

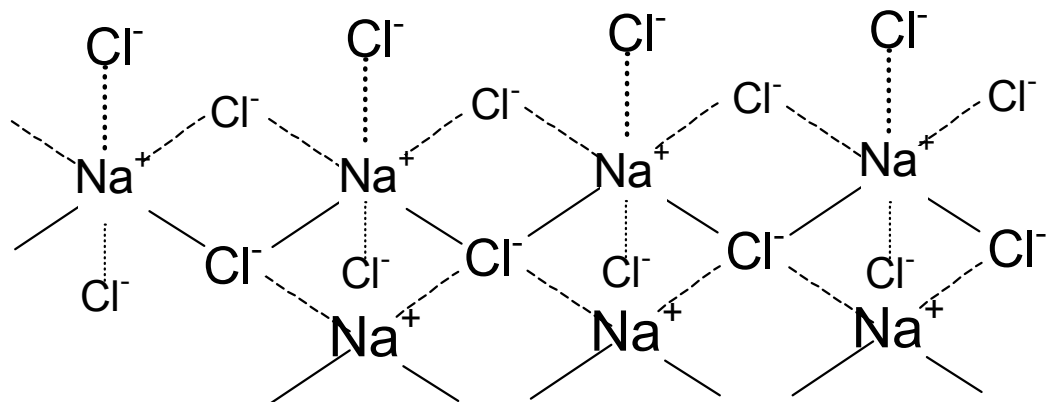
Bonding

Types of Bonding

Ionic

Metal cations and nonmetal anions (sometimes polyatomic) arranged in an alternating *lattice* of cations and anions maximizing the strong *electrostatic attraction* between oppositely charged ions.

For example, NaCl(s) consists of Na^+ and Cl^- ions in an alternating cubic lattice.



Ionic materials are typically *hard, brittle solids* with *high melting points*.

Ionic compounds *dissolve in water* to form *ionic aqueous solutions*.

Covalent

Molecules are combinations of atoms, with no net charge, held together by *covalent bonds* – *shared pairs of valence electrons*.

Electrons are *unequally shared* when the electronegativities are different - *polar covalent*.

For example, in H-Cl the electrons in the bond are closer to Cl, facilitating donation of H⁺. HCl is a strong acid.

In a molecular material, molecules are held together by *intermolecular forces*.

Intermolecular forces are *weaker*: lower melting and boiling points than (most) ionic materials.

Examples: CO₂(g) , H₂S(g), H₂O(l) and sucrose, C₁₂H₂₄O₁₂(s).

Intermolecular forces depend on size: large molecules generally form solid materials at room temperature.

Network covalent materials have repeating patterns of covalent bonding extending across an entire crystal. They are *hard, resilient solids* with *very high melting point*.

C(diamond) has the highest melting point (3500°C) of all materials.

Polyatomic ions, such as CO_3^{2-} and NO_3^- , are also held together by covalent bonds. However, they have a net charge and appear in ionic compounds.

Metallic

Metal cations are arranged in a crystal lattice, with remaining electrons shared between them in a “sea of electrons” – *metallic bonding*.

Metals are typically *solid*, *often* with *high melting points*. They are also *shiny*, and mostly silver-colored. They *conduct electricity* and are at least somewhat *malleable*.

Lewis Structures

The *electronic structure* of a set of *covalently bonded atoms*.

Valence electrons are arranged around the core of each atom (nucleus plus inner shell electrons) *in pairs* (mostly) – *lone pairs* (held by just one atom) and *bonding pairs* (shared between atoms).

Start with a *skeletal structure* – bonded atoms are linked with single bonds (each corresponding to one pair of electrons). Skeletal structure *rules*:

Hydrogen makes only one bond – H is always *terminal* (a non-central atom).

Fluorine is similarly terminal.

The *central atom* is generally the *least electronegative*.

Steps to a *Lewis structure*:

- (1) Add the valence electrons from all atoms – i.e., *sum* the group A numbers.

Add an extra electron for each minus net charge – in case of a polyatomic anion.

Subtract an electron for each plus net charge – in case of a polyatomic cation.

- (2) Use the electrons, in pairs, to form the *skeletal structure* of the molecule.

- (3) Use the remaining electrons as *lone pairs* on atoms – start with the *most electronegative* peripheral atom – until each atom has an *octet* – four electron pairs in the valence shell (include shared bonding pairs).

- (4) If there is an atom remaining *without* an octet, shift lone pair(s) from a bonded atom into the associated bond to make double or triple bonds.

Exceptions: Be, B or Al (e.g., BeH_2 , BF_3 , AlCl_3 – in the gas phase) – i.e., atoms in groups 2 and 3.

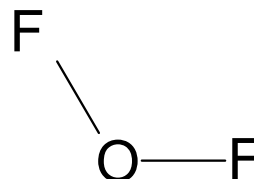
(5) To come ...

Lewis structure of F_2O – constructed with the first three steps:

(1)

$$6 + 2 \times 7 = 20 \text{ electrons}$$

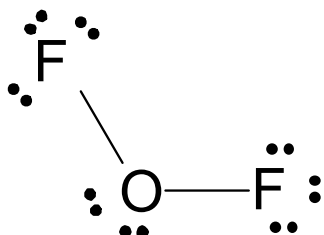
(2)



Skeletal structure - two bonds use 4 electrons.

There are 16 electrons left.

(3)



Lewis structure - every atom has an octet. $4 + 2 \times 6 = 16$ electrons are used.

There are no electrons left.

The Lewis structure of CO₂ requires step (4).

(1)

$$4 + 2 \times 6 = 16 \text{ electrons}$$

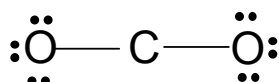
(2)



Skeletal structure - two bonds use 4 electrons.

12 electrons left.

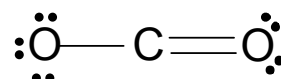
(3)



Remaining 12 electrons make octets on the oxygen atoms - the more electronegative atom.

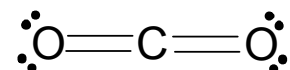
No electrons left. However, the carbon atom has only 4 electrons in its valence shell in this structure.

(4)



A lone pair (2 nonbonding electrons) on the right oxygen becomes a second bond from that oxygen to carbon.

The carbon atom now has 6 valence electrons.



Repeat this process on the left.

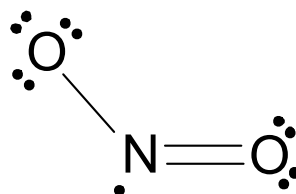
The carbon atom now has an octet. This is the Lewis structure of CO₂.

The octet is a stable valence electron configuration – the noble gas valence configuration.

However, when there are an odd number of electrons, not every atom can have an octet.

In this case, the least electronegative atom has less than eight electrons in its valence shell.

For example, in NO_2 (17 valence electrons) less electronegative nitrogen has 7 electrons in its valence shell:



Example: Draw Lewis structures for the following compounds.

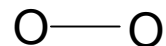
(a) O_2 (b) N_2 (c) CS_2

(a)

(1)

$2 \times 6 = 12$ electrons

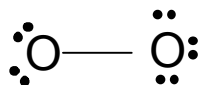
(2)



Skeletal structure - one bond uses 2 electrons.

10 electrons left.

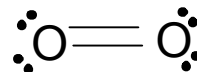
(3)



Not enough electrons for an octet on both oxygen atoms.

Remove a lone pair from the right oxygen atom, and make a bonding pair.

(4)



The Lewis structure of O_2 . Now, both atoms have an octet.

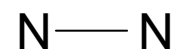
A limitation of Lewis structures: Oxygen is a diradical, better described with a triple bond and an "antibond", giving a net bond order of 2.

(b)

(1)

$2 \times 5 = 10$ electrons

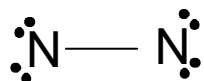
(2)



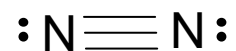
Skeletal structure - one bond uses 2 electrons.

There are 8 electrons left.

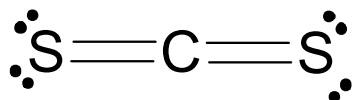
(3)



(4)



(c)

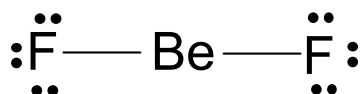


isoelectronic with CO_2

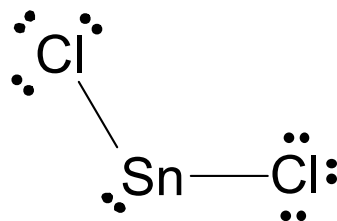
Metal atoms have low electronegativity and bring few valence electrons to the structure.

The metal atom typically has only 4 or 6 electrons in its valence shell – e.g., in the Lewis structures of beryllium and tin (near the edge of the metal region of the periodic table – bonding with nonmetals is covalent) compounds with nonmetals.

For example, BeF_2 and SnCl_2 exist as molecules in the gas phase with the following structures:

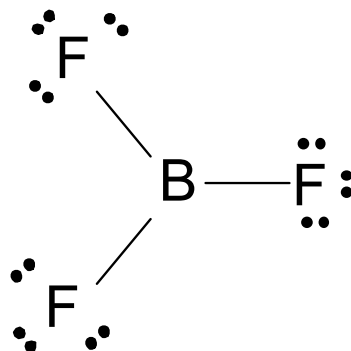


Beryllium has only four (shared) electrons in its valence shell.



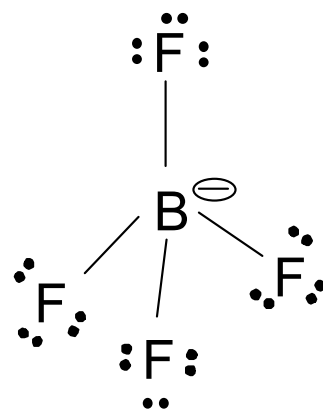
Tin has only six electrons in its valence shell.

Also, boron has less than an octet in *some* Lewis structures – e.g., BF_3 :



The vacancy in the valence shell of boron in BF_3 provides a source of reactivity.

BF_3 is a *Lewis acid*. It combines with F^- to form BF_4^- :



Formal Charge

An idealized *charge distribution*.

Formal charge on each an atom is computed as follows:

$$\text{formal charge} = \text{core charge} - (\text{number of non-bonding electrons}) - (\text{number of bonds})$$

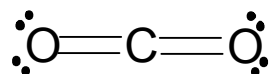
Note: number of bonds = $\frac{1}{2}$ number of shared bonding electrons

Formal charge corresponds to bonding electrons *equally* shared.

Formal charge is useful because the best Lewis structure – sometimes more than one is possible – has formal charges as close to zero as possible:

minimization of charge.

For example, the alternative structure of CO₂, with a single and triple bond, rather than two double bonds, is rejected because it has formal charges. The best structure has zero formal charges – it is the *charge minimized* structure.



Carbon:

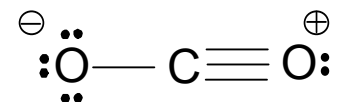
$$4 - (0 \times 2 + 4 \times 1) = 0$$

core charge 0 lone pairs + 4 bonds (1 electron each)

Oxygen:

$$6 - (2 \times 2 + 2 \times 1) = 0$$

core charge 2 lone pairs + 2 bond (1 electron each)



Carbon:

$$4 - (0 \times 2 + 4 \times 1) = 0$$

core charge 0 lone pairs + 4 bonds

Oxygen on left:

$$6 - (3 \times 2 + 1 \times 1) = -1$$

core charge 3 lone pairs + 1 bond

Oxygen on right:

$$6 - (1 \times 2 + 3 \times 1) = +1$$

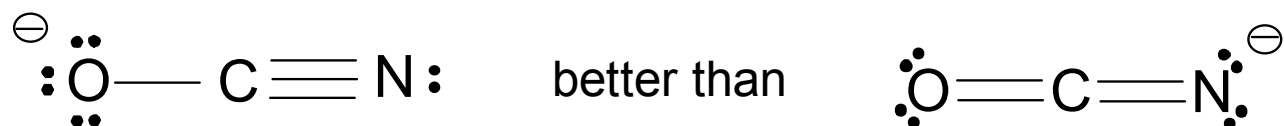
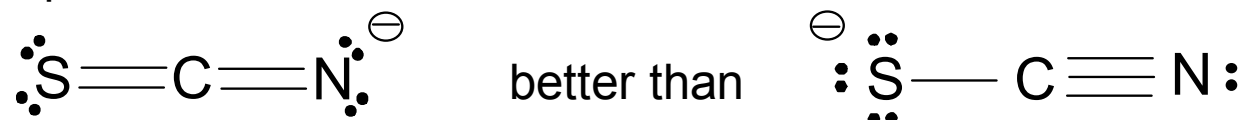
core charge 1 lone pair + 3 bonds

Sometimes there is *more than one* charge minimized structure.

When a *minus formal charge* can appear on atom A or atom B, the preferred structure has the minus formal charge on the *more electronegative atom*. Similarly, a *plus formal charge* is better on the *less electronegative atom*.

This rule does *not* supercede the *octet* rule – step (4) above.

For example,



Elements in the *third row and below* can *expand their valence shell* beyond an octet.

The octet represents filled s and p subshells. Atoms below the second row also have a *d subshell* of orbitals available which can accommodate additional electrons.

