub>2</sub> O <sub>4</sub> $\rightleftharpoons$ 2 <u>N</u> O <sub>2</sub>	<u>N</u> <sub>2</sub> O	<u>N</u> O <sub>3</sub> <sup>1-</sup>
d) <u>Chlorine variations</u>	<u>Cl</u> <sub>2</sub> O	<u>Cl</u> O <sub>2</sub>	H <u>Cl</u> O <sub>3</sub>	<u>Cl</u> O <sub>4</sub> <sup>1-</sup>
e) <u>Group V multiple choices</u>	Al <u>P</u> O <sub>4</sub>	<u>As</u> (OH) <sub>3</sub>	Ga( <u>N</u> O <sub>2</sub> ) <sub>3</sub>	Na <u>Sb</u> O <sub>3</sub> <sup>2-</sup>

**Example** Pyro Phosphate  $\text{P}_2\text{O}_7^{4-}$   $\rightarrow$   $\left[ \overset{x}{\text{P}}_2 \overset{-2}{\text{O}}_7 \right]^{4-} \rightarrow \text{P}_2 \overset{-2}{\text{O}}_7$  Overall Charge = 4-

If  $2x + (-14) = 4^-$   
Then  $2x = +10$  for P<sub>2</sub> atoms  
 $\therefore x = +5$  for each single P atom

## Oxidation State for Transition Elements

- There is **zero expectation** to recall the Allen electronegativity values  $\chi$  shown in the Periodic Table below.
- The values are the experiment-based evidence for the **electronegativity trends** you **do** need to learn.

$\chi$ Allen Electronegativity values (with Pauling units)																		Non-Metals					${}^2\text{He}$ n/a
${}^1\text{H}$ 2.30	Electronegativity increases left-to-right across each Period. However, some transition elements vary with slight decreases as well: <b>nickel Ni</b> $\rightarrow$ <b>copper Cu</b> $\rightarrow$ <b>zinc Zn</b> is a $\chi$ decrease.																${}^5\text{B}$ 2.05	${}^6\text{C}$ 2.55	${}^7\text{N}$ 3.07	${}^8\text{O}$ 3.61	${}^9\text{F}$ 4.19	${}^{10}\text{Ne}$ n/a	
${}^3\text{Li}$ 0.91	${}^4\text{Be}$ 1.58																	${}^{13}\text{Al}$ 1.61	${}^{14}\text{Si}$ 1.92	${}^{15}\text{P}$ 2.25	${}^{16}\text{S}$ 2.59	${}^{17}\text{Cl}$ 2.87	${}^{18}\text{Ar}$ n/a
${}^{11}\text{Na}$ 0.87	${}^{12}\text{Mg}$ 1.29	${}^{21}\text{Sc}$ 1.19	${}^{22}\text{Ti}$ 1.38	${}^{23}\text{V}$ 1.53	${}^{24}\text{Cr}$ 1.65	${}^{25}\text{Mn}$ 1.75	${}^{26}\text{Fe}$ 1.80	${}^{27}\text{Co}$ 1.84	${}^{28}\text{Ni}$ 1.88	${}^{29}\text{Cu}$ 1.85	${}^{30}\text{Zn}$ 1.59	${}^{31}\text{Ga}$ 1.76	${}^{32}\text{Ge}$ 1.99	${}^{33}\text{As}$ 2.21	${}^{34}\text{Se}$ 2.42	${}^{35}\text{Br}$ 2.69	${}^{36}\text{Kr}$ n/a						
${}^{37}\text{Rb}$ 0.71	${}^{38}\text{Sr}$ 0.96	<b>Transition Elements</b>										${}^{47}\text{Ag}$ 1.87	${}^{48}\text{Cd}$ 1.52	${}^{49}\text{In}$ 1.66	${}^{50}\text{Sn}$ 1.82	<b>Metalloids</b>	G8 atoms do not attract electrons						
${}^{55}\text{Cs}$ 0.66	${}^{56}\text{Ba}$ 0.88	Electronegativity usually decreases down each Group. However, some transition elements vary with slight increases as well: Transition element $\chi$ variations are caused by non-symmetric filling of d-subshell $e^-$ orbitals.										<b>copper Cu</b> $\downarrow$ <b>silver Ag</b> $\downarrow$ <b>gold Au</b> is a $\chi$ increase	${}^{79}\text{Au}$ 1.92	${}^{80}\text{Hg}$ 1.76	${}^{81}\text{Tl}$ 1.79			${}^{82}\text{Pb}$ 1.85	<b>Metals</b>				
${}^{87}\text{Fr}$ 0.67	${}^{88}\text{Ra}$ 0.89	<b>Metals</b>																					

**Q11** Use the Allen Electronegativity Periodic Table above along with the Three OS Rules to determine the **oxidation state** of the underlined transition elements:

**Examples using Iron Fe:** Oxygen remains **-2** even when the other element, iron Fe, is being weird

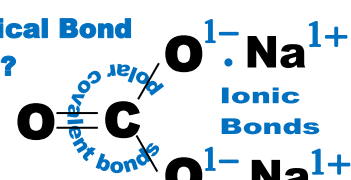
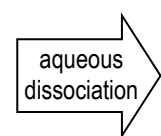
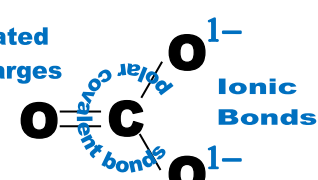
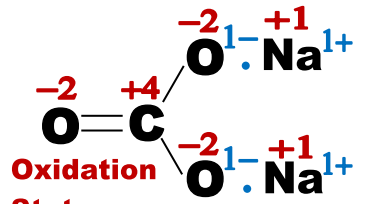
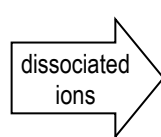
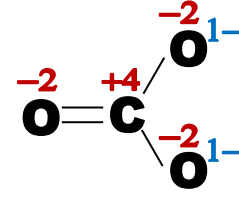
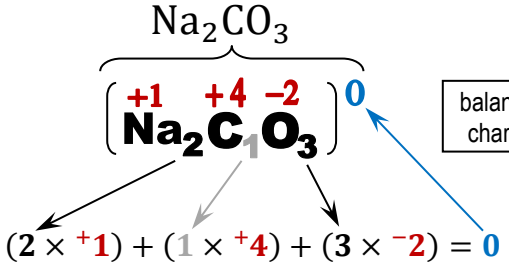
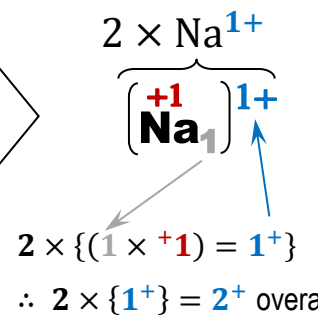
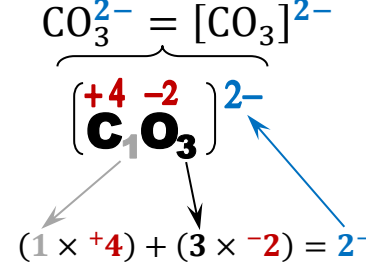
<b>Ferrous Oxide <math>\underline{\text{Fe}}\text{O}</math></b> Electronegativity Fe < O	<b>Ferric Oxide <math>\underline{\text{Fe}}_2\text{O}_3</math></b> Electronegativity Fe < O	<b>Magnetite <math>\underline{\text{Fe}}_3\text{O}_4</math></b> Electronegativity Fe < O
$\begin{array}{ccc} x & -2 & \\ \text{Fe} & \text{O} & \\ \times 1 & \times 1 & \end{array} \rightarrow \begin{array}{ccc} \text{Fe} & \text{O} & \\ x & -2 & \end{array} = 0$ <p>Overall Charge = 0</p> <p>If <math>x + (-2) = 0</math> Then <math>x = +2</math> for the single Fe atom as:</p> <p><math>\overset{+2}{\text{Fe}} \overset{-2}{\text{O}}</math> Iron (II) Oxide</p>	$\begin{array}{ccc} x & -2 & \\ \text{Fe}_2 & \text{O}_3 & \\ \times 2 & \times 3 & \end{array} \rightarrow \begin{array}{ccc} \text{Fe}_2 & \text{O}_3 & \\ 2x & -6 & \end{array} = 0$ <p>Overall Charge = 0</p> <p>If <math>2x + (-6) = 0</math> Then <math>2x = +6</math> for the two Fe atoms, with <math>x = \frac{+6}{2} = +3</math> for each single Fe atom as:</p> <p><math>\overset{+3}{\text{Fe}}_2 \overset{-2}{\text{O}}_3</math> Iron (III) Oxide</p>	$\begin{array}{ccc} x & -2 & \\ \text{Fe}_3 & \text{O}_4 & \\ \times 3 & \times 4 & \end{array} \rightarrow \begin{array}{ccc} \text{Fe}_3 & \text{O}_4 & \\ 3x & -8 & \end{array} = 0$ <p>Overall Charge = 0</p> <p>If <math>3x + (-8) = 0</math> Then <math>3x = +8</math> for the three Fe atoms, with <math>x = \frac{+8}{3} = +2\frac{2}{3}</math> <math>+2\frac{2}{3} - 2</math> for each Fe atom as: <math>\overset{+2\frac{2}{3}}{\text{Fe}}_3 \overset{-2}{\text{O}}_4</math> Magnetite is a crystalline combination of Iron (II) and Iron (III)</p>

a) <u>M</u> anganese variations	<u>Mn</u> Cl <sub>2</sub>	<u>Mn</u> <sub>2</sub> O <sub>3</sub>	<u>Mn</u> <sub>3</sub> O <sub>4</sub>	<u>Mn</u> O <sub>4</sub> <sup>1-</sup>
b) <u>C</u> hromium variations	<u>Cr</u> O <sub>2</sub>	<u>Cr</u> Cl <sub>2</sub>	<u>Cr</u> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	<u>Cr</u> <sub>2</sub> O <sub>7</sub> <sup>2-</sup>
c) Transition ion silicates	<u>Fe</u> SiO <sub>4</sub>	<u>Sc</u> <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Ca <sub>3</sub> <u>Fe</u> <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	Ca <u>Cr</u> <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> <sup>4-</sup>
d) Rare Earth <u>U</u> ranium	<u>U</u> F <sub>6</sub>	<u>U</u> O <sub>2</sub>	<u>U</u> <sub>3</sub> O <sub>8</sub>	<u>U</u> O <sub>2</sub> <sup>2-</sup>

## Part 2 Redox Reactions: Assigning Oxidation States in Reactions

Assigning oxidation states for reagents (reactants → products) in a chemical reaction will let you know if the reaction is Redox, or not. Oxidation states need to change if a reaction is Redox.

Consider the dissolving of solid sodium carbonate  $\text{Na}_2\text{CO}_3(\text{s})$  in water.

