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Inorganic chemistry

Particle

- Particle can be a simple atom system, *i.e.*:

 atom (usually of metal element, *e.g.* Cu, Na, Fe, but also Ar);
 - simple molecule (e.g. O₂, S₈, CO₂);
 - simple cation (*e.g.* Na^+ , H_3O^+);
 - simple anion (e.g. SO_4^{2-} , OH⁻, ClO₄⁻).
- Ligand is a particle possessing (usually) a free electron pair donating its electrons to a particle which has a free electron orbitals (so-called central atom). In inorganic chemistry a very popular ligand is oxygen ligand (O²⁻) as well as sulfur ligand (S²⁻).

Oxidation state

- Oxidation state is a charge on atom in a compound, if one would assume all its bonds are ionic.
- It is only a formal term, although it is reflecting an essence of atom's bonds, even if the compound is of covalent nature. It is also helping in determining given compound reactivity (if reactions are based on electron exchange or ligands as well).

Oxidation state

In sulfuric acid (H_2SO_4) we determine sulfur as having a +6 "charge". Individually such cation cannot exist. However, we know that theoretically sulfur has got such a charge because hydrogen has single positive charge (+1; H⁺) and oxygen has double negative charge (-2; O²⁻). If we count all charges in the sulfuric acid so far: $2 \cdot (+1) + 4 \cdot (-2) = -6$ Molecule has to be neutral, so sulfur has to possess (formally) +6 charge.

Oxygen and hydrogen have also just a formal charge (oxidation state), because they cannot exist individually. *E.g.* in water they most often exist in OH⁻ i H_3O^+ form, respectively.

Oxidation state

- Hydrogen can give away just one his electron and almost always gives it away (thus +1 charge). Oxygen usually receives two electrons (-2), so oxidation state is a reflection of reality on the atomic electron structure level.
- As an exception, hydrogen can meet elements that are more willing to give the electron away, *e.g.* lithium, sodium or magnesium (I and II periodic table group). As a result, those are donating their electron(s) and hydrogen is receiving it (it has -1 oxidation state then), *e.g.* LiH, MgH₂.
- The only element more electron-drawing than oxygen is fluorine. Oxygen is donor of electrons only in fluorine compounds and has +2 or +1 oxidation state (*e.g.* OF₂ or O₂F₂).

Reaction types

Particle can be a subject to three types of reactions. All more complicated ones are in fact series of the individual reactions, each of one of the three following (only 1+2 can happen simultaneously):

Ligand binding to or detaching from central atom;
 Electrons binding to or detaching from central atom;

3. Division of the multi-core molecule intro smaller parts or merging of small one-core molecules into a bigger multi-core particle (one by one).

1

"Piano"

8 In further reaction descriptions we will be using so-called piano, i.e. table with oxidation state (G_{ov}) axis vs. number of electrons donated 6 by ligand (usually oxygen anion O²⁻) to the central 5 atom axis (e,). It is possible to describe almost 4 all inorganic compounds, as well as their 3 reactions, with just these two parameters. 2 1 0 +4 +3 +2 +1 0 -1 -2 G.

Acid-base reactions (ac-bas)

- Acid-base reactions are based on ligand exchange. To be precise, it is a change of liganddonated (usually oxygen ligand) electrons provided to central atom number. No particle/atom changes its oxidation state upon this kind of reaction.
- Detaching O²⁻ anion by a compound/ion is called base reaction (bas) (e_z decreases by 2).
- Binding O²⁻ anion by a compound/ion is called acid reaction (ac) (e_z increases by 2).

Oxygen anion cannot exist individually so it is often exchanged in a different, temporary form. However, the final effect is the same as it would be just the oxygen anion transferred.