Expansion of the valence shell results when steps (1) to (4) produce a structure with a positive formal charge on a third row (or below) atom bonded to an atom with a minus formal charge – *separation of formal charge*.

Steps (1) to (4) give the following structure for the hydrogen sulfate anion:

The formal charges in HSO_4^- .

Terminal oxygen:

$$6 - (3 \times 2 + 1 \times 1) = -1$$

core charge 3 lone pairs + 1 bond (1 electron)

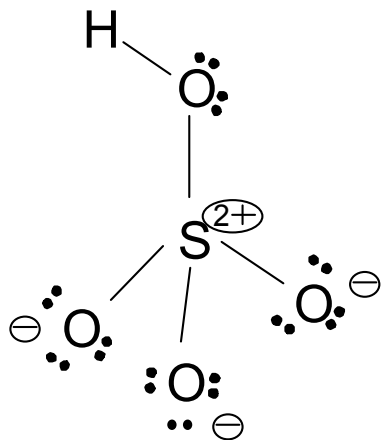
Hydroxyl oxygen:

$$6 - (2 \times 2 + 2 \times 1) = 0$$

core charge 2 lone pairs + 2 bonds

Sulfur:

$$6 - (0 \times 2 + 4 \times 1) = +2$$



The formal charge separation is reduced by converting lone pair(s) on terminal oxygen atom(s) into additional bonds to sulfur.

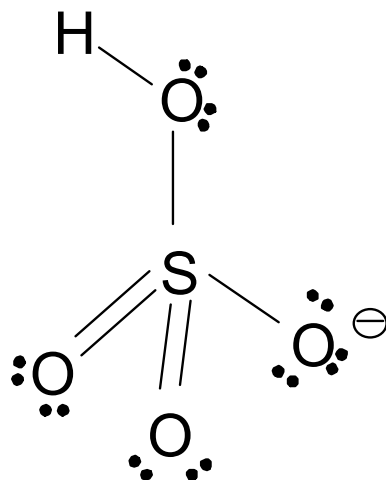
The formal charge on the oxygen atom *increases* by one.

The bonding pair counts as one electron, whereas the lone pair counted as two.

The formal charge on sulfur *decreases* by one.

The additional bond contributes an additional valence electron to sulfur.

The net effect is the *transfer of* (negative) *formal charge* from oxygen to sulfur, reducing the charge separation indicated in the structure.

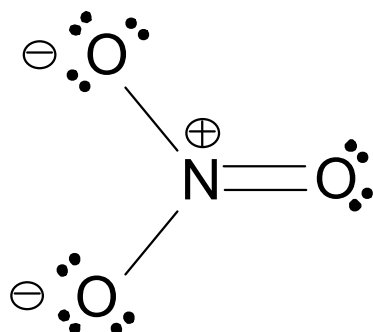


The charged-minimized **Lewis structure of HSO₄⁻**.

Charge minimization in HSO₄⁻ is possible here because sulfur is a third row element.

Nitrogen, a second row element, *cannot* expand its valence shell to accommodate more than eight electrons.

The formal charge separation cannot be eliminated in the Lewis structure of nitrate:



The last rule for constructing Lewis structures is given as follows:

(5) Minimize formal charges, to the extent possible, by allowing atoms *beyond the second row* to exceed eight electrons in the valence shell – *via* transfer of lone pairs from adjacent atoms into bonding pairs with the element expanding its valence shell.

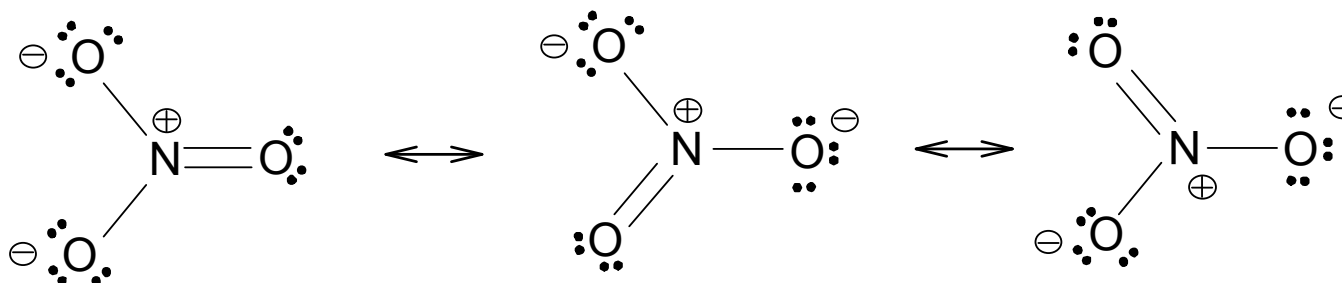
The above Lewis structure for nitrate suggests that one of the three N-O bonds is different from the other two – a double bond as opposed to a single bond.

Double bonds are *shorter* than single bonds.

However, the three N-O bonds in nitrate have *identical length*.

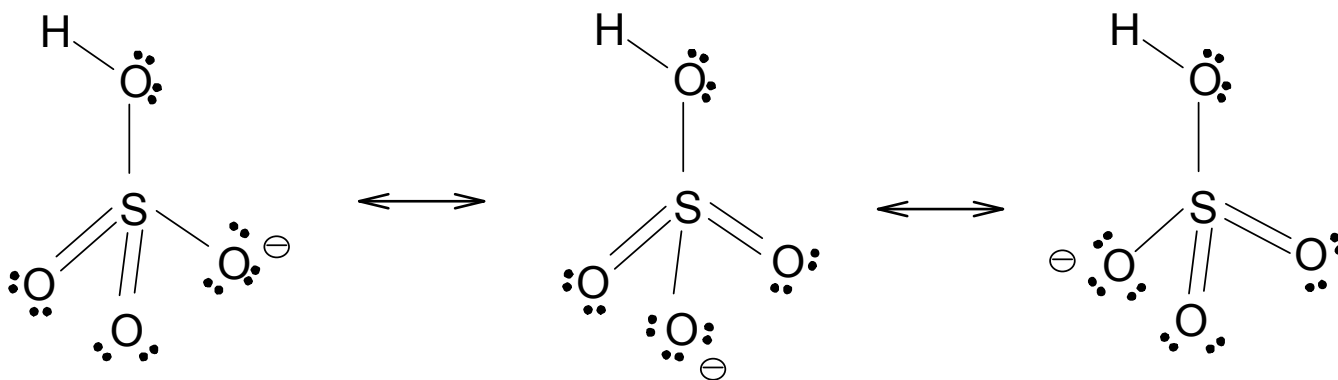
Quantum mechanics admits *superposition states* – the sum or difference of two states.

The following three Lewis structures are equivalent:



The Lewis structure of NO_3^- is the *resonance hybrid* of the three equivalent resonance structures.

Hydrogen sulfate similarly has three resonance structures:



Only *three* of the four O atoms are equivalent (the *terminal* O atoms).

The bond order (of a specific bond) is the *average bond order*.

$$\text{average bond order} = \frac{\sum_{\text{resonance structures}} \text{bond order in structure}}{\text{number of resonance structures}}$$

Equivalently,

$$\text{average bond order} = \frac{\sum_{\text{equivalent bonds}} \text{order of bond}}{\text{number of equivalent bonds}}$$

Formal charge on a specific atom in a resonance hybrid is the *average formal charge*:

$$\text{average formal charge} = \frac{\sum_{\text{resonance structures}} \text{formal charge in structure}}{\text{number of resonance structures}}$$

or

$$\text{average formal charge} = \frac{\sum_{\text{equivalent atoms}} \text{formal charge of atom}}{\text{number of equivalent atoms}}$$

Example: What are the average formal charges and bond orders in the resonance hybrid structures of (a) nitrate and (b) hydrogen sulfate?

(a) In the case of nitrate, the average formal charge on the three equivalent oxygen atoms is

$$((-1) + (-1) + 0)/3 = -2/3.$$

The average formal charge on nitrogen is +1. It is the same on all resonance structures.

The average N-O bond order is

$$(1 + 1 + 2)/3 = 4/3.$$

(b) In the case of hydrogen sulfate, the average formal charge on the three equivalent terminal oxygen atoms is

$$((-1) + 0 + 0)/3 = -1/3.$$

The average formal charge on the sulfur atom, and hydroxyl oxygen atom, is zero.

The average bond order of the three equivalent S-O bonds is

$$(1 + 2 + 2)/3 = 5/3.$$

The order of the bond between S and the hydroxyl oxygen atom is one.

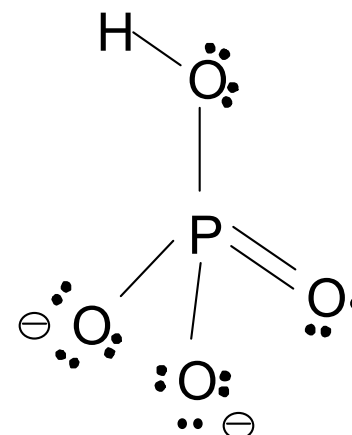
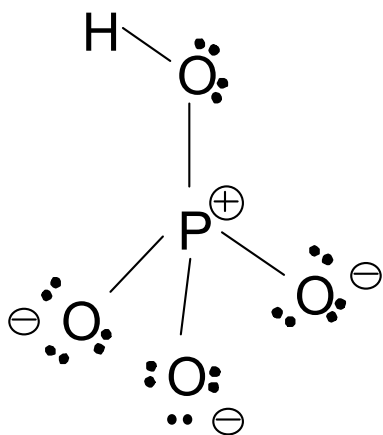
Example: Draw *charge minimized* Lewis structures, including the *formal charges*, for the following species. How many *resonance* structures are there? What are the *average* formal charges and bond orders?

(a) HPO_4^{2-} (H is bonded to O) (b) XeOF_4 (Xe is the central atom)

(a)

Steps (1), (2) and (3) - step (4) does not apply.

Step (5) - applies only once.



Three resonance structures – there are three equivalent terminal oxygen atoms.

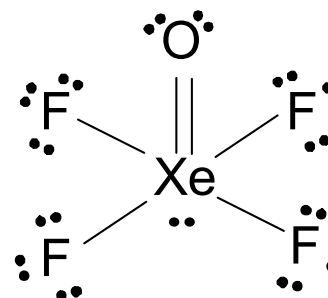
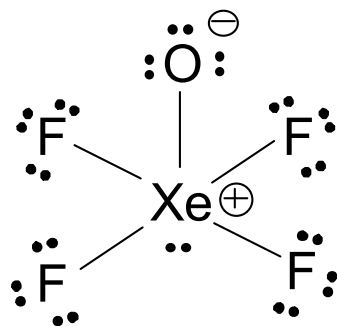
The average formal charge on the three equivalent oxygen atoms is $-2/3$.

The average P-O bond order – to a terminal oxygen – is $4/3$.

(b)

Steps (1), (2) and (3) - step (4) does not apply.

Step (5) - applies only once.



There are no additional resonance structures.

Bond orders and formal charges are as indicated in the structure.

All formal charges equal zero.

The Xe-F bonds are single bonds, and the Xe-O bond is double.

Higher order bonds are *stronger* and *shorter* – a stronger bond holds atoms closer together.

With respect to *bond length*, we have the following ordering:

triple < double < single.

With respect to *bond energy* (bond strength) the order is *reversed*:

single < double < triple.

For example, the S=O double bonds in SO₃ are stronger (have larger bond energy) and are shorter than the 5/3 order S-O bonds in HSO₄⁻, which in turn are stronger and shorter than the single S-O bond (S-O-H) in the same molecule.

Molecular Shape and Polarity

According to the *valence shell electron pair repulsion (VSEPR)* theory the shape of a molecule results from the minimization of repulsion between electron pairs (more generally, domains) in the valence shell of atoms.

Electron domains in the valence shell of each atom are maximally separated in the atoms of a stable molecule.

An electron domain is

- (1) a non-bonding pair of electrons – a *lone pair*,
- (2) the bonding pair of electrons in a single bond,
- (3) all bonding pairs of electrons in a double or triple bond, or
- (4) a single unpaired non-bonding electron.

Electron domains are arranged, in the valence shell of each atom, to give the greatest symmetry possible – minimizing electron repulsion.

Consider an atom A, within a molecule, bonded to other atoms, X.

Determine the *number of bonding electron domains*, m .

e.g.,

$$m = 2 \text{ for H}_2\text{O and CO}_2$$

$$m = 4 \text{ for CH}_4$$

Determine the *number of non-bonding electron domains*, n .

e.g.,

$$n = 2 \text{ for H}_2\text{O}$$

$$n = 0 \text{ for CH}_4 \text{ and CO}_2$$

The *shape* of a molecule (about atom A) is determined by m and n – i.e., the *VSPRE class*,



Two electron domains, in total (i.e., $m + n = 2$) – *linear geometry*:



If both of the domains are bonding, we have the

AX_2 VSEPR class ($n = 0$).

AX_2 molecules or ions have a *linear shape*.

The X-A-X bond angle equals 180° .

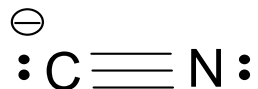
Examples:

BeF_2 has two bonding electron domains about beryllium, and is consequently linear.