<b>Balanced Reaction Equation</b>	$\text{Na}_2\text{CO}_3(\text{s}) \xrightarrow{(\text{aq})} 2\text{Na}^+_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})}$
<p>• Use the Periodic Table for valency and relative electronegativity to determine the chemical <b>bond types</b>.</p> <p><b>Chemical Bond Types?</b></p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Polyatomic Sodium Carbonate salt <math>\text{Na}_2\text{CO}_3</math></p> </div> <div style="text-align: center;"> <p>aqueous dissociation</p>  </div> <div style="text-align: center;"> <p><b>Dissociated Ionic Charges</b></p>  <p>Two mono-atomic Sodium cations <math>2\text{Na}^+</math></p> <p>Polyatomic Carbonate anion <math>\text{CO}_3^{2-}</math></p> </div> </div>	
<p>Assigning <b>oxidation states</b> for sodium carbonate <math>\text{Na}_2\text{CO}_3</math></p> <ul style="list-style-type: none"> <li>• <b>Valency:</b> Na = 1; C = 4; O = 2</li> <li>• <b>Electronegativity:</b> Na &lt;&lt; C &lt; O</li> </ul> <p><b>Oxidation states</b> <math>\overset{+1}{\text{Na}}; \overset{+4}{\text{C}}; \overset{-2}{\text{O}}</math></p> <p>• Write <b>oxidation states</b> directly above each atom in a chemical species, such as Carbonate etc.</p>	
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>Oxidation States</b></p> </div> <div style="text-align: center;"> <p>dissociated ions</p>  </div> <div style="text-align: center;">  </div> </div> $\left(2 \times \overset{+1}{\text{Na}}\right) + \left(1 \times \overset{+4}{\text{C}}\right) + \left(3 \times \overset{-2}{\text{O}}\right) = \text{charge } 0$ <p style="text-align: center;"><b>Oxidation states</b></p> $\left(1 \times \overset{+4}{\text{C}}\right) + \left(3 \times \overset{-2}{\text{O}}\right) = \text{charge } 2-$	
<p>• The arithmetic sum <math>\Sigma</math> of <b>oxidation states</b> must equal the <b>overall ionic charge</b> of that species,</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p><math>\text{Na}_2\text{CO}_3</math></p>  <p><math>(2 \times +1) + (1 \times +4) + (3 \times -2) = 0</math></p> </div> <div style="text-align: center;"> <p><math>2 \times \text{Na}^+</math></p>  <p><math>2 \times \{(1 \times +1) = 1^+\}</math></p> <p><math>\therefore 2 \times \{1^+\} = 2^+</math> overall</p> </div> <div style="text-align: center;"> <p><math>\text{CO}_3^{2-} = [\text{CO}_3]^{2-}</math></p>  <p><math>(1 \times +4) + (3 \times -2) = 2^-</math></p> </div> </div> <p style="text-align: center;">balancing charges</p>	
<ul style="list-style-type: none"> <li>• Is this a Redox reaction?             <ul style="list-style-type: none"> <li>○ None of the elements (Na, C, O) have changed oxidation state as reactant or product.</li> <li>○ There has been no flow of electrons between any reagents.</li> <li>○ Therefore, it is not a Redox reaction.</li> </ul> </li> <li>• Redox reactions need one element to lose electrons <b>and</b> another to gain electrons.             <ul style="list-style-type: none"> <li>○ <math>e^-</math> gain has a decrease in oxidation state (<b>Reduction</b>); more negative with extra <math>e^-</math>.</li> <li>○ <math>e^-</math> loss has an increase in oxidation state (<b>Oxidation</b>); more positive with less <math>e^-</math>.</li> <li>○ There is an overall balanced flow of electrons between reagents in <b>Redox</b> reactions.</li> </ul> </li> </ul>	

## Identifying a Redox Reaction using Oxidation States

Now consider the apparent dissolving of sodium metal  $\text{Na}_{(s)}$  in dilute Hydrochloric acid  $\text{HCl}_{(aq)}$ .

<p><b>Balanced Reaction Equation</b></p> $2\text{Na} + 2\text{HCl}_{(aq)} \xrightarrow{\text{metal dissolves}} \text{H}_2 + 2\text{NaCl}$		
<ul style="list-style-type: none"> <li>Use the Periodic Table for relative electronegativity and valency to determine the chemical <b>bond types</b>.</li> </ul>		
<ul style="list-style-type: none"> <li>Write <b>oxidation states</b> directly above each atom in a chemical species, such as Sodium metal etc.</li> </ul>		
<ul style="list-style-type: none"> <li>The arithmetic sum <math>\Sigma</math> of oxidation states must equal <b>ionic charge</b> of that species, <math>\text{NaCl} = [\text{Na}^{+1}\text{Cl}^{1-}]^0</math></li> </ul>		
<p><b>Is this a Redox reaction?</b></p>	<p><b>Oxidation</b> is an <b>increase</b> in <b>oxidation state</b></p> $\overset{0}{\text{Na}} \xrightarrow{\text{oxidation}} \overset{+1}{\text{Na}} + e^-$ <p style="text-align: center;">oxidation = <math>e^-</math> loss</p>	<p><b>Reduction</b> is a <b>decrease</b> in <b>oxidation state</b></p> $2 \overset{+1}{\text{H}} + 2e^- \xrightarrow{\text{reduction}} 2 \overset{0}{\text{H}}$ <p style="text-align: center;">reduction = <math>e^-</math> gain</p>
	<ul style="list-style-type: none"> <li>An equal number of electrons flow from <math>2\text{Na}</math> to <math>\text{H}_2</math>:</li> <li>Electrons 'cancel out' each side of the <math>\frac{1}{2}</math>-reactions.</li> </ul>	$2 \times \left\{ \text{Na} \xrightarrow{e^- \text{ loss}} \text{Na}^{1+} + e^- \right\}$ $2\text{H}_{(aq)}^{1+} + 2e^- \xrightarrow{e^- \text{ gain}} \text{H}_2$ <hr/> $2\text{Na} + 2\text{H}_{(aq)}^+ \rightarrow \text{H}_2 + 2\text{Na}_{(aq)}^+$
	<p>A full-redox reaction (two halves added together):</p> $\overset{-1}{\text{Cl}}^{1-} \xrightarrow{\text{unchanged}} \overset{-1}{\text{Cl}}^{1-}$ <p>The oxidation state of Chlorine remains unchanged; These spectator ions can be omitted from the reaction equation.</p>	
<p><b>Q12</b> Use <b>oxidation states</b> to identify reactions as Redox (or not Redox)</p>	$\text{H}_3\text{PO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_3$	$\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4$
	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 7\text{H}_3\text{PO}_4 \rightarrow \text{HF} + 5\text{Ca}(\text{H}_2\text{PO}_4)_2$	<p>super phosphate fertiliser</p>
	$6\text{NaOH} + \text{Al}_2\text{O}_3 + 12\text{HF} \rightarrow 9\text{H}_2\text{O} + 2\text{Na}_3\text{AlF}_6$	<p>cryolite for reduction to Al</p>



## When the Arithmetic Link Appears to Give Weird Values

The presence of same-element to same-element bonds in a compound produces oxidation state values that do not correspond with the expected valency values from the Periodic Table of Elements.

**Sodium thiosulphate**  $\text{Na}_2\text{S}_2\text{O}_3$  molecules include a single covalent bond between two sulphur atoms

$\text{Na}_2\text{S}_2\text{O}_3$  contains a variety of primary bonds:

- A single covalent bond between two sulphur atoms, contributing an oxidation state of **zero** for each sulphur;
- Polar-covalent bonds between the oxygen atoms and the central sulphur atom. Those bonds contribute an oxidation state value of **+5** to the central sulphur atom;
- There are ionic bonds between the ionically charged oxygen and sulphur atoms with the two sodium ions.

Arithmetic oxidation states in the thiosulphate anion are:

$$\text{S}_2\text{O}_3^{2-} \rightarrow \left( \overset{x}{\text{S}}_2 \overset{-2}{\text{O}}_3 \right)^{2-} \rightarrow \left( \overset{2x}{\text{S}}_2 \overset{-6}{\text{O}}_3 \right)^{2-} \text{ as the overall charge}$$

If  $2x + (-6) = 2^-$   
 Then  $2x = +4$  for  $\text{S}_2$  atoms  
 $\therefore x = +2$  overall for Sulphur

**Thiosulphate anion**  $\text{S}_2\text{O}_3^{2-}$

polar covalent bonded sulphur and oxygen with covalent sulphur

**Oxidation States**

$$\left( \overset{+2}{\text{S}}_2 \overset{-2}{\text{O}}_3 \right)^{2-}$$

$$(2 \times +2) + (3 \times -2) = 2^-$$

The structural diagram shows one sulphur atom with **oxidation state -1** and the other with **oxidation state +5**.  
 The arithmetic average of  $\frac{(-1 + +5)}{2} = \frac{(+4)}{2} = +2$  for sulphur does not apply to any individual sulphur atom.

Q13 Identify the following balanced reaction equations as being Redox, or not, by assigning oxidation state values to the <u>underlined</u> elements. Determine how many electrons are being transferred in a reaction.		Determine how many electrons are transferred during each identified Redox reaction
(a)	$2\text{H}_2\underline{\text{O}}_2 \rightarrow \underline{\text{O}}_2 + 2\text{H}_2\underline{\text{O}}$ <p style="text-align: center;">colourless                      effervescence</p>	
(b)	$\text{K}_2\underline{\text{Cr}}_2\text{O}_7 + 2\underline{\text{KOH}} \rightarrow 2\text{K}_2\underline{\text{Cr}}\text{O}_4 + \text{H}_2\underline{\text{O}}$ <p style="text-align: center;">orange                      alkaline                      yellow</p>	
(c)	$\underline{\text{Cu}} + 4\underline{\text{HNO}}_3 \rightarrow \underline{\text{Cu}}(\underline{\text{NO}}_3)_2 + 2\underline{\text{NO}}_2 + 2\text{H}_2\text{O}$ <p style="text-align: center;">copper      concentrated                      blue                      brown fumes</p>	
(d)	$\text{Na}_2\underline{\text{S}}_2\text{O}_3 + 2\underline{\text{HCl}} \rightarrow \underline{\text{S}}\text{O}_2 + \underline{\text{S}} + \text{H}_2\text{O} + 2\underline{\text{NaCl}}$ <p style="text-align: center;">colourless                      acidified                      yellow ppt</p>	
(e)	$\underline{\text{H}}_2\underline{\text{S}}_2\text{O}_7 + \underline{\text{H}}_2\text{O} \rightarrow 2\underline{\text{H}}_2\underline{\text{S}}\text{O}_4$ <p style="text-align: center;">oleum                      sulphuric acid</p>	
(f)	$2\underline{\text{S}}\text{O}_2 + \underline{\text{O}}_2 \xrightarrow{\text{V}_2\text{O}_5 \text{ Catalyst}} 2\underline{\text{S}}\underline{\text{O}}_3$ <p style="text-align: center;">sulphur dioxide                      sulphur trioxide</p>	
(g)	$\underline{\text{Cr}}_2\underline{\text{O}}_7^{2-} + 8\underline{\text{HCl}} + 3\underline{\text{H}}_2\underline{\text{O}}_2 \rightarrow 2\underline{\text{Cr}}\text{Cl}_3 + 3\underline{\text{O}}_2 + 7\text{H}_2\text{O} + 2\underline{\text{Cl}}^{1-}$ <p style="text-align: center;">orange                      acidified                      green                      effervescence</p>	

**Q14** These reactions are redox. The two examples at the start and finish demonstrate how the number of electrons being transferred during Reduction equals the number of electrons shifted during Oxidation.

- Reduction and oxidation is also represented as separate [reactant | product] Redox conjugate pairs.
- [reactant | product] retains the same left-to-right [reactant → product] representation as the reaction equation.
- Oxidation states are written above  $\overset{0}{\text{Cu}}$  and below  $\underset{0}{\text{Zn}}$  individual redox species for visual clarity of electron transfer.

Your **task** is to demonstrate how many electrons are being transferred in the remaining Redox reactions.