Ac-bas reactions

$$\begin{split} & \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (\text{transfer of } \text{O}^{2\text{-}} \text{ to } \text{SO}_3 \text{ thus forming } \text{SO}_4^{2\text{-}}), \text{ acid reaction (ac).} \\ & \text{ZnSO}_3 \xrightarrow{\Delta T} \text{SO}_2 + \text{ZnO} \quad (\text{SO}_3^{2\text{-}} \rightarrow \text{SO}_2 + \text{O}^{2\text{-}}) \quad (\text{bas}) \\ & \text{Cl}_2\text{O}_7 + \text{K}_2\text{O} \rightarrow 2\text{KCIO}_4 \quad (\text{Cl}_2\text{O}_7 + \text{O}^{2\text{-}} \rightarrow 2\text{CIO}_4^{-}) \quad (\text{ac}) \\ & \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \quad (\text{CO}_2 + \text{O}^{2\text{-}} \rightarrow \text{CO}_3^{2\text{-}}) \quad (\text{ac}) \\ & \text{AT} \end{split}$$

 $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta T} \text{CO}_2 + \text{Li}_2\text{O} (\text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}^{2-}) \text{ (bas)}$

$$\begin{split} \mathsf{Na_2CO_3} + \mathsf{SiO_2} &\to \mathsf{Na_2SiO_3} + \mathsf{CO_2} \\ (\mathsf{CO_3^{2^{-}}} + \mathsf{SiO_2} &\to \mathsf{CO_2} + \mathsf{SiO_3^{2^{-}}}) \text{ (ac-bas)} \end{split}$$





Ac-bas reactions







Ac-bas reactions



Ac-bas reactions

- Acid-base reaction could be donating/receiving of proton as well (reaction with H_3O^+ or OH^- particle). Proton possess a positive charge, so we use the same notation as for oxygen anion, although adding proton would decrease e_z (e_z is a number of ligand-donated electrons and proton is accepting one):
- Donating H⁺ (e.g. by H₃O⁺) is called acid reaction (ac – going up in a "piano");
- (bas going down in a "piano");
- There is a logical explanation for such reaction names $HCl_{(aq)}$ or $H_2SO_{4(aq)}$ are forming acids by detaching their protons. NH₃ has basic properties and can bind protons and thus forming NH₄⁺.

e,	-2	Gox
0	(0²·)	Ĺ
-1	OH.	
-2	H₂O	
-3	H₃O⁺	

Ligands

Similarly to oxygen anion, one can form tables of sulfur anion (S²⁻) detaching/binding. However, chemistry of sulfides is usually less rich than that of oxides.



Reduction-oxidation (red-ox) reactions

Reduction (red)-oxidation (ox) reactions are based on valence electron(s) donating to or accepting them from central atom. Such reaction can take place when atom very eager to get rid of its electrons meets the atom very eager to accept them.

Usually (many exceptions!), atoms from left side of periodic table are giving away their electrons (donors), and those from right side are receiving them

(acceptors). In a "piano" such

reactions are noted as shifting to left (electron donation) or to right (electron acceptance).

Half-reactions

 Oxidation-reduction process can be distinguished as two separate processes – oxidation and reduction.

Hence, red-ox reaction is often written as two separate reactions. Then electron number in both equations is adjusted by multiplication and thus the reaction stoichiometry is obtained, *e.g.*:

$$\begin{split} &\mathsf{Na}_{(s)} \rightarrow \mathsf{Na}^{+} + e^{-} \ /\cdot 2 \quad (\mathsf{reductant} - \mathsf{sodium} - \mathsf{oxidizes}) \\ &\mathsf{Cl}_{2(g)} + 2e^{-} \rightarrow 2\mathsf{Cl}^{-} /\cdot 1 \quad (\mathsf{oxidant} - \mathsf{chlorine} - \mathsf{reduces}) \\ & 2\mathsf{Na}_{(s)} + \mathsf{Cl}_{2(g)} \rightarrow 2\mathsf{NaCl}_{(s)} \end{split}$$

18

Red-ox reactions

Typical red-ox reactions are those between metals:

 $\begin{array}{l} 2\mathsf{F}\mathsf{e}^{3+}{}_{(\mathsf{aq})}+\mathsf{Sn}^{2+}{}_{(\mathsf{aq})} \xrightarrow{} 2\mathsf{F}\mathsf{e}^{2+}{}_{(\mathsf{aq})}+\mathsf{Sn}^{4+}{}_{(\mathsf{aq})} \\ \mathsf{F}\mathsf{e}^{3+}+\mathsf{e}^{-} \xrightarrow{} \mathsf{F}\mathsf{e}^{2+} \end{array}$