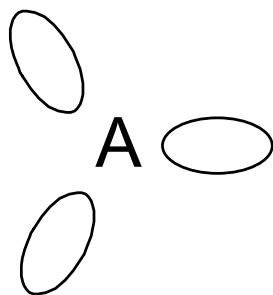
CO_2 and are also linear.

AXE molecules are diatomic – all diatomics are linear.

Example: Cyanide, CN^- ,

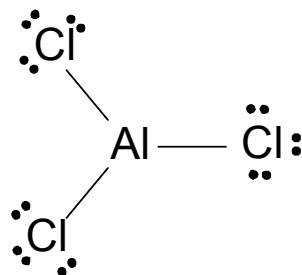


Three electron domains – *trigonal planar geometry*.



AX_3 class – *trigonal planar shape*

Examples: Boron in BF_3 and nitrogen in nitrate. Al in $AlCl_3$.



The *ideal bond angles* are all 120° - bond angles are ideal in symmetrical AX_3 molecules and ions such as BF_3 , $AlCl_3$ and NO_3^- .

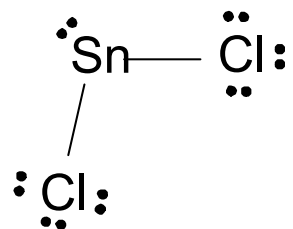
AX₂E class – *bent shape*

Examples: Tin in SnCl₂ and nitrogen in NO₂.

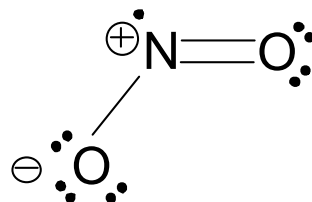
The ideal bond angle is 120°.

The **lone pair** in SnCl₂ exerts *greater repulsion* than the bonding pairs

– the bond angle is 95° < 120°.



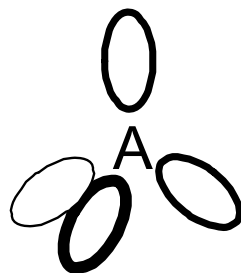
In the case of NO_2 , one of the non-bonding domains is a single electron.



- the bond angle is $134^\circ > 120^\circ$
 - a **single non-bonding** electron has *less repulsion* than bonding electron pairs

AXE_2 are diatomic and therefore linear.

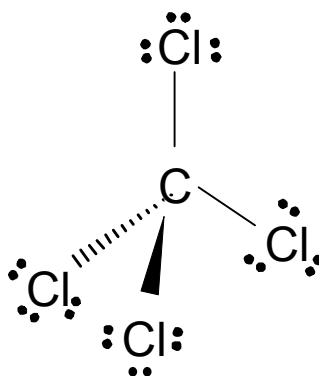
Four electron domains about A - *tetrahedral geometry*.



AX_4 class – *tetrahedral shape*.

The ideal bond angle is 109.5° .

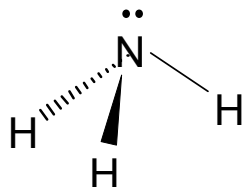
Examples: CH_4 , CCl_4



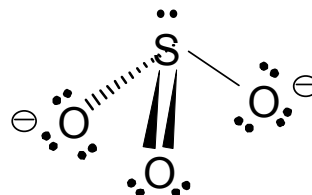
Note: The *dash* and *wedge* bonds.

AX₃E class – *trigonal pyramidal shape*

Examples: Ammonia, NH₃, and sulfite, SO₃²⁻



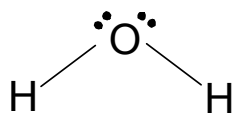
ammonia



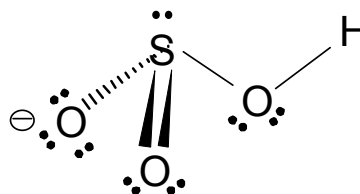
sulfite - there are three equivalent resonance structures

AX₂E₂ class – *bent shape*

Examples: Water, H₂O, F₂O and the hydroxyl group in hydrogen sulfate (the shape about the H-O oxygen atom).



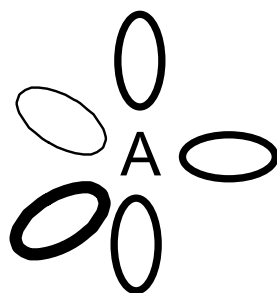
water



hydrogen sulfite - bent at the hydroxyl oxygen atom

Bond angles in AX_3E and AX_2E_2 molecules are generally *less than* 109.5° because non-bonding electron pairs exert greater repulsion than bonding pairs.

Five electron domains about A - *trigonal bipyramidal geometry*

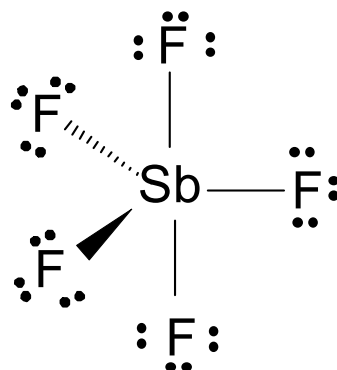


Two *axial* (vertical) and three *equatorial* positions

Ideal equatorial bond angles are 120° . Axial to equatorial bond angles are 90° .

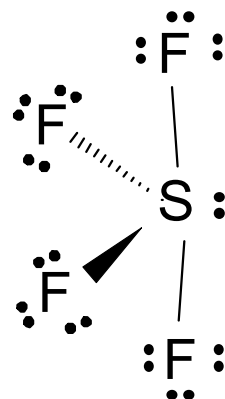
AX_5 class – *trigonal bipyramidal shape*

Example: Antimony pentafluoride, SbF_5



AX_4E class - *seesaw shape*

Example: Sulfur tetrafluoride, SF_4



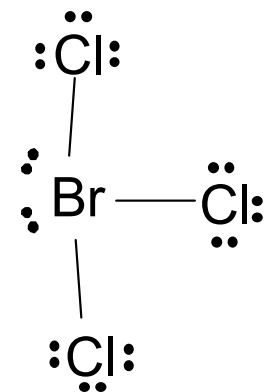
The lone pair is in an *equatorial* position - it needs more space in the valence shell of A than the bonding domains.

Bond angles are *less than* ideal values (i.e., $<90^\circ$ and $<120^\circ$) – except the axial to axial bond angle is $> 180^\circ$.

AX_3E_2 class – *T-shaped*

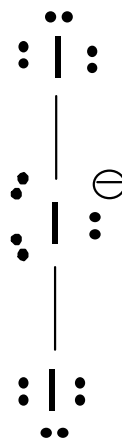
Example: $BrCl_3$

Bond angles are less than ideal ($<90^\circ$)

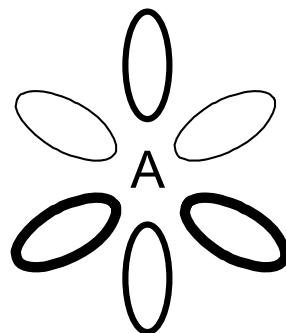


AX_2E_3 class – linear

Example: I_3^-

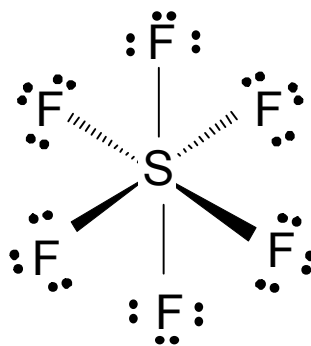


Six electron domains about A – *octahedral geometry*



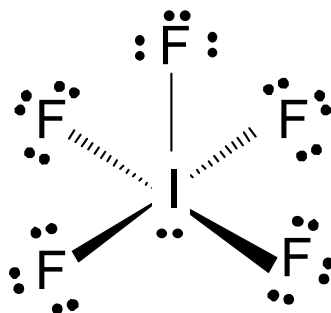
Ideal bond angle is 90°

AX_6 class – *octahedral shape*
Example: Sulfur hexafluoride



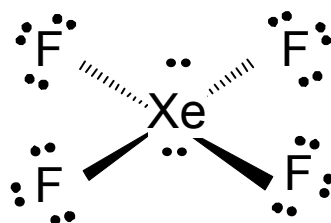
AX_5E class – *square pyramidal shape*

Example: IF_5



AX_4E_2 class – it is *square planar shape*

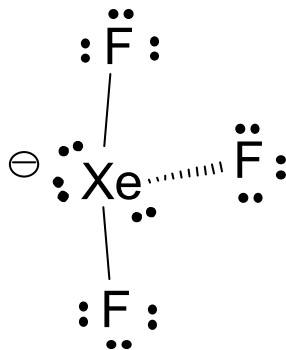
Example: Xenon tetrafluoride, XeF_4



Repulsion is minimized with two lone pairs in the two axial positions.

AX_3E_3 class – *T-shaped*

Example: Xenon trifluoride anion, XeF_3^-



Bond angles are less than ideal ($<90^\circ$).

Molecular Polarity

Polar covalent bonds have a *bond dipole*,

a vector pointing towards the more electronegative element

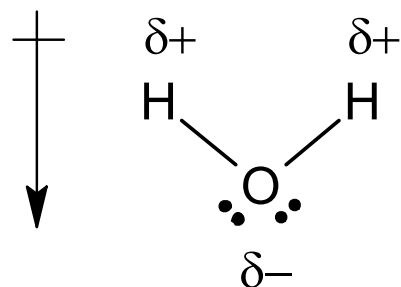
– i.e., from net positive charge to net negative charge.

Magnitude of a bond dipole is proportional to the bond polarity – i.e., amount of charge separated.

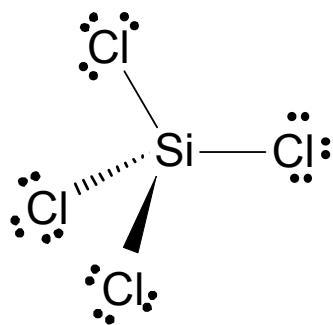
Asymmetrical molecules are *polar*

– they have a *net permanent dipole* because the bond dipoles do not cancel.

Example: Water is polar



In contrast, SiCl₄ has *no net dipole* – although it has polar covalent bonds.



SiCl₄ is symmetrical – it has a *center of symmetry*. The bond dipoles cancel and SiCl₄ is *non-polar*.

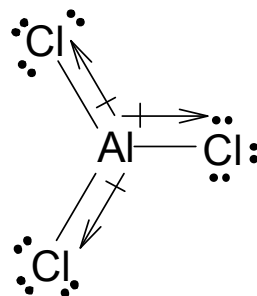
Molecules with a center of symmetry – AX_n , AX_2E_3 and AX_4E_2 molecules with one type of X atom – are **non-polar**.

Molecules with polar bonds, without a center of symmetry – all other classes, and/or more than one X atom – are **polar**.

Example: For the following molecules, determine the VSEPR class and shape. Is it a polar or non-polar molecule?

(a) $AlCl_3$ (b) $HCCl_3$ (c) SO_2 (d) IF_3 (e) SeF_6

(a)

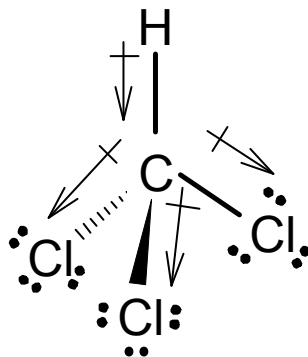


AX_3 – trigonal planar shape.

Al-Cl bonds are polar, but the molecule is symmetrical – the bond dipoles cancel.

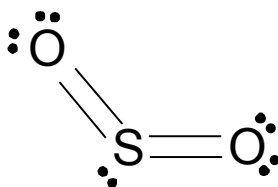
AlCl_3 molecules (in the gas phase) are non-polar.

(b)



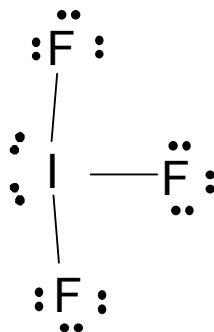
AX_4 – tetrahedral. No center of symmetry - the C-H bond dipole is different (in magnitude and direction) from the C-Cl bond dipoles – the dipoles do not cancel. Trichloromethane (chloroform) is polar.

(c)



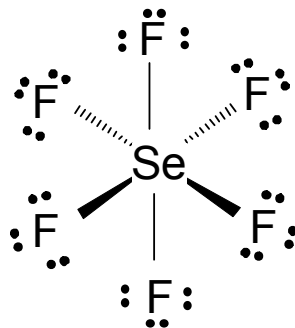
AX_2E – bent shape. Polar S-O bonds – asymmetric. SO_2 is polar.

(d)



AX₃E₂ – T-shaped – asymmetric and polar.

(e)



AX₆ – octahedral – symmetric and non-polar.