<b>ex #1</b>	$\overset{+2}{\text{Cu}}\text{SO}_4 + \underset{0}{\text{Zn}} \xrightarrow[\text{(oxidation)}]{\text{(reduction) gain } 1 \times 2e^-} \overset{0}{\text{Cu}} + \underset{+2}{\text{Zn}}\text{SO}_4$	Redox reagent pair: • copper (II) $\text{Cu}^{2+}   \text{Cu}$ copper metal and • zinc $\text{Zn}   \text{Zn}^{2+}$ zinc (II) <b>two electrons transferred</b>
(a)	$2\text{AgCl} + \text{Zn} \rightarrow 2\text{Ag} + \text{ZnCl}_2$	Redox reagent pair: • silver (I) $\text{Ag}^{1+}   \text{Ag}$ silver metal and • zinc $\text{Zn}   \text{Zn}^{2+}$ zinc (II)
(b)	$2\text{Fe}_2\text{O}_3 + 3\text{C} \xrightarrow{\text{blast furnace}} 4\text{Fe} + 3\text{CO}_2$	Redox reagent pair: • iron (III) $\text{Fe}^{3+}   \text{Fe}$ iron metal and • carbon $\text{C}   \text{CO}_2$ carbon dioxide
(c)	$\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^{1+} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{O}_2$	Redox reagent pair: • dichromate $\text{Cr}_2\text{O}_7^{2-}   \text{Cr}^{3+}$ and • hydrogen peroxide $\text{H}_2\text{O}_2   \text{O}_2$ oxygen
(d)	$\text{Cu}_2\text{O} + 2\text{HNO}_3 + 4\text{H}^{1+} \rightarrow 2\text{Cu}^{2+} + 2\text{NO}_2 + 3\text{H}_2\text{O}$	Redox reagent pair: • nitrate $\text{NO}_3^{1-}   \text{NO}_2$ nitrogen dioxide • copper (I) $\text{Cu}^{1+}   \text{Cu}^{2+}$ copper (II)
(e)	$2\text{CrO}_4^{2-} + 16\text{H}^{1+} + 3\text{Zn} \rightarrow 2\text{Cr}^{3+} + 8\text{H}_2\text{O} + 3\text{Zn}^{2+}$	Redox reagent pair: • chromate $\text{CrO}_4^{2-}   \text{Cr}^{3+}$ chromium (III) • zinc $\text{Zn}   \text{Zn}^{2+}$ zinc (II)
(f)	$\text{Fe}_2(\text{SO}_4)_3 + \text{Mg} \rightarrow 2\text{FeSO}_4 + \text{MgSO}_4$	Redox reagent pair: • iron (III) $\text{Fe}^{3+}   \text{Fe}^{2+}$ iron (II) • magnesium $\text{Mg}   \text{Mg}^{2+}$
<b>ex #2</b>	$\overset{+7}{\text{Mn}}\text{O}_4^{1-} + 5\underset{+2}{\text{Fe}}^{2+} + 8\text{H}^{1+} \xrightarrow[\text{(oxidation) lose } 5 \times 1e^-]{\text{(reduction) gain } 1 \times 5e^-} \overset{+2}{\text{Mn}}^{2+} + 5\underset{+3}{\text{Fe}}^{3+} + 4\text{H}_2\text{O}$	Redox reagent pair: • permanganate $\text{MnO}_4^{1-}   \text{Mn}^{2+}$ and • iron (II) $\text{Fe}^{2+}   \text{Fe}^{3+}$ iron (III) <b>five electrons transferred</b>

# Making Sense of Organic Reactions with Redox

Yeast contains an enzyme that converts simple sugars  $C_6H_{12}O_6$  into ethanol ( $C_2H_5OH \overset{\text{equivalent}}{\text{to}} C_2H_6O$ ) and carbon dioxide  $CO_2$ .

Bacteria in the system can then convert the ethanol into ethanoic acid ( $CH_3COOH \equiv C_2H_4O_2$ ) if oxygen is present (aerobic conditions).

**Q15** Write the redox reagent pairs as in **Q14** for these reactions.

Apply the three **oxidation state** rules:

- **Elements** have **zero** value OS.
  - **Oxygen** is **-2** (except for peroxides).
  - **Hydrogen** is **+1** (except with metals).
- All other elements adjust to these rules.

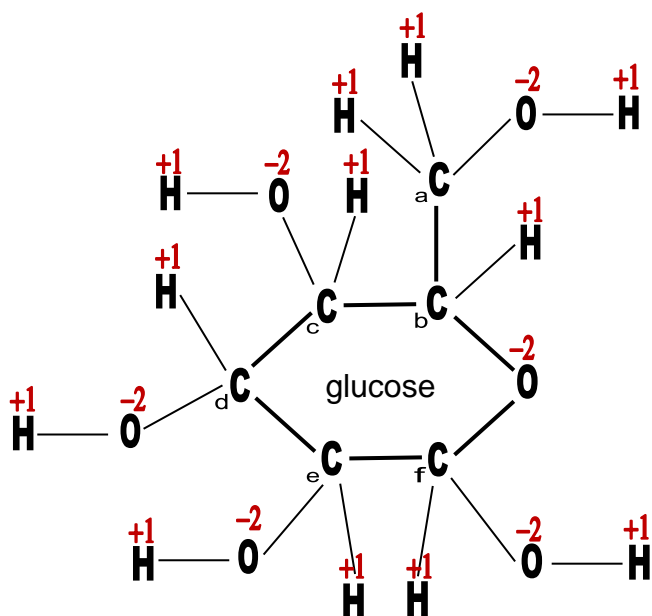
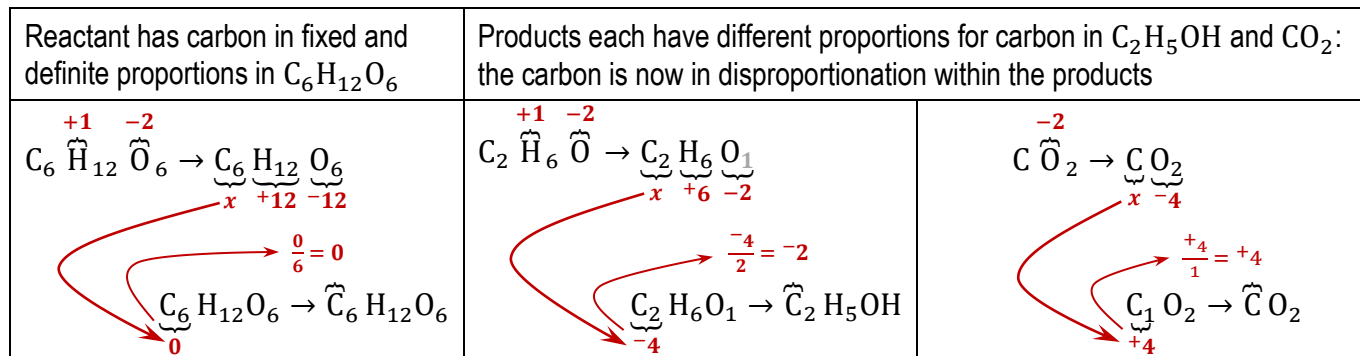
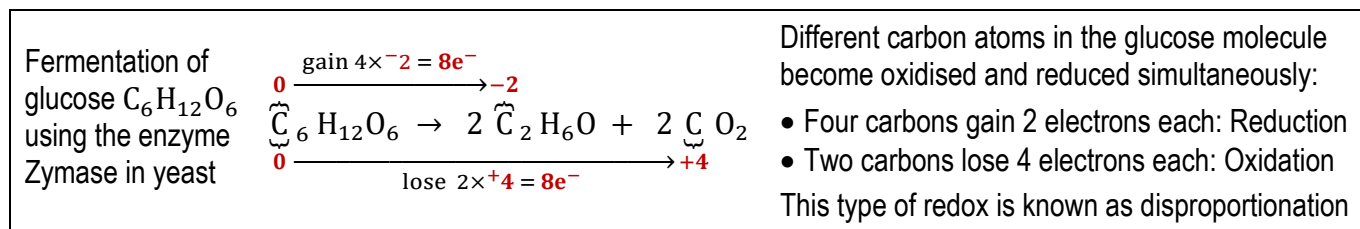
Yeast fermentation	$\begin{array}{c} \overset{0}{\text{C}}_6\text{H}_{12}\text{O}_6 \rightarrow 2 \overset{-2}{\text{C}}_2\text{H}_6\text{O} + 2 \overset{+4}{\text{C}}\text{O}_2 \\ \text{gain } 2(2 \times -2) = 8e^- \quad \text{lose } 2 \times +4 = 8e^- \end{array}$	Redox reaction pairs: <ul style="list-style-type: none"> <li>• Reduction</li> <li>• Oxidation</li> </ul>
Bacterial oxidation	$\overset{-2}{\text{C}}_2\text{H}_6\text{O} + \overset{0}{\text{O}}_2 \rightarrow \overset{0}{\text{C}}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O}$ $\begin{array}{c} \text{lose } 2 \times -2 = 4e^- \quad \text{gain } 2 \times -2 = 4e^- \end{array}$	Redox reaction pairs: <ul style="list-style-type: none"> <li>• Reduction</li> <li>• Oxidation</li> </ul>

Carbon having an **oxidation state** of **+4** in carbon dioxide  $CO_2$  makes sense because carbon is in Group 4 of the Periodic Table of elements, so that it can move four electrons depending on the relative electronegativity of the other reactant. But how can carbon have an **oxidation state** of **-2** in ethanol or **0** in simple sugar and ethanoic acid?

Comparing the correct, but overly complicated, molecular bond analysis with the much simpler arithmetic link rule.

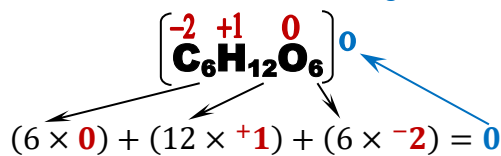
Molecular bond analysis (bond-by-bond within the molecule)	<ul style="list-style-type: none"> <li>• Identify <b>bond types</b></li> <li>• Initial <b>oxidation states</b>:               <ul style="list-style-type: none"> <li>○ Electronegativity: <math>O \gg C &gt; H</math></li> <li>○ Oxygen <b>-2</b></li> <li>○ Hydrogen <b>+1</b></li> </ul> </li> </ul>	<b>Ethanol</b> oxidised by bacteria becomes <b>Ethanoic acid</b> as product of oxidation
	Consider the oxidation state <b>contribution</b> made by each bond made by each Carbon: <ul style="list-style-type: none"> <li>• Carbon-to-Carbon <b>0</b></li> <li>• Carbon-to-Hydrogen <b>-1</b> per bond</li> <li>• Carbon-to-Oxygen <b>+1</b> per bond</li> </ul> Take arithmetic average on all Carbons in the molecule for the <b>final</b> Carbon oxidation state	<b>The average oxidation state for Carbon in ethanol is -2</b> $\frac{(-3) + (-1)}{2} = -2$
Arithmetic link between: <ul style="list-style-type: none"> <li>• <b>Oxidation states</b></li> <li>• <b>Molecular formulae</b></li> <li>• <b>Overall ionic charge</b> provides easier OS solutions</li> </ul>	$C_2H_5OH \quad \left( \overset{-2}{C} \overset{+1}{H} \overset{-2}{O} \right) \rightarrow CH_3COOH \quad \left( \overset{0}{C} \overset{+1}{H} \overset{-2}{O} \right)$ $ethanol \quad \left( C_2H_6O \right) \quad \rightarrow \quad ethanoic acid \quad \left( C_2H_4O_2 \right)$ $(2 \times -2) + (6 \times +1) + (1 \times -2) = 0 \quad \quad \quad (2 \times 0) + (4 \times +1) + (2 \times -2) = 0$	
The change in OS for carbon identifies this as a redox reaction, with carbon being oxidised ( $-2 \xrightarrow{\text{OS increase}} 0$ )		

**Organic and biological reactions** can be quite complicated because of the complex nature of the molecules involved. The following redox analysis of the fermentation of glucose  $C_6H_{12}O_6$  shows how these complex reactions follow the same fundamental redox rules to explain how electron transfer is driving the reaction forward.