 $Sn^{2+} \rightarrow Sn^{4+} + 2e^{-}$

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$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

lons are not in a vacuum, so the real reaction takes place in a medium and with counter-ions, *e.g.* (example for above reaction):

 $CuSO_{4(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$

Red-ac and ox-bas reactions (mixed/linked)

- In reality, many reactions are linked red-ox and ac-bas reactions. They are often both exchanging ligands (ac-bas) and electrons (red-ox) between reactants.
- Formation of sodium sulfate is an example of such linked reaction:

Na₂S + 2O₂ $\xrightarrow{\Delta T}$ Na₂SO₄ 4 phases, including: I: S²⁻ → S + 2e⁻ / O₂ + 4e⁻ → 2O²⁻ / S + O²⁻ → SO²⁻ IV: SO₃²⁻ → SO₃ + 2e⁻ / O₂ + 4e⁻ → 2O²⁻ / SO₃ + O²⁻ → SO₄²⁻

Red-ac and ox-bas reactions



Red-ac and ox-bas reactions

Reactions that take place inside the lead-acid battery (in that case proton is written as a $H^+_{(aq)}$, which notation is equal to " H_3O^{+*} " without the need of balancing water molecules in a reaction equation):

$$\begin{split} & \mathsf{Pb}_{(s)} + \mathsf{H}_2\mathsf{SO}_{4(aq)} \to \mathsf{PbSO}_{4(s)} + 2\mathsf{H}^+_{(aq)} + 2\mathsf{e}^- (\mathsf{Pb} \to \mathsf{Pb}^{2+} + 2\mathsf{e}^-) \\ & \mathsf{PbO}_{2(s)} + \mathsf{H}_2\mathsf{SO}_{4(aq)} + 2\mathsf{H}^+_{(aq)} + 2\mathsf{e}^- \to \mathsf{PbSO}_{4(s)} + 2\mathsf{H}_2\mathsf{O} \\ & (\mathsf{Pb}^{4+} + 2\mathsf{e}^- \to \mathsf{Pb}^{2+}) (2\mathsf{O}^{2-} + 4\mathsf{H}^+ \to 2\mathsf{H}_2\mathsf{O}) \end{split}$$

Also thermite burning (e.g. $Fe_2O_3 + 2AI \rightarrow 2Fe + Al_2O_3$)

Red-ac and ox-bas reactions

 Potassium permanganate (violet/purple is going clear/light pink in acid becomes colorless/pale pink), whole reaction takes place in water, so there is no need to write (aq) at each reagent:

 $2KMnO_4 + 3H_2SO_4 + 5KNO_2 \rightarrow 2MnSO_4 + 5KNO_3 + K_2SO_4$ $(8H_3O^+ + MnO_4^- +5e^- \rightarrow Mn^{2+} + 12H_2O) / \cdot 2$ $(NO_2^- + 3H_2O \rightarrow NO_3^- + 2H_3O^+ + 2e^-) / \cdot 5$

 $(16H_{3}O^{+} + 2MnO_{4}^{-} + 10e^{-} \rightarrow 2Mn^{2+} + 24H_{2}O)$ $(5NO_{2}^{-} + 15H_{2}O \rightarrow 5NO_{3}^{-} + 10H_{3}O^{+} + 10e^{-})$

Red-ac and ox-bas reactions





Red-ac and ox-bas reactions

Acids, bases, oxidants, reductants

- Acid can receive oxygen anion or donate proton.
- Base can donate oxygen anion or receive proton.
- Oxidant oxidizes other atoms/compounds (reduces itself). Oxidant receives electrons (taking away from other atoms).
- Reductant reduces other atoms/compounds (oxidizes itself). Reductant gives away its electrons to other atoms.