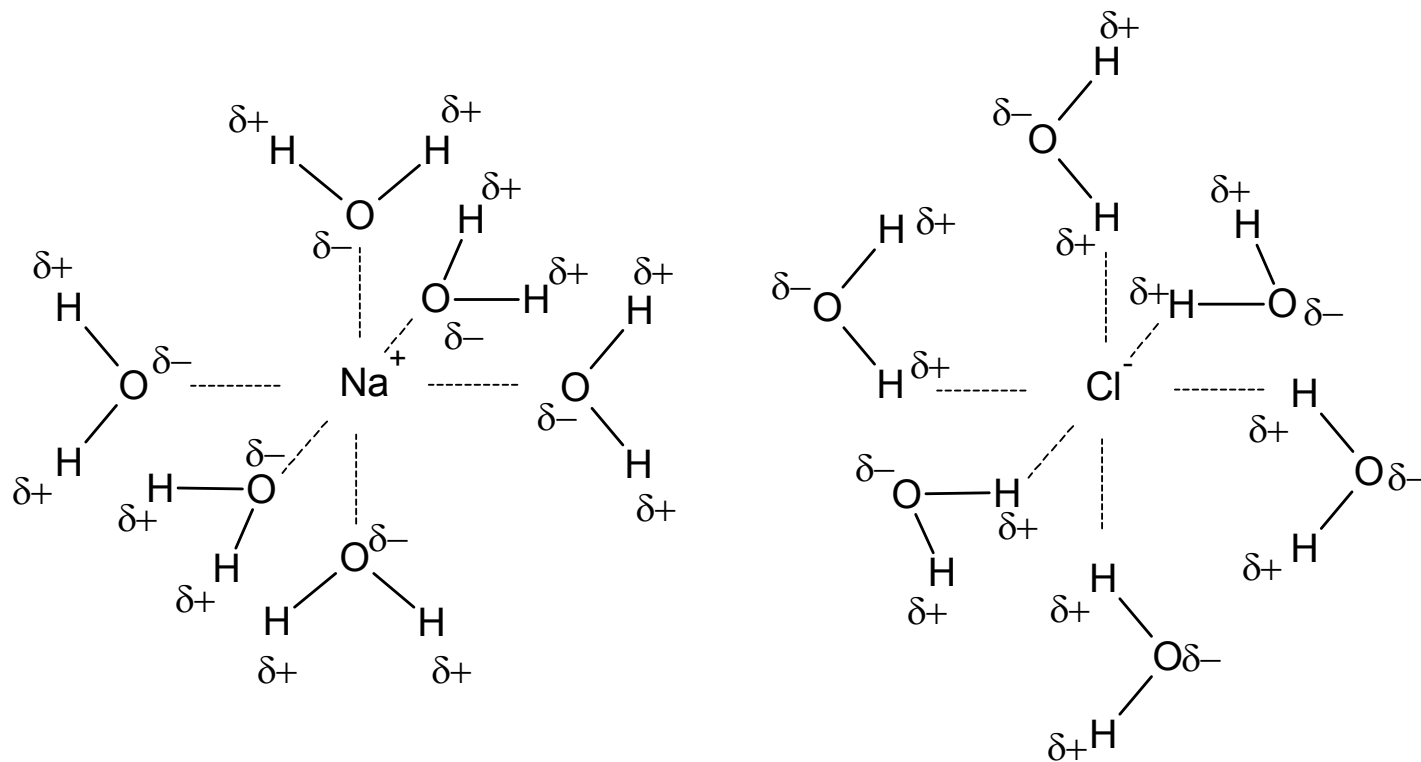
Types of Reactions

Aqueous Solutions

Salts *dissolve* in water to form *electrolyte solutions* – though some have extremely small *solubility*.

Dissolution results because the polar solvent, water, *solvates* the ions.

Example: NaCl(aq)



Electrolyte solutions conduct electricity.

Ions move around freely in the *aqueous* solution.

Ionic solids *do not* conduct electricity as the ions are *fixed* in *lattice* positions.

Solubility and Precipitation Reactions

Solubility

Solubility is the *maximum concentration* of salt that can be achieved.

Very low solubility = *insoluble*

Solubility (mol L^{-1})

< 0.01	<i>insoluble</i>
0.01 to 0.1	slightly <i>soluble</i> (count as soluble)
>0.1	<i>soluble</i>

Soluble or insoluble depends on the strength of the bonding in the ionic solid compared with the strength of aqueous solvation of the ions – sometimes a delicate balance.

Solubility rules for common salts:

1. Alkali metal (Li^+ , Na^+ , K^+ , Rb^+) and ammonium (NH_4^+) salts are *soluble*.
2. Nitrate (NO_3^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), hydrogen carbonate (HCO_3^-) and ethanoate (CH_3COO^-) salts are *soluble*.
3. Sulfate (SO_4^{2-}) salts are *soluble*, *except* for the calcium (Ca^{2+}), strontium (Sr^{2+}) and barium (Ba^{2+}) (i.e., alkaline earth metals other than magnesium) salts which are *insoluble*.
4. Chloride (Cl^-), bromide (Br^-) and iodide (I^-) salts are *soluble*, *except* for the silver (Ag^+), lead (Pb^{2+}) and mercury I (Hg_2^{2+}) salts which are *insoluble* (see rule 5 below).

5. Silver (Ag^+), lead (Pb^{2+}) and mercury I (Hg_2^{2+}) salts are *insoluble*, except for the salts already covered by rules 2 and 3 above.
6. Sulfide (S^{2-}) salts are *insoluble*, *except* for the alkali metal, ammonium (covered by rule 1 above), and alkaline earth salts (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) which are *soluble*.
7. Oxide (O^{2-}) and hydroxide (OH^-) salts are *insoluble*, *except* for the alkali metal, ammonium (see rule 1 above), calcium (Ca^{2+}), strontium (Sr^{2+}) and barium (Ba^{2+}) salts which are *soluble* – though CaO and $\text{Ca}(\text{OH})_2$ are only slightly soluble.
8. Carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts are *insoluble*, *except* for the alkali metal and ammonium salts (covered by rule 1 above).

	Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ NH ₄ ⁺	Mg ²⁺	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺	other
NO ₃ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , HCO ₃ ⁻ , CH ₃ COO ⁻	soluble	soluble	soluble	soluble	soluble
SO ₄ ²⁻	soluble	soluble	insoluble	soluble	soluble
Cl ⁻ , Br ⁻ , I ⁻	soluble	soluble	soluble	insoluble	soluble
S ²⁻	soluble	soluble	soluble	insoluble	insoluble
O ²⁻ , OH ⁻	soluble	insoluble	soluble	insoluble	insoluble
CO ₃ ²⁻ , PO ₄ ³⁻	soluble	insoluble	insoluble	insoluble	insoluble

Example: Which of the following salts are soluble?

- (a) NaCl (b) AgCl (c) Ba(OH)₂ (d) Pb(NO₃)₂ (e) CaCO₃ (f) PbSO₄
 (g) SrSO₄ (h) Hg₂(CH₃COO)₂

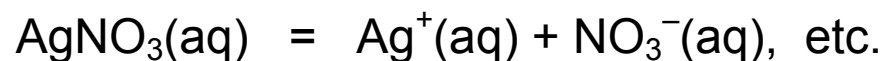
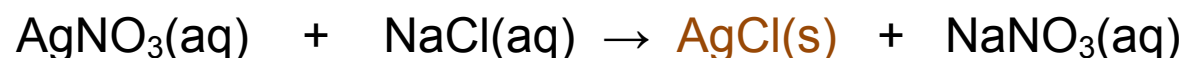
- (a) Sodium salts are soluble. Therefore, NaCl is soluble.
- (b) While most chlorides are normally soluble, silver chloride is not. AgCl is insoluble.
- (c) While most hydroxides are insoluble, barium hydroxide is not. Ba(OH)_2 is soluble.
- (d) Nitrates are soluble. Therefore, $\text{Pb(NO}_3)_2$ is soluble.
- (e) Carbonates are generally insoluble. Since the cation (calcium here) is not an alkali metal or ammonium, CaCO_3 is insoluble.
- (f) Sulfates are generally soluble. Since the cation (lead here) is not calcium, strontium or barium, PbSO_4 is insoluble.
- (g) SrSO_4 is an insoluble sulfate.
- (h) Ethanoates are soluble. Therefore, $\text{Hg}_2(\text{CH}_3\text{COO})_2$ is soluble.

Precipitation Reactions

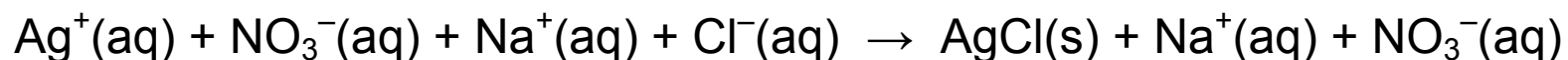
Supersaturated solutions are sometimes obtained when two solutions are mixed.

A *precipitation reaction* results.

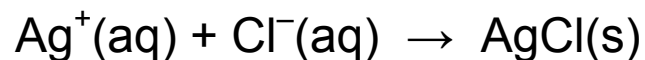
Example: Mixing solutions of silver nitrate and sodium chloride produce silver chloride *precipitate*. Balanced chemical reaction:



Ionic form:



or



net ionic equation

The sodium and nitrate ions are *spectator ions*.

Example: Which of the following sets of solutions produce precipitation reactions when mixed? If there is a precipitation reaction, what is the precipitate?

- (a) $\text{MgBr}_2(\text{aq}) + \text{Rb}_2\text{S}(\text{aq})$
- (b) $\text{Ba}(\text{CH}_3\text{COO})_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq})$
- (c) $\text{Cu}(\text{ClO}_3)_2(\text{aq}) + 2 \text{NaOH}(\text{aq})$
- (d) $\text{LiNO}_3(\text{aq}) + (\text{NH}_4)_3\text{PO}_4(\text{aq})$
- (e) $\text{Na}_2\text{CO}_3(\text{aq}) + \text{ZnClO}_4(\text{aq})$

(a) MgS and RbBr are both soluble salts. Therefore, there is *no* precipitation reaction.

(b) NaCH_3COO is soluble, while BaSO_4 is insoluble. Therefore, $\text{BaSO}_4(\text{s})$ *precipitates*.

(c) NaClO_3 is soluble, while $\text{Cu}(\text{OH})_2$ is insoluble. Cu^{2+} is in the “other” column of the Solubility Rules Table. $\text{Cu}(\text{OH})_2(\text{s})$ is the *precipitate*.

(d) $(\text{Li})_3\text{PO}_4$ and NH_4NO_3 are both soluble salts. Therefore, there is *no* precipitation reaction. Since all lithium and nitrate salts are soluble, adding $\text{LiNO}_3(\text{aq})$ to any other solution will not produce a precipitation reaction.

(e) $\text{ZnCO}_3(\text{s})$ is the *precipitate*. Zn^{2+} is in the “other” column of the table.

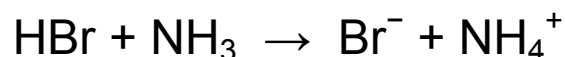
Precipitation reactions can be used to identify ions present in solutions.

Example: Consider three sample solutions, A, B and C. One contains magnesium, one contains calcium and one contains silver. Can you match the metal ions to the sample solutions using “test solutions”, $\text{Na}_2\text{SO}_4(\text{aq})$. and $\text{NaCl}(\text{aq})$?

Upon mixing samples with test solution, $\text{Na}_2\text{SO}_4(\text{aq})$, only the sample solution containing calcium gives a precipitate. $\text{NaCl}(\text{aq})$ produces a precipitate with silver, but not magnesium or calcium.

Brønsted-Lowry Theory of Acid-Base Reactions

According to the *Brønsted-Lowry* definition of acids and bases, an acid reacts with a base by exchanging an H^+ . For example,



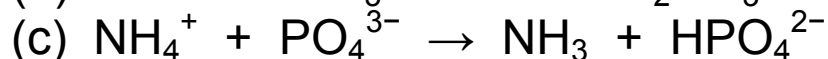
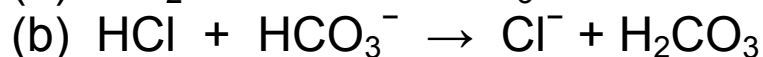
HBr is the H^+ *donor* – the *acid*

NH_3 is the H^+ *acceptor* – the *base*

Acids have polarized bonds with a partial positive charge on H.

Bases have lone pairs that can accept H^+ .

Example: Identify the acid and base in the following reactions:



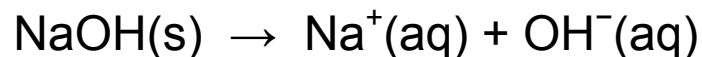
- (a) HF loses an H^+ . It is the H^+ donor – i.e., it is the *acid*. NH_2^- accepts the H^+ . It is the *base*. Note that an acid always has an H bonded to an electronegative atom (N, O, F, S, Cl, Br or I – often it is O). A base must have a lone pair of electrons to accept the H^+ . The lone pair is usually on an N atom (often seen for uncharged basic molecules) or an O atom (mostly seen for anionic bases).
- (b) HCl is the *acid* – it loses an H^+ . HCO_3^- is the *base* – it accepts the H^+ .
- (c) NH_4^+ is the *acid* – it loses an H^+ . PO_4^{3-} is the *base* – it accepts the H^+ .

Acids and bases form *acidic* and *basic* aqueous solutions, respectively.

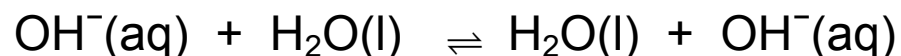
Acids and bases can be molecules or ions.

Salts form aqueous solutions by splitting into positive and negative ions that are solvated by water.