Determining oxidation state for Carbon in glucose $C_6H_{12}O_6$	Contribution to <b>oxidation state</b> for each $C_6H_{12}O_6$ carbon atom			
	Carbon to carbon bond	Carbon to hydrogen bond	Carbon to oxygen bond	Sub Total per carbon atom
a <b>C</b>	0	-1 -1	+1	-1
b <b>C</b>	0 0	-1	+1	0
c,d,e <b>C</b>	0 0	-1	+1	0
f <b>C</b>	0	-1	+1 +1	+1
Average	$\frac{(1 \times -1) + (4 \times 0) + (1 \times +1)}{6} =$			0

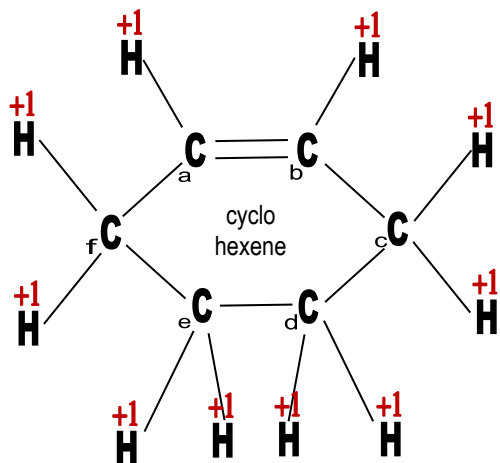
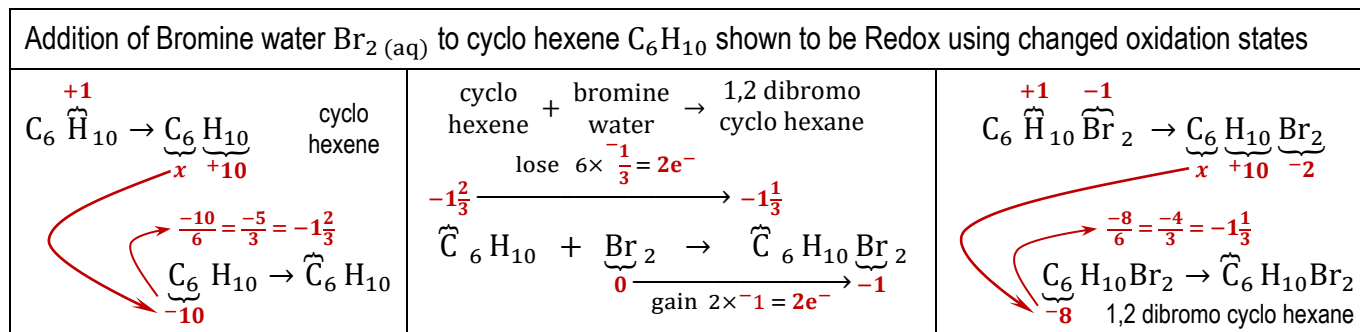
$C_6H_{12}O_6$  overall molecular charge zero:



**Q16** Identify the electron shift and redox reagent pairs for these organic reactions:

Photosynthesis	$6CO_2 + 6H_2O \xrightarrow{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$
Combustion	$2C_8H_{18} + 25O_2 \xrightarrow{\text{ignition}} 16CO_2 + 18H_2O$
Breathalyser	$2K_2Cr_2O_7 + 16HCl + 3C_2H_5OH \rightarrow 4CrCl_3 + 3CH_3COOH + 11H_2O + 4KCl$

**Addition reactions** can involve the insertion of Group VII Halogens across multiple carbon-to-carbon bonds.



Determining oxidation state for Carbon in cyclohexene  $\text{C}_6\text{H}_{10}$

	Carbon to carbon bond	Carbon to hydrogen bond	Sub Total per carbon atom
a,b <b>C</b>	0 0	-1	-1
c,d,e,f <b>C</b>	0 0	-1 -1	-2
Average	$\frac{(2 \times -1) + (4 \times -2)}{6} = \frac{-10}{6}$		$-1\frac{2}{3}$

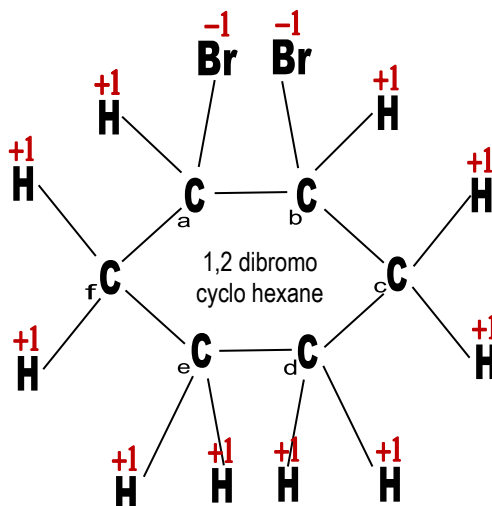
Determining oxidation state for Carbon in 1,2 dibromo cyclohexane  $\text{C}_6\text{H}_{10}\text{Br}_2$

	Carbon to carbon bond	Carbon to hydrogen bond	Carbon to bromine bond	Sub Total per carbon atom
a,b <b>C</b>	0 0	-1	+1	0
c,d,e,f <b>C</b>	0 0	-2		-2
Average	$\frac{(2 \times 0) + (4 \times -2)}{6} = \frac{-8}{6}$			$-1\frac{1}{3}$

$\text{C}_6\text{H}_{10}$  overall molecular charge zero:

$$\left( -1\frac{2}{3} + 1 \right) \text{C}_6\text{H}_{10} \text{O}$$

$$(6 \times -1\frac{2}{3}) + (10 \times +1) = 0$$



$\text{C}_6\text{H}_{10}\text{Br}_2$  overall molecular charge zero:

$$\left( -1\frac{1}{3} + 1 - 1 \right) \text{C}_6\text{H}_{10}\text{Br}_2 \text{O}$$

$$(6 \times -1\frac{1}{3}) + (10 \times +1) + (2 \times -1) = 0$$

**Q17** Identify the electron transfer and redox reagent pairs for these organic addition reactions:

Preparation of vinyl chloride	ethylene $\text{C}_2\text{H}_4 + \text{Cl}_2 \xrightarrow{\text{FeCl}_3 \text{ catalyst}} \text{C}_2\text{H}_4\text{Cl}_2$ vinyl chloride
Preparation of vinyl acetate	acetic acid $2\text{C}_2\text{H}_4\text{O}_2 + 2\text{C}_2\text{H}_4 + \text{O}_2 \xrightarrow{\text{Pd catalyst}} 2\text{H}_2\text{O} + 2\text{C}_4\text{H}_6\text{O}_2$ vinyl acetate

## Part 3 Electrochemistry: Writing Redox Equations

Redox reactions are best balanced using the five step ½-equation method described below.

- Identify the redox species changing oxidation states as redox conjugate pairs [reactant | product].
  - Balance the number of atoms changing oxidation state on each side of [reactant → product].
- Account for missing Oxygen atoms between Reactants and Products.
  - Convert unaccounted Oxygen atoms to H<sub>2</sub>O with the addition of H<sup>1+</sup> ions (aka acidic conditions).
- Determine the arithmetic value of total ionic charge on each side of [reactant → product] the reaction.
  - Add ēlectrons to the side with the lowest negative charge until both sides have equal total ionic charge.

Steps 1 to 3 will produce two redox ½-equations, with one showing Reduction while the other shows Oxidation.

- Determine the Lowest Common Multiple (LCM) for both ½-equations with respect to the ēlectrons.
  - Use LCM to generate equal numbers of ēlectrons on each side of [reactant → product] for elimination.
- Algebraically cancel excess H<sup>+</sup> and H<sub>2</sub>O from each side of [reactant → product] the reaction equation.
  - Add remaining reagents from each ½-equation to obtain a balanced Redox reaction equation.

**Example:** Acidified violet permanganate reacts with hydrogen peroxide to form colourless Manganese (II) with oxygen effervescence. The presence of oxygen has been confirmed with a positive glowing splint test.

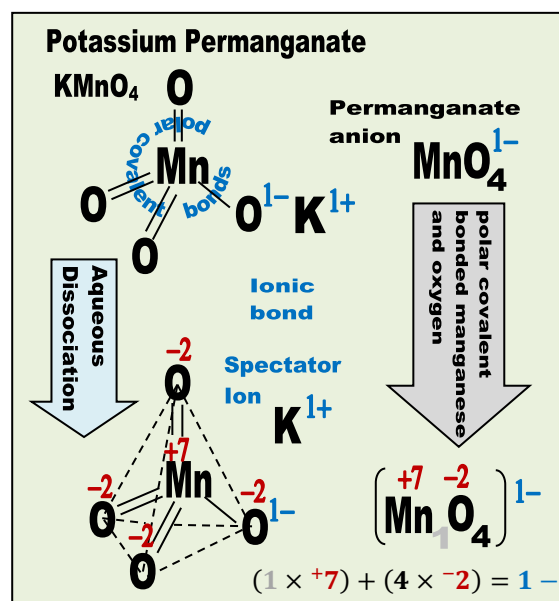
1	Reduction conjugate pair is gaining $1 \times 5e^-$ $\overset{+7}{\text{Mn}}\text{O}_4^{1-}   \overset{+2}{\text{Mn}}^{2+}$	Oxidation conjugate pair is losing $2 \times 1e^-$ $\overset{-1}{\text{H}_2}\overset{0}{\text{O}}_2   \overset{0}{\text{O}}_2$
2	$\text{MnO}_4^{1-} \rightarrow \text{Mn}^{2+}$ $\text{MnO}_4^{1-} \rightarrow \text{Mn}^{2+} + (4\text{H}_2\text{O})$ $\text{MnO}_4^{1-} + (4 \times 2\text{H}^{1+}) \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$\text{H}_2\text{O}_2 \rightarrow \text{O}_2$ $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{1+}$
3	$(1 \times -1) + (8 \times +1) = 7+ \neq (1 \times +2) = 2+$ $\text{MnO}_4^{1-} + 8\text{H}^{1+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $\text{MnO}_4^{1-} + 8\text{H}^{1+} + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $(-1) + (+8) + (5 \times -1) = 2+ \quad (+2) = 2+$	$0 \neq (2 \times +1) = 2+$ $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{1+}$ $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{1+} + 2e^-$ $0 \quad (+2) + (2 \times -1) = 0$

Two redox ½-equations, one showing Reduction while the other shows Oxidation, are now ready for balancing

4	$[\text{MnO}_4^{1-} + 8\text{H}^{1+} + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}] \times 2$ $[\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{1+} + 2e^-] \times 5$	$2\text{MnO}_4^{1-} + 16\text{H}^{1+} + 10e^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ $5\text{H}_2\text{O}_2 \rightarrow 5\text{O}_2 + 10\text{H}^{1+} + 10e^-$
5	The mass and charge balanced full Redox reaction equation with observations.	$2\text{MnO}_4^{1-} + 6\text{H}^{1+} + 5\text{H}_2\text{O}_2 \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$ Violet                      acidified                      colourless                      effervescence

**Q18** Balance the following Redox reactions with manganese.

a)	$\text{MnO}_4^{1-} \rightarrow \text{Mn}^{2+}$ $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ _____ _____ _____
b)	$\text{MnO}_4^{1-} \rightarrow \text{MnO}_2$ $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$ _____ _____ _____
c)	$\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}^{2+}$ $\text{Cu}^{1+} \rightarrow \text{Cu}^{2+}$ _____ _____ _____



**Q19** Complete the Redox reactions using the redox conjugate pairs provided.

	Conjugate pairs	Using ½-equation method to balance full redox reaction equation
a)	Ca   Ca <sup>2+</sup> with H <sub>2</sub> O   H <sub>2</sub>	$\begin{array}{l} \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^{-} \\ \_ \text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2 + 2\text{OH}^{1-} \\ \hline \rightarrow \end{array}$
b)	PbO   Pb with Br <sub>2</sub>   BrO <sub>3</sub> <sup>1-</sup>	$\begin{array}{l} \text{PbO} \rightarrow \text{Pb} \\ \text{Br}_2 \rightarrow \_ \text{BrO}_3^{1-} \\ \hline \rightarrow \end{array}$
c)	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>   Cr <sup>3+</sup> with Fe <sup>2+</sup>   Fe <sup>3+</sup>	$\begin{array}{l} \text{Cr}_2\text{O}_7^{2-} \rightarrow \_ \text{Cr}^{3+} \\ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \\ \hline \rightarrow \end{array}$
d)	MnO <sub>2</sub>   Mn <sub>2</sub> O <sub>3</sub> with Fe <sup>2+</sup>   Fe <sup>3+</sup>	$\begin{array}{l} \_ \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \\ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \\ \hline \rightarrow \end{array}$
e)	C <sub>2</sub> H <sub>5</sub> OH   CH <sub>3</sub> COOH with MnO <sub>4</sub> <sup>1-</sup>   Mn <sup>2+</sup>	$\begin{array}{l} \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOH} \\ \text{MnO}_4^{1-} \rightarrow \text{Mn}^{2+} \\ \hline \rightarrow \end{array}$

The reactions show that Redox can be identified from the following three possible criteria:

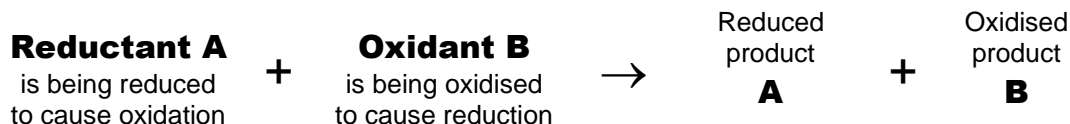
- Electron loss or gain
  - Hydrogen loss or gain
  - Oxygen loss or gain (This was the original definition for Redox reactions).
- } → Often summarised together as Oxidation Is Loss / Reduction Is Gain = **OILRIG**