Disproportionation /symproportionation reactions

- Reactions in which atoms of the same element are undergoing red-ac and ox-bas reactions, exchanging electrons and/or ligands:
 - If initially atoms had different oxidation state (and/or different ligands number) they are all forming the same particle at the end (symproportionation);
 - If initially all atoms were forming same particle, then they end up as a two (usually) different particles (disproportionation).
- These reactions are usually proceeding over diagonal directions in "pianos".

Disproportionation reaction

• Thermal decompositions are typical disproportionation reactions:

 $\begin{aligned} &\mathsf{CaC_2O_{4(s)}} \rightarrow \mathsf{CaCO_{3(s)}} + \mathsf{CO}_{(g)} \\ &(\mathrm{I:} \ \mathrm{C_2O_4^{2^-}} \rightarrow \mathrm{CO_2} + \mathrm{CO_2^{2^-}}) \\ &(\mathrm{II:} \ \mathrm{CO_2} + \mathrm{CO_2^{2^-}} \rightarrow \mathrm{CO_3^{2^-}} + \mathrm{CO}) \\ &\mathsf{MgC_2O_{4(s)}} \rightarrow \mathsf{MgO_{(s)}} + \mathsf{CO_{(g)}} + \mathsf{CO_{2(g)}} \\ &(\mathrm{I:} \ \mathrm{C_2O_4^{2^-}} \rightarrow \mathrm{CO_2^{\uparrow}} + \mathrm{CO_2^{2^-}}) \\ &(\mathrm{II:} \ \mathrm{CO_2^{2^-}} + \mathrm{Mg^{2^+}} \rightarrow \mathrm{MgO_{(s)}} + \mathrm{CO^{\uparrow}}) \end{aligned}$



Disproportionation reaction

Symproportionation reactions

Carbon dioxide reaction with carbon under limited amount of (lack of) oxygen is another example:





Reactions and their visualization



Complexes

- Complex is a system comprising **central atom** (or identical central atoms) - so-called **coordination center** and atoms or atomic groups bound to it, so-called **ligands**.
- Coordination center of a given complex is usually metal atom from the middle of periodic table (Fe, Co, Ni, Ag, Al), often transition metal, but other metals and non-metals happen as well.
- In a complex, ligands are usually simple anions or neutral particles (Cl⁻,S²⁻,O²⁻,OH⁻,H₂O,NH₃), less often proton (H₃O⁺/H⁺).

32

Complexing reactions

 Very specific type of ac-bas reaction is complexing reaction (complex formation reaction). It is characteristic because of coordination bonds forming between central atom and ligands. There is no mutual electron sharing in this bond. New bond between ligand and central atom is formed only from ligand's electrons.

Complexing reactions

- Ligands are often simple anions or neutral molecules containing free electron pairs.
- Complex compounds are often of a limited stability. Upon encounter with a ligand more willing to give away its electrons, these ligands are let into central atom <u>coordination sphere</u> in place of the present ligand.
- One central atom can be bonded with different ligands at the same time.

Complexing reactions

Both complex formation and dissociation are multi-step processes, *i.e.* addition or separation is realized by only one ligand at the time, *e.g.*:

 $\begin{aligned} & \operatorname{Fe}^{3+} + \operatorname{CN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{CN})]^{2+} \\ & [\operatorname{Fe}(\operatorname{CN})]^{2+} + \operatorname{CN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{CN})_{2}]^{+} \\ & [\operatorname{Fe}(\operatorname{CN})_{2}]^{+} + \operatorname{CN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{CN})_{3}] \\ & [\operatorname{Fe}(\operatorname{CN})_{3}] + \operatorname{CN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{CN})_{4}]^{-} \\ & [\operatorname{Fe}(\operatorname{CN})_{4}]^{-} + \operatorname{CN}^{-} \rightleftharpoons [\operatorname{Fe}(\operatorname{CN})_{5}]^{2-} \\ & [\operatorname{Fe}(\operatorname{CN})_{5}]^{2-} + \operatorname{CN}^{-} \nleftrightarrow [\operatorname{Fe}(\operatorname{CN})_{6}]^{3-} \end{aligned}$

Complexing reactions



By the way – "breathing" in plants is performed using the same compound, only iron atom is substituted with magnesium.