For example,

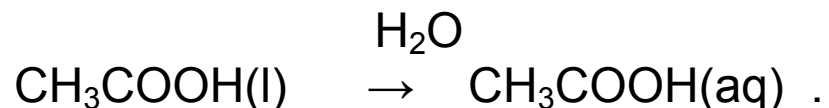


This solution is basic because it contains the *strong base*, OH^- .

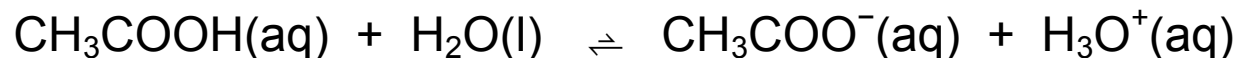


Molecular compounds form aqueous solutions by becoming solvated by water.

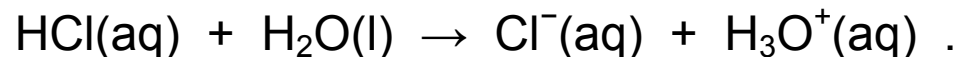
For example, ethanoic acid (vinegar) dissolves in water,



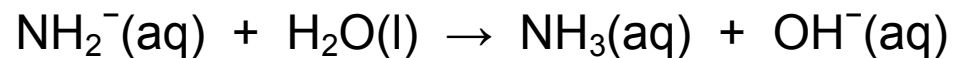
The solvated ethanoic acid, $\text{CH}_3\text{COOH}(\text{aq})$, is a weak acid.



Acids and bases react with water in aqueous solution. For example,



Here, H_2O acts as a base. It accepts an H^+ .

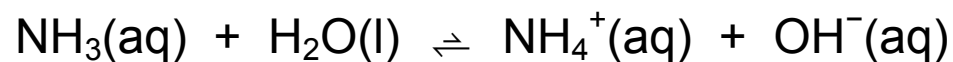


Here, H_2O acts as an acid. It donates an H^+ .

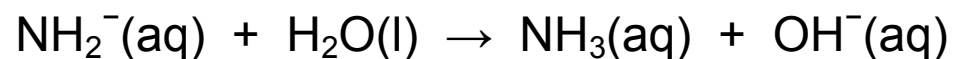
Water can behave as either acid or base – it is *amphoteric*.

Strong and Weak Acids and Bases

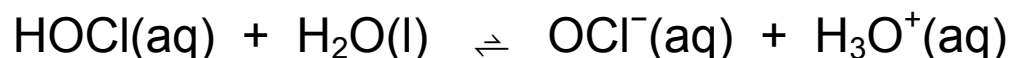
Ammonia, NH_3 , is a *weak base*:



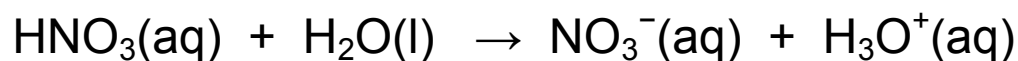
Amide, NH_2^- , is a *strong base*:



Hypochlorous acid, HOCl, is a *weak acid*:



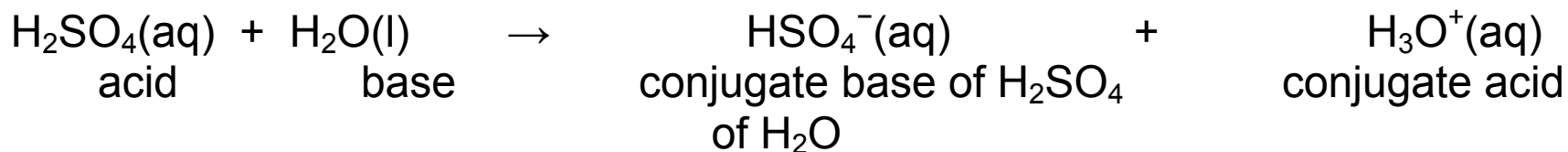
Nitric acid is *strong acid*:



The reverse of an acid-base reaction is itself an acid-base reaction.

The *conjugate base* of the acid, and the *conjugate acid* of the base, are the *base* and *acid* in the *reverse reaction*.

For example,

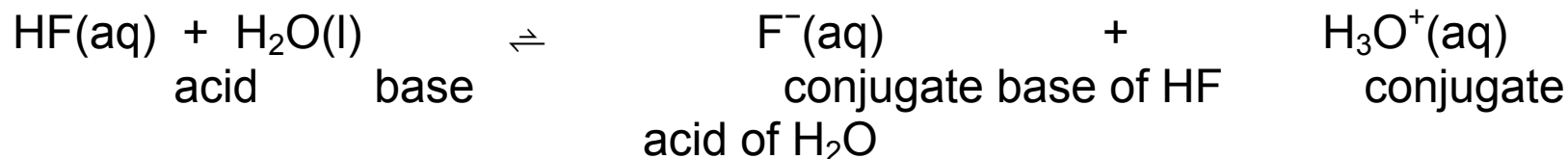


H₂SO₄ is a stronger acid than H₃O⁺.

Equilibrium is always shifted *away from* the *stronger acid*.

Hydronium, H_3O^+ , is the prototype strong acid. Any acid *stronger than* H_3O^+ is also a *strong acid*.

H_2SO_4 is a *strong acid*.



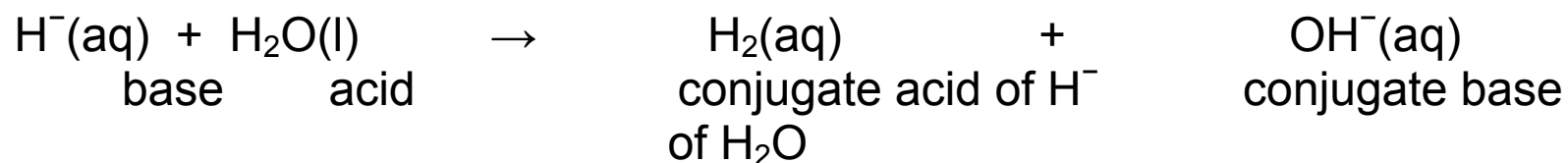
HF is *weaker than* H_3O^+ .

HF is a *weak acid*.

Alkali metal (group 1) or alkaline earth (group 2) metal hydroxides produce $\text{OH}^-(\text{aq})$ when dissolved in water. Hydroxide, OH^- , is the prototype *strong base*.

MgO and $\text{Mg}(\text{OH})_2$ are insoluble, and produce very small concentrations of hydroxide. However, they readily dissolve and react with acids – they are basic oxides.

Amides and hydrides are also strong bases.

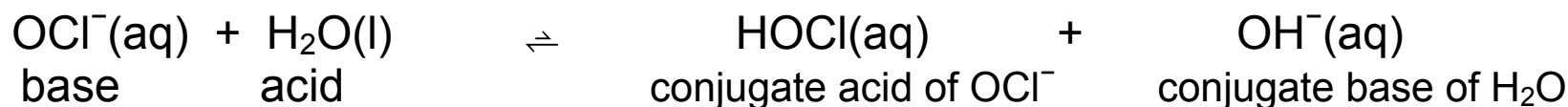


Any base stronger than OH^- , is also a strong base.

- (1) the equilibrium always shifts *away* from the stronger base, is equivalent to
- (2) the equilibrium always shifts *away* from the stronger acid.

The stronger acid and stronger base are *always* on the same side of the reaction.

Sodium hypochlorite, NaOCl, dissolves in water to produce aqueous hypochlorite ions, $\text{OCl}^- (\text{aq})$. Hypochlorite is a weak base:



Strong acids

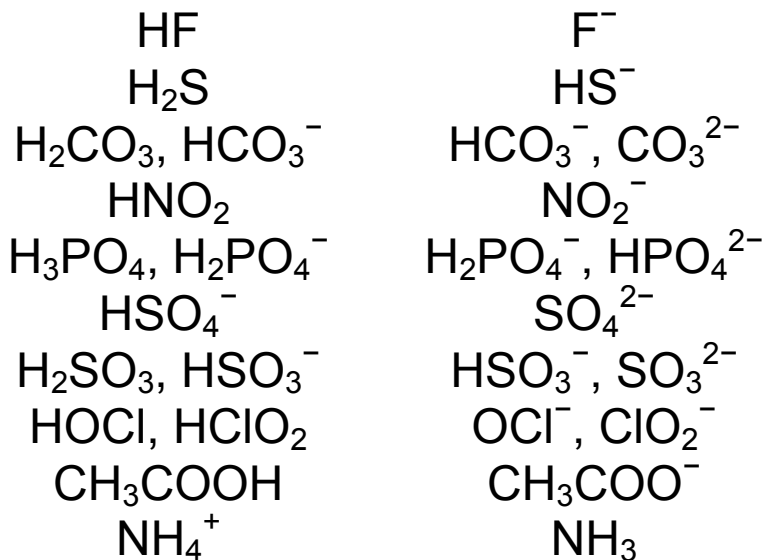
	Acids	Conjugate Bases	
Strong Acids	HCl, HBr, HI	Cl^- , Br^- , I^-	The conjugate bases are very weak bases
	HNO_3	NO_3^-	
	H_2SO_4	HSO_4^-	
	HClO_3 , HClO_4	ClO_3^- , ClO_4^-	

Some weak acids

Weak Acids

Acids

Conjugate Bases



The conjugate bases are
weak bases

Strong bases and some weak bases

	Bases	Conjugate Acids	
Strong Bases	O^{2-} , oxide ion (e.g., Li_2O , Na_2O , CaO , SrO)	OH^-	The conjugate acids are very weak acids
	OH^- , hydroxide ion (e.g., LiOH , NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$)	H_2O	
	NH_2^- , amide ion (e.g., NaNH_2)	NH_3	
	H^- , hydride ion (e.g., LiH)	H_2	
	S^{2-}	HS^-	

Weak
Bases

Bases

NH_3 , ammonia
 CH_3NH_2 ,
methylamine
 HS^-
 F^-
 CO_3^{2-} , HCO_3^-
 HPO_4^{2-} , H_2PO_4^-
 OCl^- , ClO_2^-
 CH_3COO^-

Conjugate Acids

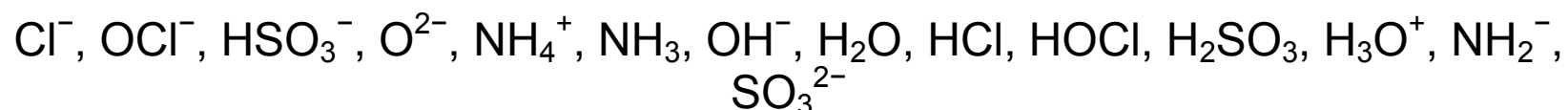
NH_4^+ , ammonium
 CH_3NH_3^+ ,
methyllumonium
 H_2S
 HF
 HCO_3^- , H_2CO_3
 H_2PO_4^- , H_3PO_4
 HOCl , HClO_2
 CH_3COOH

The conjugate acids
are **weak acids**

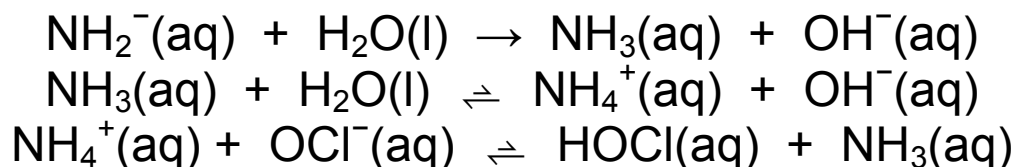
Acid and base strength of conjugate pairs

Acid Strength ↑	Acid	↔	Conjugate	Base Strength ↓
	Conjugate	↔	Base	
	Acid		Base	
	Strong	↔	Very Weak	
	Weak	↔	Weak	
	Very Weak	↔	Strong	

Example: Identify the conjugate acid and base pairs within the following set of species:



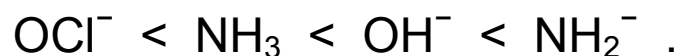
Example: Given that



(a) Order the bases (the species acting as a base in either the forward or reverse of one of these reactions) according to increasing strength as a base (from weakest to strongest).

(b) Order the acids according to increasing strength.

(a) In order of increasing strength as a base, we have



(b) According to strength as an acid,



Types of Acids and Bases

Binary Acids

Hydrosulfuric acid (H_2S)

Hydrohalic acids: hydrofluoric acid (HF), hydrochloric acid (HCl), hydrobromic acid (HBr) and hydroiodic acid (HI).