Reduction can be:	Redox	Oxidation can be:
ēelectron gain $\begin{array}{l} \text{Cu}^{2+} + 2\bar{e} \rightarrow \text{Cu} \\ \text{Cl}_2 + 2\bar{e} \rightarrow 2\text{Cl}^{-} \\ 2\text{H}_2\text{O} + 2\bar{e} \rightarrow \text{H}_2 + 2\text{OH}^{-} \end{array}$	Oxidation Is Loss Reduction Is Gain OILRIG only for (ē / H)	ēelectron loss $\begin{array}{l} \text{Ca} \rightarrow \text{Ca}^{2+} + 2\bar{e} \\ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \bar{e} \\ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^{+} + 4\bar{e} \end{array}$
Hydrogen gain $\begin{array}{l} \text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 \\ \text{Si} + 4\text{H}^{+} + 4\bar{e} \rightarrow \text{SiH}_4 \\ \text{P} + 3\text{H}^{+} + 3\bar{e} \rightarrow \text{PH}_3 \end{array}$		Hydrogen loss $\begin{array}{l} 2\text{Na} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 \\ \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{+} + 2\bar{e} \\ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^{+} + 2\bar{e} \end{array}$
Oxygen loss $\begin{array}{l} 2\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Fe} + 3\text{CO}_2 \\ \text{PbO} + 2\text{H}^{+} + 2\bar{e} \rightarrow \text{Pb} + \text{H}_2\text{O} \\ \text{H}_2\text{O}_2 + 2\text{H}^{+} + 2\bar{e} \rightarrow 2\text{H}_2\text{O} \end{array}$	Oxidation is the gaining of oxygen!	Oxygen gain $\begin{array}{l} 2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO} \\ \text{Br}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{BrO}_3^{-} + 12\text{H}^{+} + 10\bar{e} \\ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^{+} + 4\bar{e} \end{array}$

**Oxidation State ±n** behaves as a vector quantity describing the electromotive chemical force caused by the transfer of  $e^{-}$  during reactions and the voltage effect produced by that transfer.

Redox Grammar			
Verb		Noun	
transitive	intransitive	Proper	Conjugate
To <b>OXIDIZE</b> is to unite with oxygen, resulting in $\bar{e}$ loss for a reactant.	<b>OXIDATION</b> is the loss of $\bar{e}$ for a reactant; often due to gaining oxygen.	An <b>OXIDANT</b> is that reactant which is being oxidized.	An <b>OXIDIZING AGENT</b> causes oxidation by itself being Reduced.
To <b>REDUCE</b> is to disunite with oxygen, resulting in $\bar{e}$ gain for a reactant.	<b>REDUCTION</b> is the gain of $\bar{e}$ for a reactant; often due to losing oxygen.	A <b>REDUCTANT</b> is that reactant which is being reduced.	A <b>REDUCING AGENT</b> causes reduction by itself being Oxidized.

- Oxidation is  $\bar{e}$  loss for one reactant so that the other reactant can gain those  $\bar{e}$  for their own Reduction.



- The reductant is causing the other reactant to be Oxidized. The reductant is an Oxidising Agent.
- The oxidant is causing reduction the other reactant to be Reduced. The oxidant is a Reducing Agent.

<b>Reduction</b> $\text{Cu}_{(\text{aq})}^{2+} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$ <b>Oxidation</b> $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + 2\text{e}^-$ <b>Redox</b> $\text{Zn}_{(\text{s})} + \text{Cu}_{(\text{aq})}^{2+} \rightarrow \text{Zn}_{(\text{aq})}^{2+} + \text{Cu}_{(\text{s})}$ <div style="display: flex; justify-content: space-around; font-size: small;"> <span><math>\text{Zn}_{(\text{s})}</math> oxidant</span> <span><math>\text{Cu}_{(\text{aq})}^{2+}</math> reductant</span> </div>	Copper (II) cations can only be reduced while zinc metal can only be oxidised during Redox	The reductant $\text{Cu}_{(\text{aq})}^{2+}$ is an oxidising agent because it makes $\text{Zn}_{(\text{s})}$ oxidise
Reduction $\text{H}_2\text{O}_2 + 2\text{H}^{1+} + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ Oxidation $[\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-] \times 2$ Redox $\text{H}_2\text{O}_2 + 2\text{H}^{1+} + 2\text{Fe}^{2+} \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}^{3+}$ <div style="display: flex; justify-content: space-around; font-size: small;"> <span><math>\text{H}_2\text{O}_2</math> reductant</span> <span><math>2\text{Fe}^{2+}</math> oxidant</span> </div>	Hydrogen peroxide can be an oxidant or a reductant depending on the reduction potential of its redox pairing	The reductant $\text{H}_2\text{O}_2$ is an oxidising agent because it makes $\text{Fe}^{2+}$ oxidise
Oxidation $[\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^{1+} + 2\text{e}^-] \times 5$ Reduction $[\text{MnO}_4^{1-} + 8\text{H}^{1+} + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}] \times 2$ Redox $5\text{H}_2\text{O}_2 + 6\text{H}^{1+} + 2\text{MnO}_4^{1-} \rightarrow 5\text{O}_2 + 8\text{H}_2\text{O} + 2\text{Mn}^{2+}$ <div style="display: flex; justify-content: space-around; font-size: small;"> <span><math>5\text{H}_2\text{O}_2</math> oxidant</span> <span><math>2\text{MnO}_4^{1-}</math> reductant</span> </div>	Permanganate can only be an oxidising agent by itself being reduced	The oxidant $\text{H}_2\text{O}_2$ is an reducing agent because it makes $\text{MnO}_4^{1-}$ reduce

**Q20** Complete these redox reactions and identify the oxidant/reductant and the oxidising agent/reducing agent.

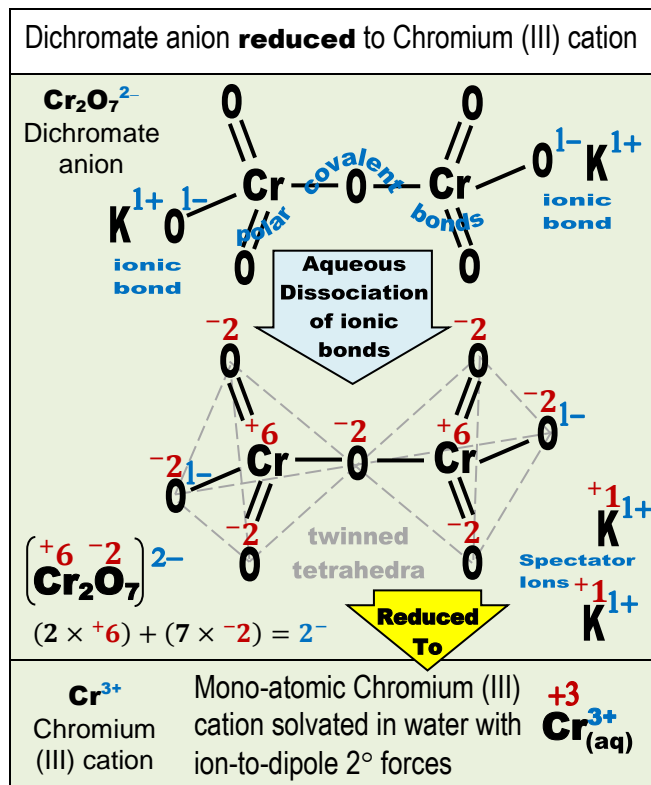
	Oxidant	Reductant	Redox conjugate pairs	Oxidising Agent	Reducing Agent
a)			Chromate, $\text{CrO}_4^{1-}$   $\text{Cr}(\text{OH})_3$ with Zinc, $\text{Zn}$   $\text{Zn}^{2+}$ $\text{CrO}_4^{1-} \rightarrow \text{Cr}(\text{OH})_3$ $\text{Zn} \rightarrow \text{Zn}^{2+}$ <hr/> $\rightarrow$		
b)			Copper (I) oxide, $\text{Cu}_2\text{O}$   $\text{Cu}^{2+}$ with Nitric acid, $\text{HNO}_3$   $\text{NO}_2$ $\rightarrow$ $\rightarrow$ <hr/> $\rightarrow$		



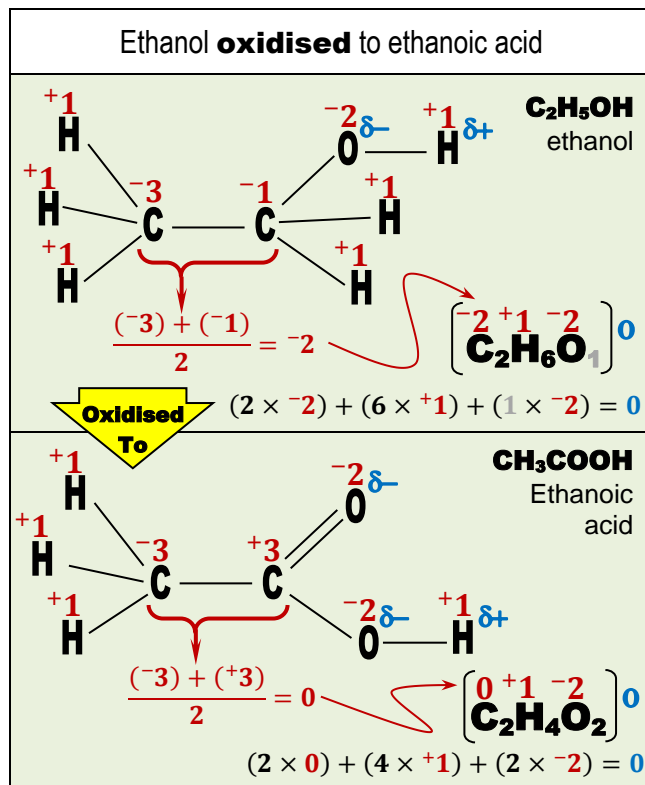
# The Method Works, Even for 'Silly' Numbers

Alcohol breathalyser units used by the Police to test car drivers once used a very brightly coloured Redox reaction:

- A redox reaction happens when alcohol (as ethanol  $C_2H_5OH$ ) vapours from the lungs of a driver are blown through an aqueous solution containing dichromate ( $Cr_2O_7^{2-}$ ) anions.
- The  $Cr_2O_7^{2-}$  anion is **reduced** from bright orange dichromate to dark green chromium (III) cations  $Cr^{3+}$ .
- The  $C_2H_5OH$  ethanol is **oxidised** to become ethanoic acid  $CH_3COOH$ .



Reduction and Oxidation occur simultaneously as Redox



**Example:** Acidified potassium dichromate  $K_2Cr_2O_7$  reacts with ethanol  $C_2H_5OH$  to produce a solution containing green Chromium (III) cations  $Cr^{3+}$  and ethanoic acid  $CH_3COOH$ . ( $K_{(aq)}^{1+}$  have been omitted as spectator ions)

①	Reduction conjugate pair is gaining $2 \times 3e^-$	$\overset{+6}{Cr_2} \overset{-2}{O_7}   \overset{+3}{Cr}^{3+}$	Oxidation conjugate pair is losing $2 \times 2e^-$	$\overset{-2}{C_2} H_6 O   \overset{0}{C_2} H_4 O_2$
②	$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + (7H_2O)$ $Cr_2O_7^{2-} + (7 \times 2H^{1+}) \rightarrow 2Cr^{3+} + 7H_2O$		Ethanol $C_2H_5OH \rightarrow CH_3COOH$ ethanoic acid $C_2H_6O \rightarrow C_2H_4O_2$ $C_2H_6O + H_2O \rightarrow C_2H_4O_2$ $C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H^{1+}$	
③	$(1 \times -2) + (14 \times +1) = 12+ \neq (2 \times +3) = 6+$ $Cr_2O_7^{2-} + 14H^{1+} \rightarrow 2Cr^{3+} + 7H_2O$ $Cr_2O_7^{2-} + 14H^{1+} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $(-2) + (+14) + (6 \times -1) = 6+$ $(+6) = 6+$		$0 \neq (4 \times +1) = 4+$ $C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H^{1+}$ $C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H^{1+} + 4e^-$ $0$ $(+4) + (4 \times -1) = 0$	

Two redox  $\frac{1}{2}$ -equations, one showing Reduction while the other shows Oxidation, are now ready for balancing

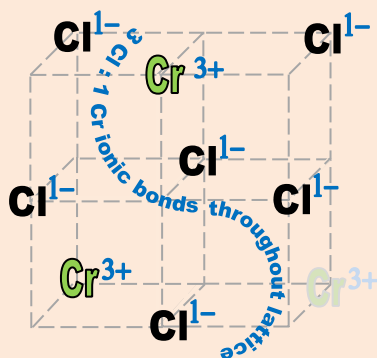
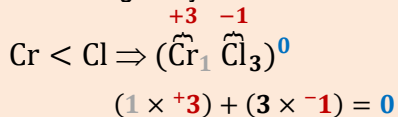
④	$[Cr_2O_7^{2-} + 14H^{1+} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O] \times 2$ $2Cr_2O_7^{2-} + 28H^{1+} + 12e^- \rightarrow 4Cr^{3+} + 14H_2O$ $[C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 4H^{1+} + 4e^-] \times 3$ $3C_2H_6O + 3H_2O \rightarrow 3C_2H_4O_2 + 12H^{1+} + 12e^-$	
⑤	The mass and charge balanced full Redox reaction equation with observations.	$2Cr_2O_7^{2-} + 16H^{1+} + 3C_2H_5OH \rightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$ orange      acidified      ethanol      green      ethanoic acid

**Chromium** has a variable oxidation state because the valence shell configuration of Transition elements includes the five d-subshell orbitals along with a single s-subshell orbital. This subshell arrangement provides a large variety of closely spaced energy levels for electrons to move between during chemical reactions.