Oxoacids and Oxoanions

Oxoacid	1 st Conjugate Base	2 nd Conjugate Base	3 rd Conjugate Base
H_2CO_3 carbonic acid	HCO_3^- hydrogen carbonate	CO_3^{2-} carbonate	
HNO_2 nitrous acid	NO_2^- nitrite		
HNO_3 nitric acid	NO_3^- nitrate		
H_3PO_3 phosphorous acid	H_2PO_3^- dihydrogen phosphite	HPO_3^{2-} hydrogen phosphite	
H_3PO_4 phosphoric acid	H_2PO_4^- dihydrogen phosphate	HPO_4^{2-} hydrogen phosphate	PO_4^{3-} phosphate

H_2SO_3
sulfurous acid

HSO_3^-
hydrogen sulfite

SO_3^{2-}
sulfite

H_2SO_4
sulfuric acid

HSO_4^-
hydrogen sulfate

SO_4^{2-}
sulfate

HClO
hypochlorous
acid

OCl^-
hypochlorite

HClO_2
chlorous acid

ClO_2^-
chlorite

HClO_3
chloric acid

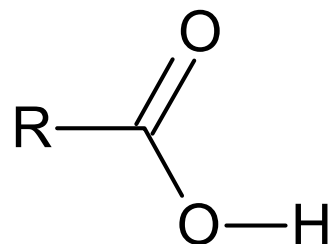
ClO_3^-
chlorate

HClO_4
perchloric acid

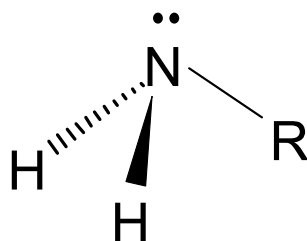
ClO_4^-
perchlorate

Organic Acids and Bases

Carboxylic acids are *weak acids*, with structure of the form,



Amines are *weak bases*. *Primary* amines have structures of the form,



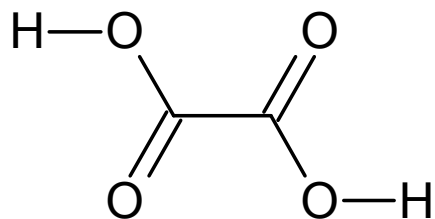
Some simple organic acids and bases

Alkane	Alkanoic acid	Conjugate Base - Alkanoate	Amine
CH ₄ methane	HCOOH methanoic acid (also known as formic acid)	HCOO ⁻ methanoate (also known as formate)	CH ₃ NH ₂ methanamine
C ₂ H ₆ ethane	CH ₃ COOH ethanoic acid (also known as acetic acid)	CH ₃ COO ⁻ ethanoate (also known as acetate)	CH ₃ CH ₂ NH ₂ ethanamine
C ₃ H ₈ propane	CH ₃ CH ₂ COOH propanoic acid	CH ₃ CH ₂ COO ⁻ propanoate	CH ₃ CH ₂ CH ₂ NH ₂ Propanamine

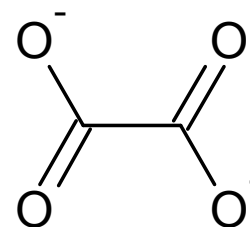
C_4H_{10} butane	$CH_3CH_2CH_2COOH$ butanoic acid	$CH_3CH_2CH_2COO^-$ butanoate	$CH_3CH_2CH_2CH_2NH_2$ Butanamine
C_5H_{12} pentane	$CH_3CH_2CH_2CH_2COOH$ pentanoic acid	$CH_3CH_2CH_2CH_2COO^-$ pentanoate	$CH_3CH_2CH_2CH_2CH_2NH_2$ Pentanamine
C_6H_{14} hexane	$CH_3CH_2CH_2CH_2CH_2COOH$ hexanoic acid	$CH_3CH_2CH_2CH_2CH_2COO^-$ hexanoate	$CH_3CH_2CH_2CH_2CH_2CH_2NH_2$ Hexanamine

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$ is a dicarboxylic acid.

The associated 2nd conjugate base is oxalate, $\text{C}_2\text{O}_4^{2-}$.



oxalic acid

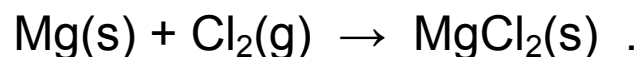


oxalate

Oxidation-Reduction Reactions

An *oxidation-reduction* (*redox*) reaction is an *electron transfer reaction*.

For example,



Magnesium chloride consists of Mg^{2+} and Cl^- ions in an alternating lattice.

Two electrons were transferred from each Mg atom – to two chlorine atoms.

Half reactions:



The redox reaction is the sum of the *oxidation* and *reduction* half reactions, written with the same number of electrons.

Above, magnesium gets *oxidized*, while chlorine gets *reduced*.

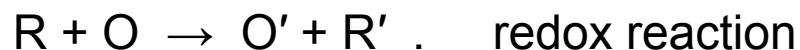
Magnesium is the *reducing agent* chlorine is the *oxidizing agent*.

Reducing agents donate electrons.

Oxidizing agents accept electrons.

The *reverse* of a redox reaction is itself a redox reaction, with the electrons given back to reform the oxidizing and reducing agents on the left, O and R.

When R loses electrons , it forms O'. When O loses electrons, it forms R':



Redox reactions (that are seen) are typically strongly product-favored.

The redox reaction proceeds away from the stronger oxidizing (reducing) agent.

In the above reaction, R is a stronger reducing agent than R' while O is a stronger oxidizing agent than O'.

Apply this to the above example with $R = \text{Mg(s)}$, $O = \text{Cl}_2(\text{g})$, $O' = \text{Mg}^{2+}$ and $R' = \text{Cl}^-$.

Mg(s) is a *stronger reducing agent* than Cl^- (within MgCl(s)).

$\text{Cl}_2(\text{g})$ is a *stronger oxidizing agent* than Mg^{2+} (within MgCl(s)).

Oxidation Numbers

Analogous to formal charge:

oxidation number = core charge

- (number of non-bonding electrons)
- (number of bonding electrons in bonds to less electronegative element(s))

In CO_2 ,

oxidation number of O = $6 - 4 - 4 = -2$, for each O atom

and

oxidation number of C = $4 - 0 - 0 = +4$, for each C atom

Alternatively, there are *rules* that work for simple compounds.

1. The sum of all the oxidation numbers in a species equals its charge zero for a neutral molecule
2. Atoms in elemental form (e.g., $\text{Br}_2(\text{l})$, $\text{Fe}(\text{s})$, $\text{O}_2(\text{g})$) have oxidation number zero.
3. Fluorine (the most electronegative element) has oxidation number, -1 , in all of its compounds.
4. Oxygen (the next most electronegative element) has oxidation number, -2 , in its compounds – except in peroxides (A-O-O-B compounds such as H_2O_2) where it has oxidation number, -1 , and in F_2O where it has oxidation number, $+2$.
5. Chlorine, bromine and iodine have oxidation number -1 , unless bonded to a more electronegative element.
6. Group 16 elements, such as sulfur and selenium, have oxidation number -2 , unless bonded to a more electronegative element. Group 15 elements, such as

nitrogen and phosphorus, have oxidation number -3 , unless bonded to a more electronegative element.

7. Hydrogen has oxidation number, $+1$, when bonded to non-metals (e.g., H_2O and NH_3), except hydrogen has oxidation number, -1 , in PH_3 . Hydrogen has oxidation number -1 in main group metal (groups I and II, Al, Ga, In, Tl, Sn, Pb and Bi) and semimetal (B, Si, Ge, As, Sb, Te and Po) hydrides.

Some transition metals (e.g., Au) have higher electronegativity than hydrogen, and hydrogen has oxidation $+1$ in the associated compound.

Example: Assign oxidation numbers for the atoms of the following species.

- (a) $\text{SO}_2(\text{g})$
- (b) $\text{H}_2\text{SO}_3(\text{aq})$
- (c) $\text{HSO}_3^-(\text{aq})$
- (d) $\text{H}_2\text{SO}_4(\text{aq})$
- (e) $\text{CH}_3\text{COOH}(\text{aq})$ ethanoic acid

(a) Both oxygen atoms have $\text{ON}(\text{O}) = -2$, and

$$\text{ON}(\text{S}) + 2 \text{ON}(\text{O}) = 0$$

$$\text{ON}(\text{S}) + 2 \times (-2) = 0 \text{ or } \text{ON}(\text{S}) = +4 .$$

The oxidation number of sulfur is +4. We call this is the +IV state of sulfur.

(b) Hydrogen has $\text{ON}(\text{H}) = +1$. Also, $\text{ON}(\text{O}) = -2$ and

$$2 \text{ON}(\text{H}) + \text{ON}(\text{S}) + 3 \text{ON}(\text{O}) = 0$$

or

$$\text{ON}(\text{S}) = +4 .$$

In sulfurous acid, sulfur is in the +IV oxidation state – the same as sulfur in SO_2 .

Hydration is *not* a redox reaction

(c) Here,

$$\text{ON}(\text{H}) + \text{ON}(\text{S}) + 3 \text{ON}(\text{O}) = -1$$

or

$$\text{ON}(\text{S}) = +4 .$$

Again, sulfur is in the +IV oxidation state.

Acid-base reactions are *not* a redox reaction.

(d) Here,

$$2 \text{ON}(\text{H}) + \text{ON}(\text{S}) + 4 \text{ON}(\text{O}) = 0$$

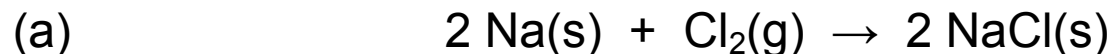
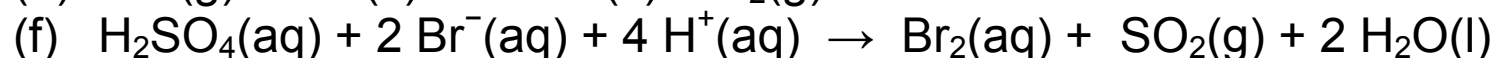
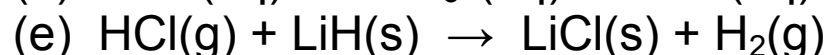
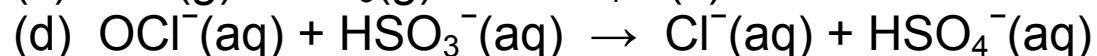
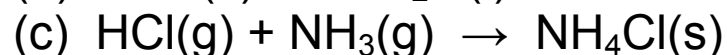
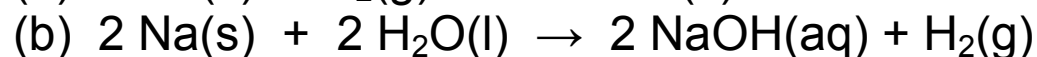
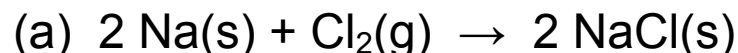
or

$$\text{ON}(\text{S}) = +6 .$$

The oxidation number of sulfur in sulfuric acid is +6. This is the +VI oxidation state of sulfur (the highest oxidation state of sulfur – it equals the core charge).

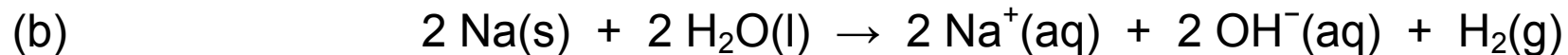
A reaction producing sulfuric acid from sulfurous acid is a redox reaction.

Example: Which of the following reactions are redox reactions? How many electrons are transferred in each redox reaction? Identify the oxidizing and reducing agents.



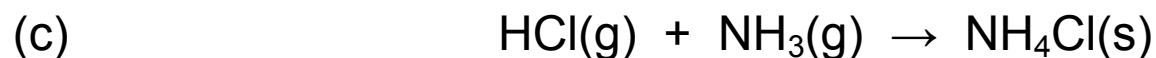
Oxidation numbers: 0 0 +1 -1

Redox. Sodium loses electrons (it gets oxidized) – it is the reducing agent. Chlorine gains electrons (it gets reduced) – it is the oxidizing agent. Two electrons are transferred.



Oxidation numbers: 0 +1 -2 +1 -1 +1 0

Redox. Sodium loses electrons (it gets oxidized) – it is the reducing agent. Two of the hydrogen atoms in two water molecules gain electrons (H_2O gets reduced) – water is the oxidizing agent. Two electrons are transferred.



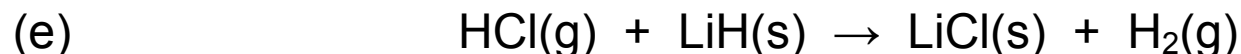
Oxidation numbers: +1 -1 -3 +1 -3 +1 -1

Not a redox reaction. It is an acid-base reaction.



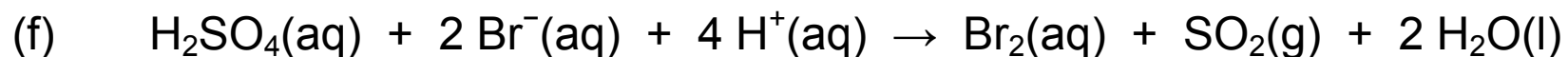
Oxidation numbers: -2 +1 +1 +4 -2 -1 +1 +6 -2

Redox. Sulfur in hydrogen sulfite loses electrons (HSO_3^- gets oxidized) – it is the reducing agent. Chlorine in hypochlorite gains electrons (OCl^- gets reduced) – water is the oxidizing agent. Two electrons are transferred.



Oxidation numbers: +1 -1 +1 -1 +1 -1 0

Redox reaction. The hydride ion loses one electron (H^- gets oxidized) – hydride is the reducing agent. Hydrogen in hydrogen chloride gains one electron (HCl gets reduced) – hydrogen chloride is the oxidizing agent. One electron is transferred.



+1 +6 -2 -1 +1 0 +4 -2 +1 -2

Redox reaction.

Some oxidizing and reducing agents

Oxidizing Agent product (reducing agent in reverse reaction)	Reducing Agent product (oxidizing agent in reverse reaction)
<p>O_2</p> <p>O^{2-} (or compound with $ON(O) = -2$)</p> <p>H_2O_2</p> <p>H_2O</p> <p>F_2, Cl_2, Br_2 and I_2</p> <p>F^-, Cl^-, Br^- and I^-</p> <p>H_2SO_4, HNO_3 $HClO_3, HClO_4,$ $HBrO_3$</p> <p>SO_2, NO Cl^-, Br^-</p>	<p>H_2</p> <p>H^+ (or compound with $ON(H) = +1$)</p> <p>$Li, Na, K, Rb,$ Cs $Mg, Ca, Sr,$ Ba, Al</p> <p>$Li^+, Na^+, K^+, Rb^+, Cs^+$ $Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}$</p> <p>$C, S, P$</p> <p>e.g., $CO, CO_2, SO_2, SO_3,$ P_4O_6, P_4O_{10}</p>

$\text{Cr}_2\text{O}_7^{2-}$ (in acid) CrO_4^{2-} (in base)	Cr^{3+} (in acid) $\text{Cr}(\text{OH})_3$ (in base)	hydrocarbons: C_nH_m	e.g., CO , CO_2
HOCl (in acid) OCl^- (in base)	Cl^-	H_2S , HS^-	e.g., SO_2
MnO_4^-	Mn^{2+} (in acid) MnO_2 (in base)	Fe , Zn	Fe^{2+} , Zn^{2+}
Ag^+ , Fe^{3+}	Ag , Fe^{2+}	Fe^{2+}	Fe^{3+}
Sn^{4+}	Sn^{2+}	I^-	I_2 or IO_3^-
H^+ with active metal	H_2	SO_3^{2-} , NO_2^-	SO_4^{2-} , NO_3^-
PbO_2	Pb^{2+} (in acid)	alcohols such as $\text{C}_n\text{H}_{2n+1}\text{OH}$	aldehyde or carboxylic acid, $\text{C}_n\text{H}_{2n}\text{O}$ or $\text{C}_n\text{H}_{2n-1}\text{OOH}$

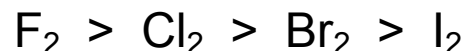
Oxidizing agents include an element whose oxidation number decreases. Higher oxidation numbers correspond to stronger oxidizing agents.

Atoms in their lowest oxidation state cannot be reduced.

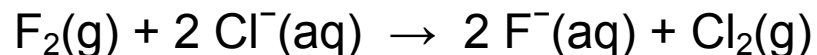
Reducing agents include an element whose oxidation number increases. Lower oxidation numbers correspond to stronger reducing agents.

Atoms in their highest oxidation state cannot be oxidized.

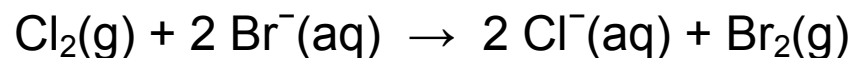
According to oxidizing strength,



Fluorine can oxidize chloride:



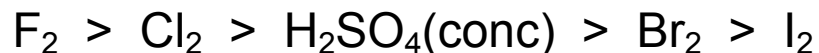
Chlorine can oxidize bromide,



According to strength as reducing agent,

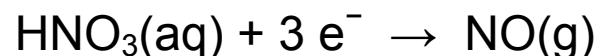


Concentrated sulfuric acid is a powerful oxidizing agent. It can oxidize bromide, but not chloride. It is therefore a stronger oxidizing agent than bromine, but weaker than chlorine. Thus, according to strength as oxidizing agent,

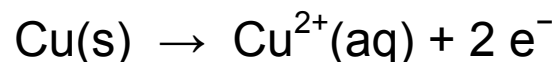


Balancing Redox Reactions

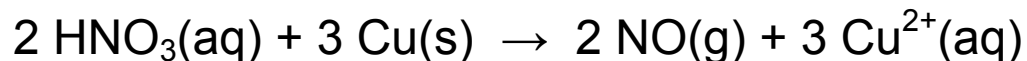
Consider nitric acid solution reacting with copper. *Unbalanced* half reactions:



and



Electrons must balance – this gives



Hydrogen and oxygen are still not balanced – there is participation of solvent (in this case water).

in Acid Solution

The following steps balance a reaction in acid:

- (1) Identify the oxygen deficient side of the reaction. Add one H_2O to that side for each missing oxygen atom.
- (2) Identify the hydrogen deficient side of the reaction. Add one H^+ to that side for each missing hydrogen atom.

in Base Solution

To balance a reaction in base, there are two strategies. The following steps provide one strategy:

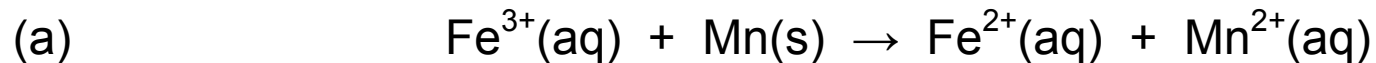
- (1) Identify the oxygen deficient side of the reaction. Add one OH^- to that side for each missing oxygen atom.
- (2) Identify the hydrogen deficient side of the reaction. Add one H_2O to that side, and one OH^- to the other side, for each missing hydrogen atom.

Alternatively, you can balance the reaction as though the solution were acidic – i.e. using H_2O and H^+ , and then add an equal amount of OH^- to *both* sides to neutralize H^+ – i.e. replace $\text{H}^+ + \text{OH}^-$ by H_2O . In the last step, you include only the net water on one side of the reaction.

The above rules can be applied to the separate half reactions, or the overall redox reaction.

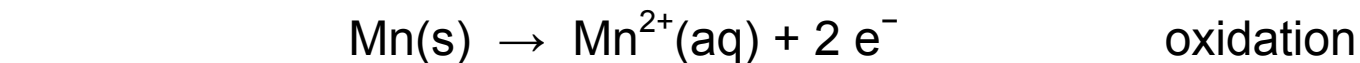
Example: Balance the following *unbalanced* redox reactions. Acidic or basic conditions are indicated where applicable. Identify the oxidizing and reducing agents.

- (a) $\text{Fe}^{3+}(\text{aq}) + \text{Mn}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq})$
- (b) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{HCOOH}(\text{aq})$ (in acid)
- (c) $\text{MnO}_4^-(\text{aq}) + \text{CH}_3\text{CH}_2\text{OH}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq})$ (in acid)
- (d) $\text{H}_2\text{O}_2(\text{aq}) + \text{Al}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{Al}^{3+}(\text{aq})$ (in acid)
- (e) $\text{MnO}_4^-(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + \text{I}_2(\text{s})$ (in base)
- (f) $\text{OCl}^-(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{BrO}_3^-(\text{aq})$ (in base)



Oxidation numbers: +3 0 +2 +2

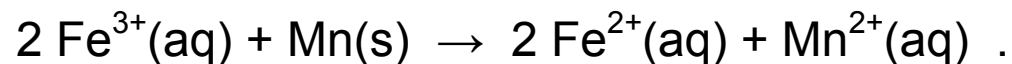
Iron III is the oxidizing agent, while elemental manganese is the reducing agent. The half reactions are

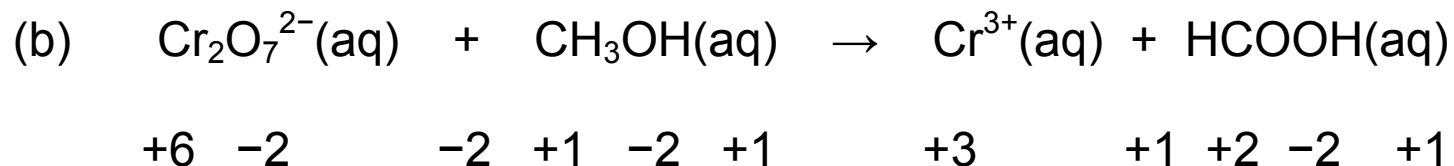


and

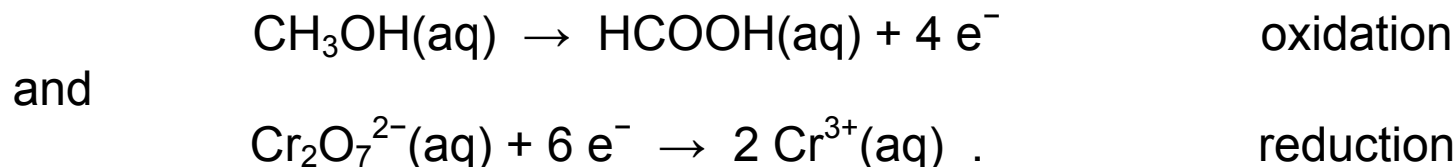


The half reactions are both balanced with respect to atoms. The balanced overall reaction is given by combining these half reactions, with the second half reaction scaled by two to balance the electrons.

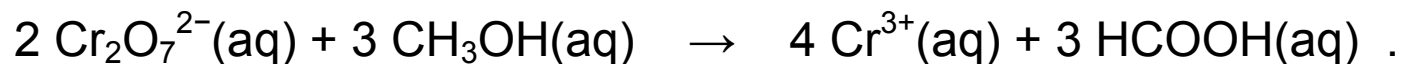




Dichromate is the oxidizing agent, while methanol is the reducing agent. The unbalanced (with respect to H and O) half reactions are



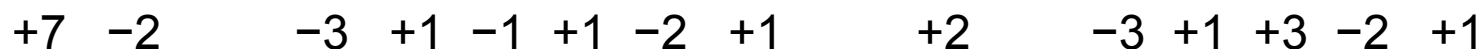
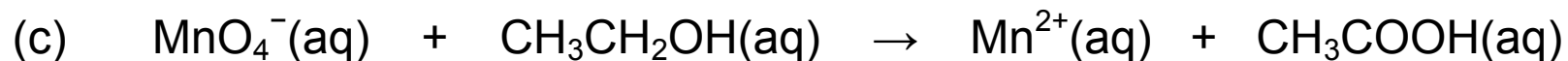
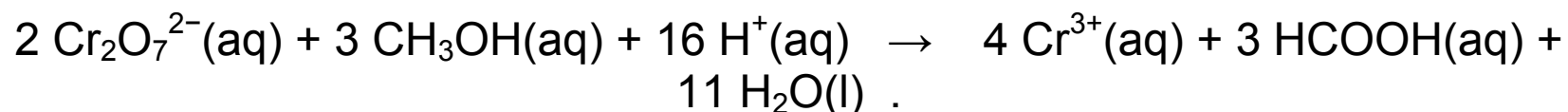
These reactions are balanced with respect to atoms other than hydrogen and oxygen. The second reaction requires a coefficient of two for chromium III, to balance the chromium atoms. To balance electrons, combine the oxidation half reaction scaled by three with the reduction half reaction scaled by two, to get



It remains to balance hydrogen and oxygen. There are 17 O atoms on the left, and 6 O atoms on the right. Therefore, we add 11 H₂O(l) to the right to balance oxygen. The result is



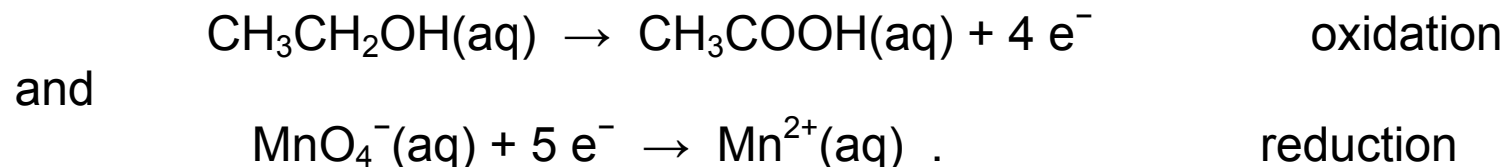
There are now 12 H atoms on the left, and 28 H atoms on the right. Therefore, we add 16 H⁺(aq) to the left to balance hydrogen. The result is



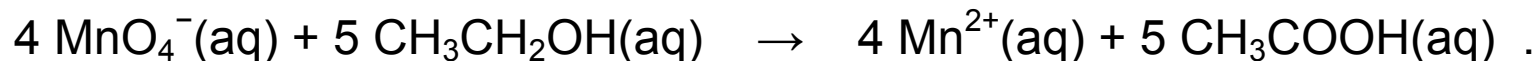
Here, oxidation numbers for atoms in ethanol and ethanoic acid are assigned using structures. This gives different values for the two carbon atoms in both compounds: -3 and -1 for carbon in ethanol, and -3 and +3 for carbon in ethanoic acid.

If the listed rules for assigning oxidation number are applied, the average oxidation number of carbon in these compounds is determined: -2 for ethanol, and 0 for ethanoic acid. Either approach – assigning oxidation numbers to individual atoms, or average oxidation number for each type of atom – gives the same number electrons transferred. With individual atom assignments, the carbon atom bonded to oxygen in ethanol loses four electrons. Using average oxidation numbers, we say that the two carbon atoms of ethanol each lose two electrons. In either case, four electrons are lost.