**Chromium (III)** forms bright green monatomic cations when dissolved in aqueous solutions.

Ionic salts such as **CrCl<sub>3</sub>** form ionic lattice with 3:1 coordination.

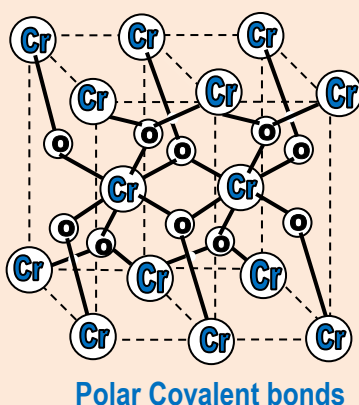
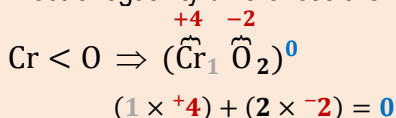
Electronegativity differences are:



**Chromium (IV) Oxide** forms a dark blue polar covalent lattice.

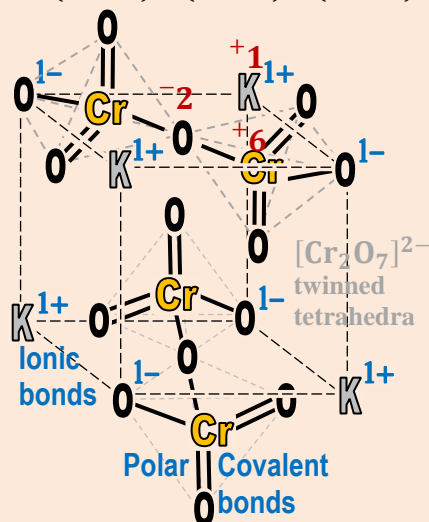
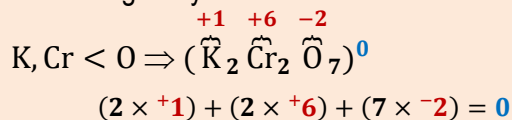
Each **CrO<sub>2</sub>** structural unit has 6:3 coordination (6 oxygen atoms per chromium with 3 chromium atoms per oxygen).

Electronegativity differences are:



**Potassium Dichromate (VI)** forms orange **[Cr<sub>2</sub>O<sub>7</sub>]<sup>2-</sup>** anions which contain twelve polar covalent bonds. Each anion forms two ionic bonds with **K<sup>1+</sup>** cations to have repeating structural unit **K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**.

Electronegativity differences are:



## Redox Reaction Equations Involving Chromium

**Q21** Complete the Redox reactions using the redox conjugate pairs provided as shown in **Q18** and **Q19**.

	Conjugate pairs	Using 1/2-equation method to balance full redox reaction equation
a)	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>   Cr <sup>3+</sup> with H <sub>2</sub> O <sub>2</sub>   O <sub>2</sub>	→ → _____
b)	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>   CrO <sub>2</sub> with Cu <sup>1+</sup>   Cu <sup>2+</sup>	→ → _____
c)	CrO <sub>2</sub>   Cr <sup>3+</sup> with H <sub>2</sub> O <sub>2</sub>   O <sub>2</sub>	→ → _____
d)	HCrO <sub>4</sub> <sup>1-</sup>   Cr <sup>3+</sup> with ClO <sub>2</sub>   ClO <sub>3</sub> <sup>1-</sup>	→ → _____

**ACTIVITY** is the term used to describe how **metals** can displace other metal cations from aqueous solution. The metal cations are gaining electrons from the solid metals.

- A metal high on the list is oxidised by losing electrons: **ex**  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- A metal cation low on the list is reduced by gaining electrons: **ex**  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- The examples above show that copper metal will be 'displaced' from solution:  
Blue copper (II) solution  $\text{Cu}_{(\text{aq})}^{2+} + \text{Zn}_{(\text{s})} \rightarrow \text{Cu}_{(\text{s})} + \text{Zn}_{(\text{aq})}^{2+}$  Brown copper precipitate
- Water is included because the metals above it will react and form hydrogen gas:
  - Calcium will react vigorously once the calcium oxide layer is dissolved
  - Iron will react with water extremely slowly, and only if oxygen is also present.
- The further away reactants are on the list, the more vigorous their reaction.

The practical investigation into displacement reactions produced the experimental evidence needed to support much of the Activity list for metals shown opposite.

**A solid metal on the list will displace any metal cation below it on the list**

<b>Most Active</b>	
Calcium	Ca
Magnesium	Mg
Aluminium	Al
Zinc	Zn
Iron	Fe
<b>Water</b>	<b>H<sub>2</sub>O</b>
Tin	Sn
Lead	Pb
Copper	Cu
Silver	Ag
Gold	Au
<b>Least Active</b>	

**REDUCTION POTENTIAL** is the term used to describe how **non-metals** can gain electrons in comparison to any other reactant during a redox reaction. These reagents are being reduced. They are called Reductants.

- A reductant is a reagent with a reaction equation showing a gaining of electrons.
- A reductant will redox with any reagent lower on the list, but the other reagent must become an Oxidant.
- An oxidant is when a reagent loses electrons. This achieved by reversing the reaction equation for a Reductant.
- Reductants lower on the list will not react with other reductants higher on the list.

Here is a list of the more commonly encountered Reduction Potential reagents.

<b>Highest Reduction Potential</b>		
Dichromate	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{1+} + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Chromium (III)
Permanganate	$\text{MnO}_4^{1-} + 8\text{H}^{1+} + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	Manganese (II)
Nitric Acid	$\text{HNO}_3 + \text{H}^{1+} + \text{e}^- \rightleftharpoons \text{NO}_2 + \text{H}_2\text{O}$	Nitrogen Dioxide
Hydrogen Peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^{1+} + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	Water
	$\text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + 2\text{H}^{1+} + 2\text{e}^-$	Oxygen
Iron (III)	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	Iron (II)
Water	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^{1-}$	Hydrogen
<b>Lowest Reduction Potential</b>		

**Q22** The Reduction Potential Series above will predict if the following combinations can produce a Redox reaction. Complete these reaction equations using the  $\frac{1}{2}$ -equation method. Not all combinations result in Redox.

a)	Permanganate with Iron (II)	
b)	Dichromate with Iron (III)	
c)	Bubbling Hydrogen gas through Hydrogen Peroxide	
d)	Hydrogen Peroxide with Iron (III)	

**Q23** Write these observed changes as balanced redox Half-Equations.

Redox description		Mnemonic	Half-Equation	
a)	Permanganate is reduced to Manganese Dioxide	$\text{MnO}_4^{1-} \mid \text{MnO}_2$	$\text{MnO}_4^{1-}$	$\rightarrow \text{MnO}_2$
b)	Sulphur dioxide is oxidised to sulphuric acid	$\text{SO}_2 \mid \text{H}_2\text{SO}_4$	$\text{SO}_2$	$\rightarrow \text{H}_2\text{SO}_4$
c)	Dichromate is reduced to Chromium (III)	$\text{Cr}_2\text{O}_7^{2-} \mid \text{Cr}^{3+}$	$\text{Cr}_2\text{O}_7^{2-}$	$\rightarrow \text{Cr}^{3+}$
d)	Ethanol is oxidised to ethanal	$\text{C}_2\text{H}_5\text{OH} \mid \text{CH}_3\text{CHO}$	$\text{C}_2\text{H}_5\text{OH}$	$\rightarrow \text{CH}_3\text{CHO}$
e)	Carbon monoxide is oxidised to carbon dioxide	$\text{CO} \mid \text{CO}_2$	$\text{CO}$	$\rightarrow \text{CO}_2$
f)	Elemental iodine is oxidised to iodic acid	$\text{I}_2 \mid \text{HIO}_3$	$\text{I}_2$	$\rightarrow \text{HIO}_3$
g)	Aluminate anion is reduced to aluminium metal	$\text{Al(OH)}_4^{1-} \mid \text{Al}$	$\text{Al(OH)}_4^{1-}$	$\rightarrow \text{Al}$
h)	Dichromate is reduced to Chromium (IV) oxide	$\text{Cr}_2\text{O}_7^{2-} \mid \text{CrO}_4$	$\text{Cr}_2\text{O}_7^{2-}$	$\rightarrow \text{CrO}_4$

**Disproportionation** happens when the same reagent both oxidises and reduces with itself simultaneously. Certain reagents can both oxidise and reduce readily, depending on the other chemical with which they are having a redox reaction. The following pairs of reactions show reagents that can react with themselves (disproportionate).

i)	Half Equations	Hydrogen peroxide reduced to water	$\text{H}_2\text{O}_2$	$\rightarrow$	$\text{H}_2\text{O}$
		Hydrogen peroxide oxidised to oxygen	$\text{H}_2\text{O}_2$	$\rightarrow$	$\text{O}_2$
	Redox full equation for $\text{H}_2\text{O}_2$ disproportionation			$\rightarrow$	
j)	Half Equations	Thiosulphate reduced to sulphur	$\text{S}_2\text{O}_3^{2-}$	$\rightarrow$	$\text{S}$
		Thiosulphate oxidised to sulphur dioxide	$\text{S}_2\text{O}_3^{2-}$	$\rightarrow$	$\text{SO}_2$
	Redox full equation for $\text{S}_2\text{O}_3^{2-}$ disproportionation			$\rightarrow$	
k)	Half Equations	Chlorine reduced to hydrochloric acid	$\text{Cl}_2$	$\rightarrow$	$\text{HCl}$
		Chlorine oxidised to hypochlorous acid	$\text{Cl}_2$	$\rightarrow$	$\text{HClO}$
	Redox full equation for $\text{Cl}_2$ disproportionation			$\rightarrow$	

**Electrochemical Reactions** are chemical reactions that produce an electrical current.

- **Electrochemistry** examines how to physically arrange chemical reagents to produce an electrical current that is external to the reagents. This external flow of electricity is known as an **electro-motive force (emf)**.
- **Electrolytic reactions** are those chemical reactions that require an input of electricity to drive the reaction.