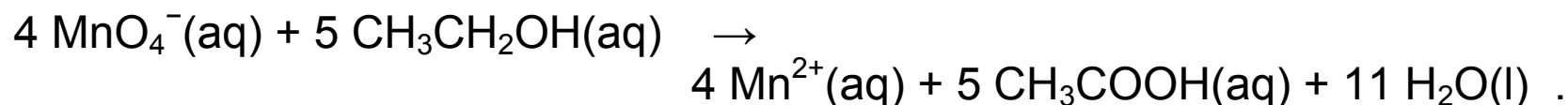
Permanganate is the oxidizing agent in the above reaction, while ethanol is the reducing agent. The unbalanced half reactions are



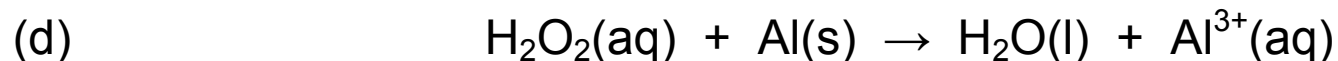
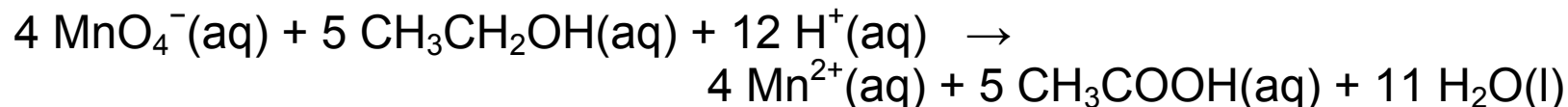
These reactions are balanced with respect to atoms other than hydrogen and oxygen. To balance electrons, combine the oxidation half reaction scaled by five with the reduction half reaction scaled by four, to get



It remains to balance hydrogen and oxygen. There are 21 O atoms on the left, and 10 O atoms on the right. Therefore, we add 11 H₂O(l) to the right to balance oxygen. The result is



There are now 30 H atoms on the left, and 42 H atoms on the right. Therefore, we add 12 H⁺(aq) to the left to balance hydrogen. The result is

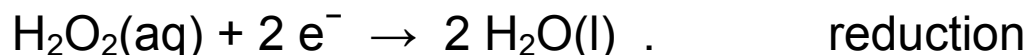


Oxidation numbers: +1 -1 0 +1 -2 +3

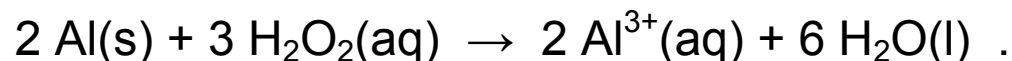
The unbalanced half reactions (the first is actually balanced) are



and

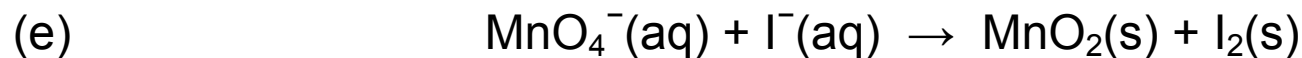


Here, aluminum is the reducing agent, while hydrogen peroxide is the oxidizing agent. In this case, it is necessary to balance the O atoms in the reduction half reaction because it is the oxygen whose oxidation number decreases. To balance the electrons, combine the half reactions, with the first half reaction scaled by two and the second scaled by three. The result is



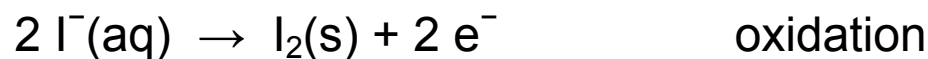
This reaction is balanced with respect to all atoms except hydrogen. There are 6 H atoms on the left, and 12 on the right. To balance the hydrogen, add 6 $\text{H}^{+}(\text{aq})$ to the left to get





Oxidation numbers: +7 -2 -1 +4 -2 0

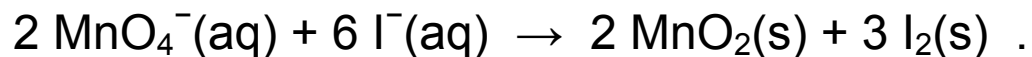
The unbalanced half reactions are



and



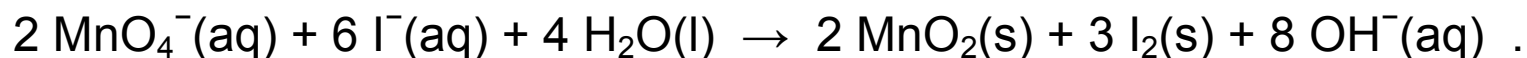
In the oxidation half reaction, a coefficient of 2 was introduced to balance the I atoms. To balance the electrons, combine the half reactions with the first scaled by three and the second scaled by two to get



Since the solution is basic, oxygen is balanced by added hydroxide. There are 8 O atoms on the left, and 4 on the right. Therefore, add 4 $\text{OH}^-(\text{aq})$ to the right.

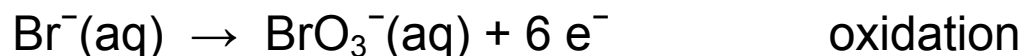


There are 4 H atoms on the right, and none on the left. To balance hydrogen, add 4 H₂O(l) to the left and 4 OH⁻(aq) to the right to get

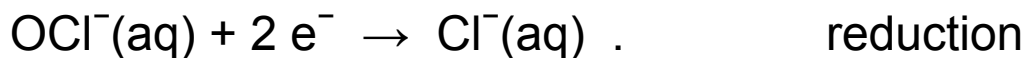


Oxidation numbers: -2 +1 -1 -1 +5 -2

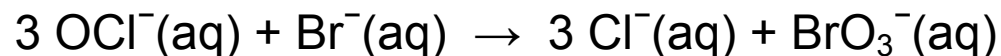
The unbalanced half reactions are



and



To balance the electrons, combine the half reactions with the second scaled by three to get

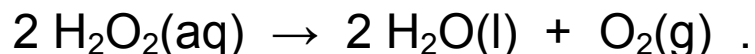


There are 3 O atoms on the left, and 3 on the right. Also, there no H atoms on either side. Therefore, the reaction is balanced as written.

Disproportionation Reactions

The oxidizing and reducing agent are the same – i.e., it reacts with itself.

Examples: Hydrogen peroxide spontaneously decomposes into water and oxygen according to the decomposition reaction (shown here in aqueous solution),



Oxidation numbers: +1 -1 +1 -2 0

This reaction is ordinarily slow and not noticeable. However, it is fast when there is a catalyst such as $\text{MnO}_2(\text{s})$.

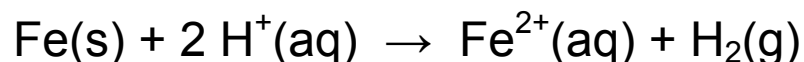
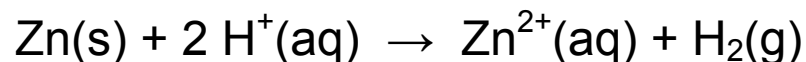
Chlorine reacts in aqueous solution:



Oxidation numbers: 0 +1 -1 +1 -1 +1 -2 +1

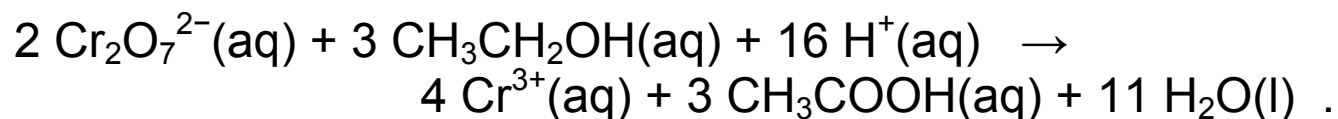
Visible Reactions

Examples:



Acid-base indicators, such as phenolphthalein, distinguish between acidic and basic solutions by changing color.

Dichromate is a *redox indicator* – the *roadside breathalyzer test*



Dichromate solution is orange. Chromium III produced is green (due to the presence of sulfate in the solution used – otherwise it is violet-blue). Sulfuric acid is added to speed up the reaction – it is a catalyst.

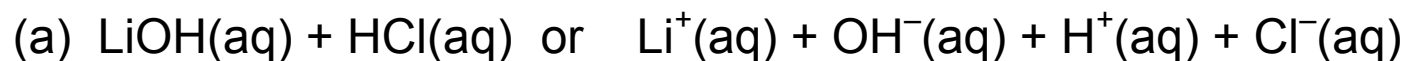
A calibrated *colorimeter* gives the ethanol concentration in the driver's blood that corresponds to the observe color.

Permanganate is also a redox indicator sensitive to a reducing environment – deep purple to pale pink in an acidic solution.

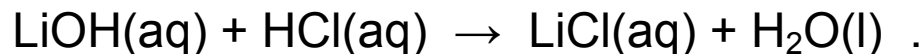
Example: Predict the type of reaction(s) (precipitation, acid-base or redox) for the following reactants. Which reactions produce a visible change?

- (a) $\text{LiOH}(\text{aq}) + \text{HCl}(\text{aq})$
- (b) $\text{LiHCO}_3(\text{aq}) + \text{HNO}_3(\text{aq})$

- (c) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{CH}_3\text{OH}(\text{aq})$
- (d) $\text{H}_2\text{O}_2(\text{aq})$ (in the presence of catalyst $\text{MnO}_2(\text{s})$)
- (e) $\text{H}_2\text{SO}_4(\text{aq}) + \text{Al}(\text{s})$
- (f) $\text{MnO}_4^{-}(\text{aq}) + \text{H}_2\text{S}(\text{aq})$ (acidic solution)
- (g) $\text{LiOH}(\text{aq}) + \text{Ca}(\text{HCO}_3)_2(\text{aq})$

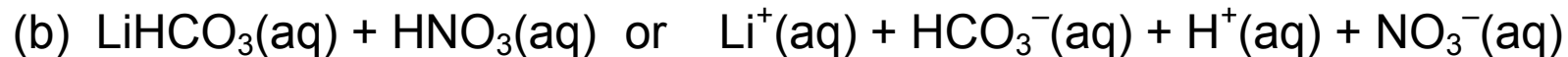


Here, we have aqueous hydroxide and hydronium ions. They neutralize in an *acid-base* reaction. The overall reaction is



This reaction produces *no* visible change.

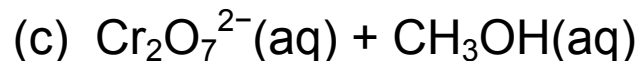
If an acid-base indicator is added to one of the solutions which is then employed as a limiting reactant – i.e., the other solution is more abundant – a color change results from this reaction. In this case, there is a visible change.



This is another *acid-base* reaction. Here, the base is hydrogen carbonate. The products are $\text{LiNO}_3(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$. The carbonic acid formed in this reaction subsequently decomposes into carbon dioxide and water. The overall reaction is



The carbon dioxide gas formed bubbles out of solution. This is *visible change*.



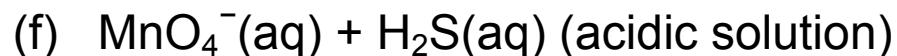
This is a *redox* reaction. Dichromate is a strong oxidizing agent and methanol is a reducing agent. This is just the breathalyzer reaction, except that the alcohol is methanol instead of ethanol. Dichromate changes color when it gets reduced – it changes from orange to blue (or green, if sulfate is present). This is a *visible change*.

(d) $\text{H}_2\text{O}_2(\text{aq})$ (in the presence of $\text{MnO}_2(\text{s})$)

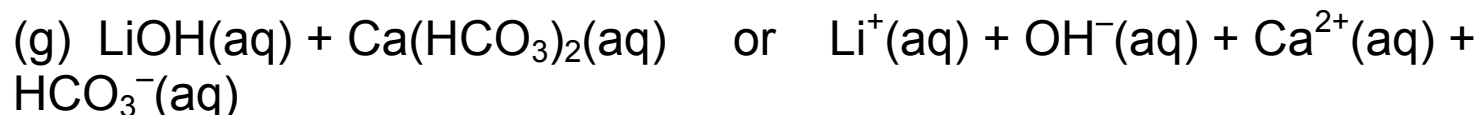
Hydrogen peroxide decomposes in the presence of $\text{MnO}_2(\text{s})$. It undergoes decomposition, and produces water and oxygen. Oxygen gas bubbles out of solution, giving a visible *change*. This reaction is exothermic – i.e., it produces heat. The heat produced by the reaction accelerates the reaction. It can be explosive.

(e) $\text{H}_2\text{SO}_4(\text{aq}) + \text{Al}(\text{s})$

This is a *redox* reaction. Aluminum is a relatively active metal – i.e., it is a strong reducing agent. The hydronium in the sulfuric acid solution is a sufficiently strong oxidizing agent to oxidize the aluminum. The product of the reduction of hydronium is hydrogen gas, which bubbles out of solution. Again, we have a *visible change*.



This is another *redox* reaction. Permanganate is a strong oxidizing agent which easily oxidizes hydrogen sulfide with sulfur in its lowest oxidation state (−II). Since permanganate is deep purple and the product of its reduction (manganese II) is pale pink, there is a *visible change*.



This is an *acid-base* reaction. Here, there is a strong base, $\text{OH}^-(\text{aq})$, that reacts with the weak acid, $\text{HCO}_3^-(\text{aq})$. We know that $\text{HCO}_3^-(\text{aq})$ is a weak acid, because it is conjugate to a weak base, $\text{CO}_3^{2-}(\text{aq})$.