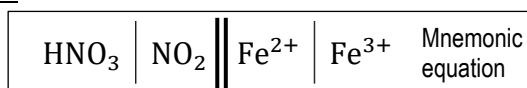
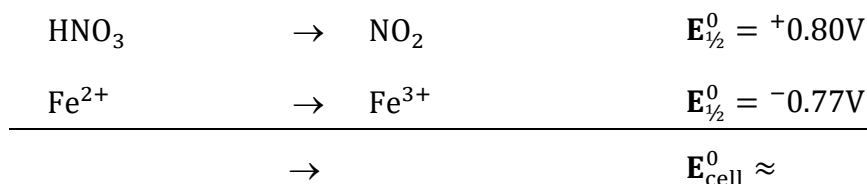
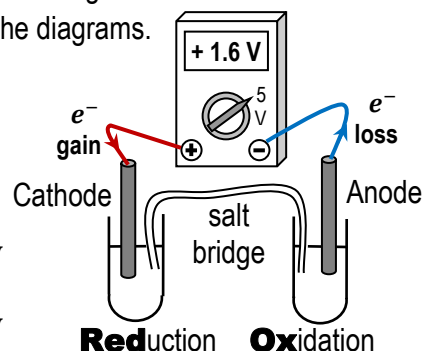
**Q24** Balance these **Electrochemical** reactions using the following  $\frac{1}{2}$  cells, salt bridge and inert graphite electrodes.

**Note:** Electrical Current **I** is defined as going from (+) to (-). Electrons  $e^-$  themselves really move (-) to (+).

- Assume acidic conditions. That means add as many  $H^+_{(aq)}$  ions as you need to balance the  $\frac{1}{2}$ -equations.
- Complete the mnemonic cell reactions for overall red<sup>n</sup> || oxid<sup>n</sup> under each diagram.
- Identify and label each electrode, including electron flow arrows, on the diagrams.

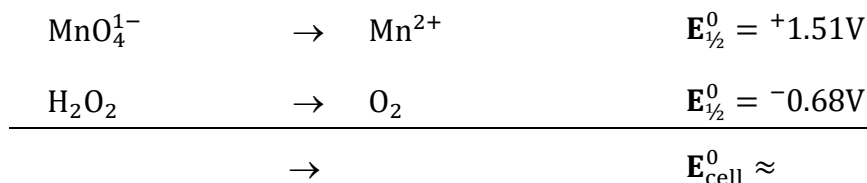
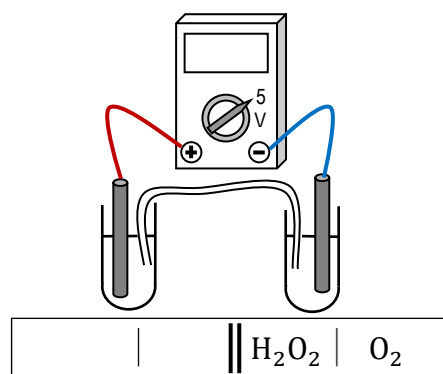
(a) Ferrous sulphate  $FeSO_4$  with concentrated nitric acid  $HNO_3$ :

- The  $Fe^{2+}$  will oxidise to  $Fe^{3+}$  rather than convert to  $Fe_{(s)}$ ;  
The  $SO_4^{2-}$  remains unreacted as a spectator ion.
- The concentrated  $HNO_3$  can now be reduced.



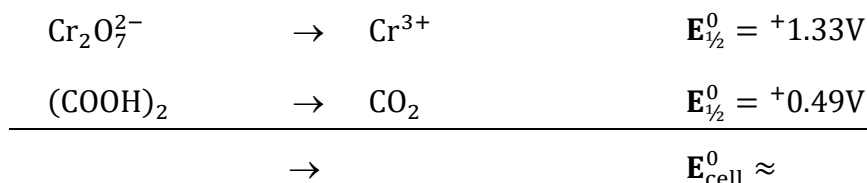
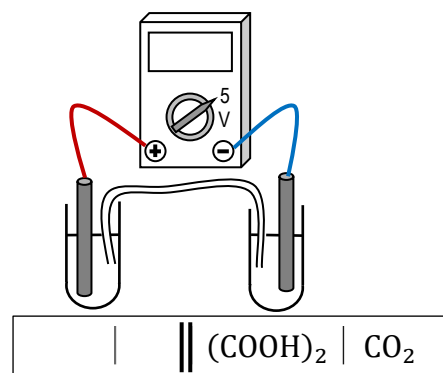
(b) Acidified potassium permanganate  $KMnO_4$  with hydrogen peroxide  $H_2O_2$ . Acidification ensures  $Mn^{2+}$  as the product.

- What does acidifying the solution do for the Redox  $\frac{1}{2}$ -reactions?
- $K^+_{(aq)}$  cations do not reduce to  $K_{(s)}$  in aqueous solutions.  
The  $K^+_{(aq)}$  remains unreacted as a spectator ion.

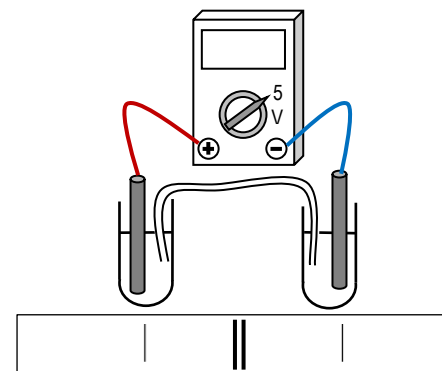
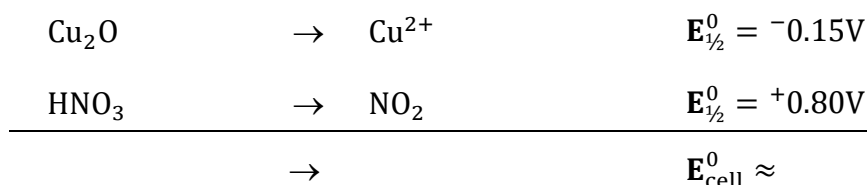


(c) Acidified potassium dichromate  $K_2Cr_2O_7$  with oxalic acid  $(COOH)_2$

- Lose  $K^+_{(aq)}$  as spectator ions now!
- The  $Cr_2O_7^{2-}$  reduces while the  $(COOH)_2$  oxidises readily.




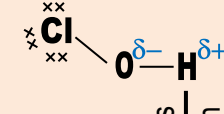
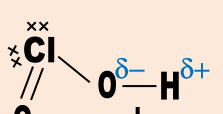
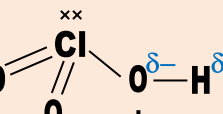
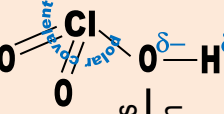
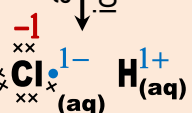
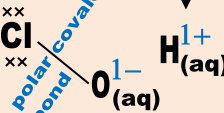
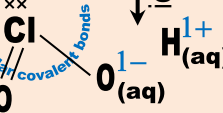

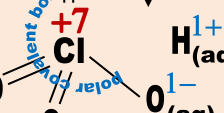
(d) Insoluble copper (I) oxide  $Cu_2O$  converts to aqueous copper (II) cations  $Cu^{2+}_{(aq)}$  in the presence of nitric acid.



**CHLORINE** has a high electronegativity and can expand its octet to form a variety of oxidation states.

- Chlorine is from Group VII Period 3 of the Periodic Table with seven valence electrons.
- The high electronegativity of Chlorine allows all seven valence electrons to form a maximum of seven bonds.
- Seven bonds represent fourteen valence electrons for Chlorine.
- Maximum electrons in a valence shell  $n$  is  $2n^2$ : Period 3 has  $\max_{e^-} = 2 \times (3)^2 = 18e^-$  maximum.
- Forming a stable valence shell with more than eight electrons is known as 'Expanding the Octet'.

The structural diagrams below represent valence shell electrons for Chlorine. Inner shell electrons are not shown.

<b>Hydrochloric acid</b>	<b>Hypochlorous acid</b>	<b>Chlorous acid</b>	<b>Chloric acid</b>	<b>Perchloric acid</b>
HCl forms a linear polar covalent molecule with respect to the Cl atom.	HClO forms a v-shaped polar covalent molecule with respect to the O atom.	HClO <sub>2</sub> forms a v-shaped polar covalent molecule with respect to both the Cl and O atoms.	HClO <sub>3</sub> forms a trigonal pyramid polar covalent molecule with respect to Cl atom.	HClO <sub>4</sub> forms a tetrahedral polar covalent molecule with respect to the Cl atom.
Relative electronegativity H < Cl	Relative electronegativity H < Cl << O	Relative electronegativity H < Cl << O	Relative electronegativity H < Cl << O	Relative electronegativity H < Cl << O
<b>Oxidation states</b> +1 -1 H Cl	<b>Oxidation states</b> +1 +1 -2 H Cl O	<b>Oxidation states</b> +1 +3 -2 H Cl O <sub>2</sub>	<b>Oxidation states</b> +1 +5 -2 H Cl O <sub>3</sub>	<b>Oxidation states</b> +1 +7 -2 H Cl O <sub>4</sub>
				
aqueous ionisation	aqueous ionisation	aqueous ionisation	aqueous ionisation	aqueous ionisation
				
<b>ionised bonds</b>	<b>ionised bonds</b>	<b>ionised bonds</b>	<b>ionised bonds</b>	<b>ionised bonds</b>

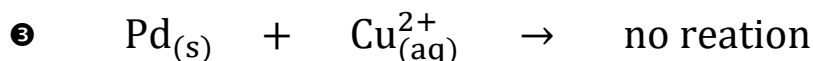
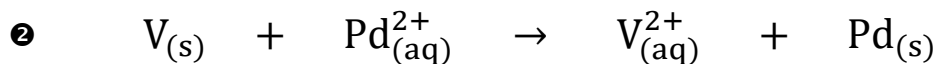
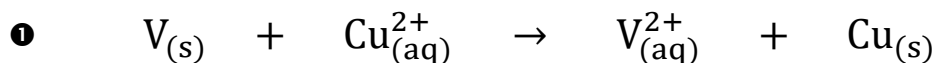
**Oxidation states** for Oxygen (-2) and for Hydrogen (+1) remain constant, as per the 'three' oxidation rules.

**Q25 Assign** oxidation states to the various halogens (F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>) and chromium (Cr) atoms in the following reactions to determine which reactions are redox and which are acid/base (not redox):

a)	$\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}_{(g)} \text{ then } \text{HCl}_{(g)} \xrightarrow{\text{aqueous}} \text{HCl}_{(aq)}$ <p>chlorine gas      hydrogen chloride      hydrochloric acid</p>	$\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HClO}$ <p>dichlorine monoxide      hypochlorous acid</p>
	$2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{HClO}_2 + \text{HClO}_3$ <p>chlorine dioxide      chlorous acid      chloric acid</p>	$\text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HClO}_4$ <p>dichlorine heptoxide      perchloric acid</p>
	$\text{F}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HFO}$ <p>oxygen difluoride      hypofluorous acid</p>	$2\text{BrO}_2 + 2\text{H}_2\text{O} \rightarrow \text{HBrO} + \text{HBrO}_3 + \text{H}_2$ <p>bromine dioxide      hypobromous acid      bromic acid</p>
b)	$2\text{Na}_2\text{CrO}_4 + 2\text{HCl} \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} + 2\text{NaCl}$ <p>yellow      pH &lt; 7      orange</p>	$\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KOH} \rightarrow 2\text{K}_2\text{CrO}_4$ <p>orange      pH &gt; 7      yellow</p>
	$\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{FeSO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4$ <p>orange      pale green      dark green      rust red</p>	
	$3\text{MnCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Mn}_3(\text{PO}_4)_2 + 3\text{CO}_2 + 3\text{H}_2\text{O}$ <p>purple      pH &lt; 7      effervescence</p>	

The following question is taken from a second semester SACE Stage 1 Chemistry exam.

**Q26** Copper (Cu), palladium (Pd) and vanadium (V) are metals used in making alloys. Three displacement tests were carried out on these three metals  $M_{(s)}$  and their corresponding salts  $M_{(aq)}^{n+}$  in solution. The results are summarised below:



(a) (i) Complete the displacement reaction equation the following combination:



(ii) Arrange the three metals in order of **increasing** reactivity: **[2 marks]**

Least Active < < Most Active

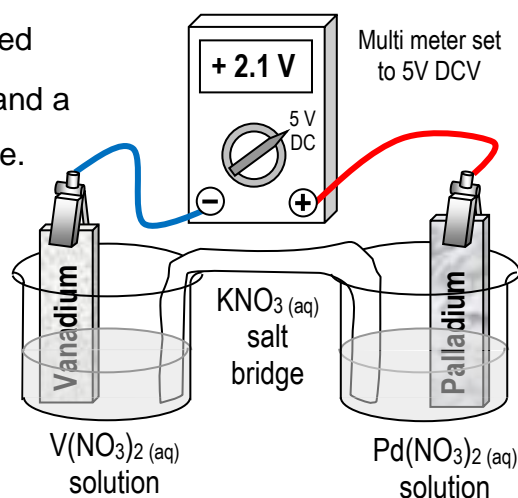
(ii) Provide a brief explanation for your answer in part (a) (ii) above. **[3 marks]**

(b) Two half cells for  $V|V^{2+}$  and  $Pd|Pd^{2+}$  are connected with a salt bridge soaked in potassium nitrate solution and a multimeter set to record DC voltages as shown opposite.

(i) Indicate the direction of the external electron flow with an arrow on the diagram opposite. **[1 mark]**

(ii) Complete the table below by referring to the (+) and (-) electrodes shown in the diagram.

**[4 marks]**



Electrode Sign		$\frac{1}{2}$ -cell $M M^{n+}$ at electrode	Electrode Half Equations	Redox Process Name (Reduction or oxidation)	Electrode Name (Cathode or Anode?)
From diagram	(+)				
	(-)				

(iii) Write full redox equation for these  $\frac{1}{2}$ -reactions

Which displacement reaction, ①, ②, ③ or ④, is represented by connecting these two half-cells? **[2 marks]**

(c) (i) The  $V|V^{2+}$  half-cell has a solution containing  $V_{(aq)}^{2+}$  and  $NO_{3(aq)}^{1-}$  ions. Which one of these ions becomes in excess in the solution as the redox reaction proceeds? [1 mark]

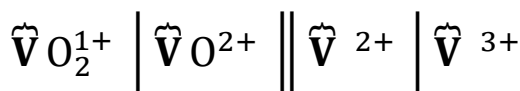
(ii) The  $Pd|Pd^{2+}$  half-cell has a solution containing  $Pd_{(aq)}^{2+}$  and  $NO_{3(aq)}^{1-}$  ions. Which one of these ions becomes in excess in the solution as the redox reaction proceeds? [1 mark]

(iii) The salt bridge contains mobile  $K_{(aq)}^{1+}$  and  $NO_{3(aq)}^{1-}$  ions. State which half-cell each of these mobile ions move to as the redox reaction proceeds. [2 marks]

$K_{(aq)}^{1+}$  moves to \_\_\_\_\_ and  $NO_{3(aq)}^{1-}$  moves to \_\_\_\_\_

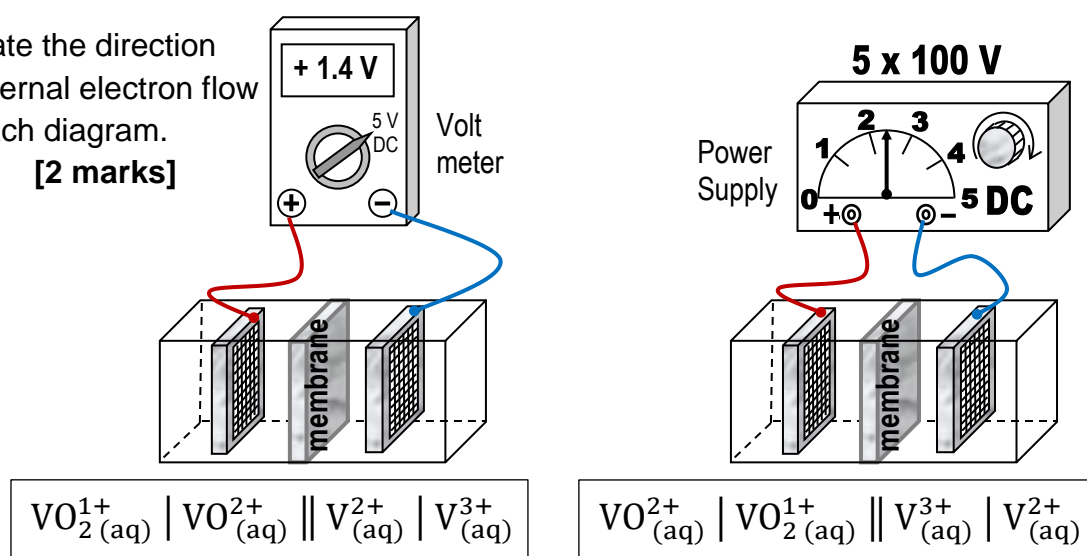
(d) The vanadium redox battery (VRB) uses vanadium salt solutions separated by a permeable plastic membrane ( || ) to allow aqueous ions to move between each half cell.

(i) State the four oxidation states of vanadium in the VRB: [3 marks]



(ii) The VRB converts chemical energy to electrical energy and can also use electrical energy to produce a chemical reaction. Refer to the two diagrams below and identify which process is occurring in each. [2 marks]

(iii) Indicate the direction of external electron flow on each diagram. [2 marks]



(iv) Use the half equation method to write the full redox reaction equation for the electrolytic VRB shown above. [3 marks]

$\frac{1}{2}$  equation →

$\frac{1}{2}$  equation →

full equation →

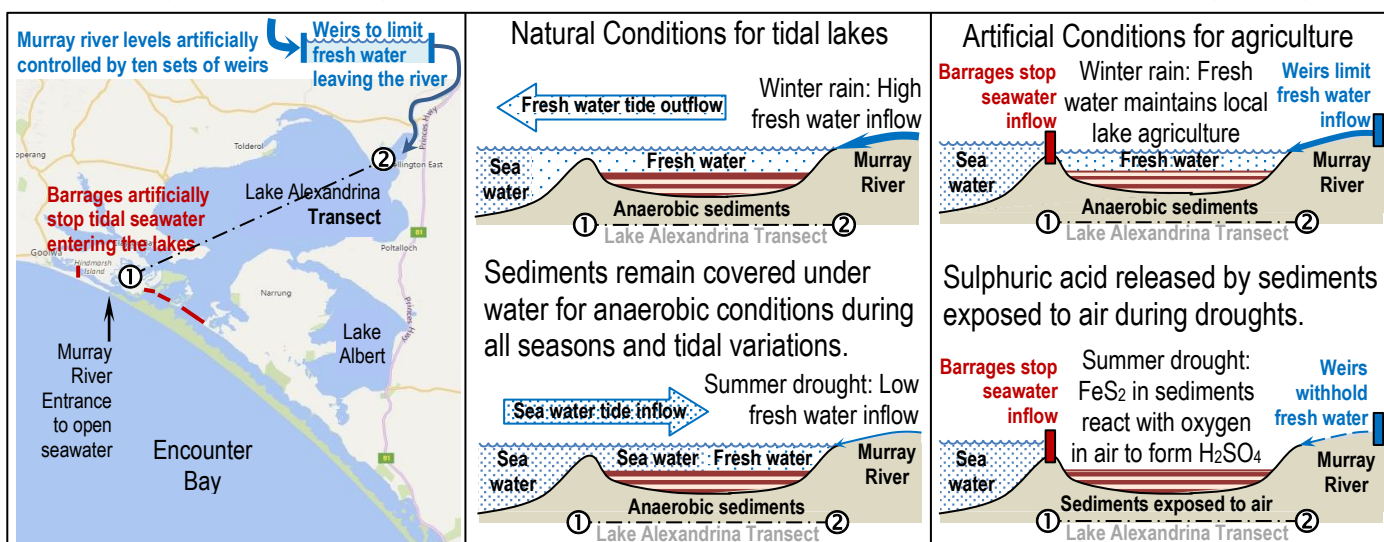


## Science as Human Endeavour (SHE) related Electrochemistry in SA

The 2,500 km Murray River flows from the Victorian alps to the South Australian Lower Lakes.

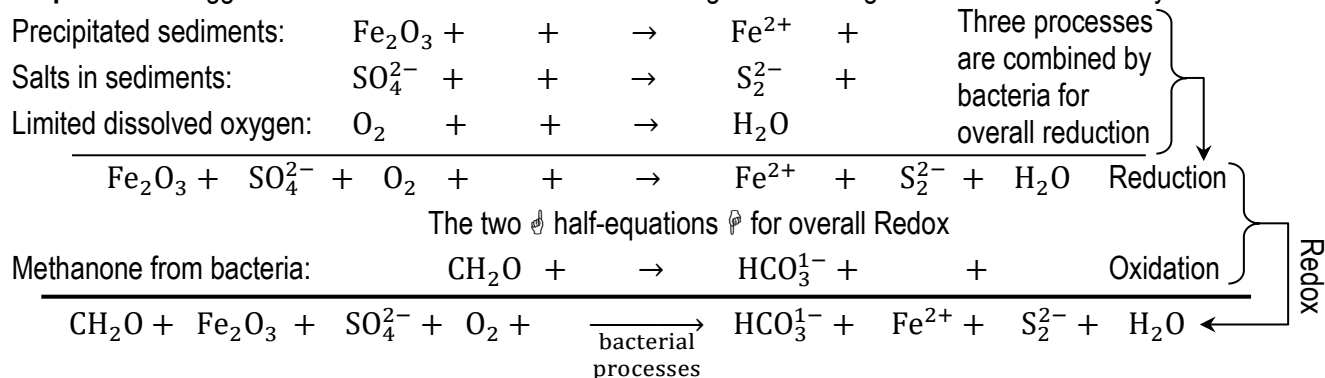
- Water run-off from arid land into the river causes many minerals, salts, soil, clay and organic materials to be transported downstream and deposited as sediments in the Lower lakes.
  - Sediments containing iron (III) oxide  $\text{Fe}_2\text{O}_3$  have accumulated over thousands of years<sup>12</sup>.
  - Water logged bacteria naturally convert the  $\text{Fe}_2\text{O}_3$  into iron (II) persulphide, pyrites,  $\text{FeS}_2$ .
- Weirs along the Murray river reduce fresh water inflow to the lakes during drought (see ②). The fresh water is retained along the river for agricultural irrigation and town water supplies<sup>13</sup>.
- Barrages at the seawater entrance artificially stop seawater inflow to the lakes (see ①).
  - $\text{FeS}_2$  in sediments exposed to the air react with oxygen to form sulphuric acid  $\text{H}_2\text{SO}_4$ .
  - The  $\text{H}_2\text{SO}_4$  can be neutralised with aerial spraying of limestone powder  $\text{CaCO}_3$ .

Alternatively,  $\text{H}_2\text{SO}_4$  production can be prevented by covering the lake sediments with seawater by opening the sea barrages. The extra salt is less harmful to the environment during drought.



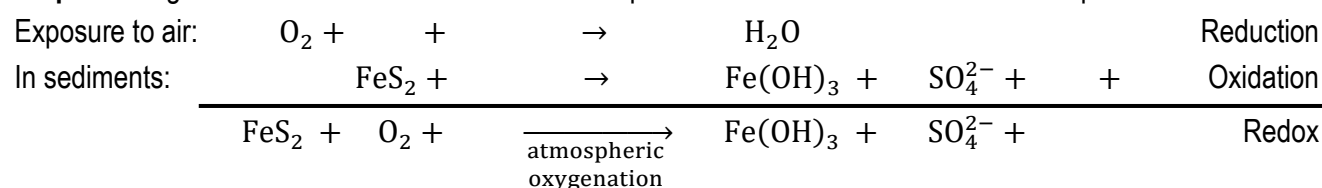
Complete the following redox half-equations and their resulting fully balanced reaction equations.

**Step 1:** Water-logged anaerobic conditions favour bacterial growth feeding from  $\text{Fe}_2\text{O}_3$  sedimentary minerals.



The products accumulate in the soil as insoluble iron (II) persulphide, pyrites,  $\text{Fe}^{2+} + \text{S}_2^{2-} \rightarrow \text{FeS}_2$ . (See Q4 h)

**Step 2:** Drought conditions lower water levels and expose  $\text{FeS}_2$  sediments to aerobic atmospheric conditions.



The products then associate to form sulphuric acid  $2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{SO}_4$  and damage the environment.

<sup>12</sup> South Australian DEWNR Report: Lower Lakes Acid Sulphate Soils Conceptual Models 2012-2013

<sup>13</sup> <http://www.lakesneedwater.org/barrages/locks-and-weirs-of-the-river-murray>