Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester

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Redox reactions and electrodes

Oxidation state

- Oxidation state is a charge on atom in a compound if assumed, that all bonds made by this atom are ionic.
- It is just a formal description of atom. However, it shows a character of this atom bonds, even if the compound is covalent in character. It also helps with understanding of the nature of the given compound reactions (if they are connected with electron exchange or ligand exchange as well).

Oxidation state

In sulfuric acid (H_2SO_4) sulfur is described as possessing +6 „charge". Individually, such cation could not exist. However, theoretically sulfur has such charge, as hydrogen atom has single positive charge (+1; H^+) and oxygen atom has double negative charge (-2; O^{2-}). If one counts charges in the sulfuric acid, it is $2\cdot(+1) + 4\cdot(-2) = -6$.
As compound has to be neutral, then sulfur has (by convention) +6 charge.
Oxygen and hydrogen have also conventional charge (oxidation state) as they cannot exist individually. For instance, in water they exist as OH^- and H_3O^+.

Oxidation state

- Hydrogen can give away only one electron and it also always does (thus, it has almost always +1 charge).
- Oxygen usually accepts two electrons (-2 charge), so the oxidation state actually corresponds to the reality from the electronic structure point of view.

Oxidation state

- Exception to the above rule exist. For instance, if hydrogen meets element more eager to give away its electron, *e.g.* lithium, sodium, magnesium (I and II group in periodic table). Then this other element is giving away the electron and hydrogen is accepting it (and has -1 oxidation state), in compounds such as LiH or MgH_2.
- The only element that has more affinity towards electrons than oxygen is fluorine. In oxygen-fluorine compounds oxygen atoms have oxidation state at +2 or +1 value (*e.g.* OF_2 or O_2F_2).

Reaction types

In reality the particle can be the subject to only three types of reactions. All more complex reactions are in fact a series combination of those reactions (together, only 1 and 2 can happen in the same time):

1. Ligand detachment or attachment from/to central atom (of particle);
2. Electron(s) detachment or attachment from/to central atom (of particle);
3. Multi-core particle division into smaller fragments or formation of multi-core particle from the number of single-core particles (in multiple steps).

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Reduction-oxidation reactions (red-ox)

Reactions of oxidation (ox)-reduction (red) consist in donation (accepting) of valence electron(s) to/from central atom. It can happen if atom that is eager to give away its electrons gives them to the atom that eagerly accepts them.
Usually (as a rule of a thumb), atoms from the left side of the periodic table give away their electrons (donors), and those on the right side usually are taking electrons (acceptors).
In the e_z-G_{ox} coordination system those reactions are pictured as a movement to the left (giving away electrons) or to the right (accepting electrons).

Half-reactions

- Oxidation-reduction process can be treated as a pair of two individual processes – oxidation and reduction (especially when they are mechanically separated).
  Due to that, redox reactions are often noted as two reactions (so-called half-reactions). Then they are balanced for number of exchanged electrons and in that way is stoichiometry of the process can be determined. *E.g.*:

$Na_{(s)} \rightarrow Na^+ + e^-$ /·2 (reductant – sodium – oxidizes itself)
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$ /·1 (oxidant – chlorine – reduces itself)
$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$

Redox reactions

- Reactions between metals are typical redox reactions:

$2Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{4+}_{(aq)}$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$
$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

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

Of course, ions are not present by themselves in the vacuum. The real reaction is (taking ions from the example) for instance:

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

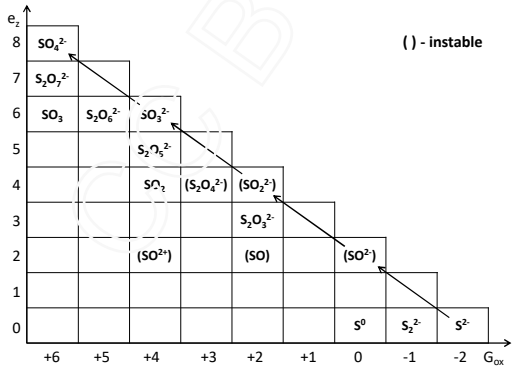
Red-ac and ox-bas reactions (mixed)

- In reality, a lot of reactions are connected reduction-oxidation and acid-base reactions. They consist in synchronous giving away ligand and accepting electron (ox-bas) or synchronous accepting ligand and giving away electron (red-ac).
- Sodium sulfate synthesis can be an example of such reaction:

$Na_2S + 2O_2 \xrightarrow{\Delta T} Na_2SO_4$ four stages, including:

I: $S^{2-} \rightarrow S + 2e^- / O_2 + 4e^- \rightarrow 2O^{2-} / S + O^{2-} \rightarrow SO^{2-}$
IV: $SO_3^{2-} \rightarrow SO_3 + 2e^- / O_2 + 4e^- \rightarrow 2O^{2-} / SO_3 + O^{2-} \rightarrow SO_4^{2-}$

Red-ac and ox-bas reactions



Red-ac and ox-bas reactions

Reactions occurring in lead-acid battery (in this case $H^+_{(aq)}$ notation is equivalent to „H_3O^+", and there is no need to balance water molecules in the chemical equation):

$Pb_{(s)} + H_2SO_{4(aq)} \rightarrow PbSO_{4(s)} + 2H^+_{(aq)} + 2e^-$ ($Pb \rightarrow Pb^{2+} + 2e^-$)
$PbO_{2(s)} + H_2SO_{4(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$
($Pb^{4+} + 2e^- \rightarrow Pb^{2+}$) ($2O^{2-} + 4H^+ \rightarrow 2H_2O$)

Or thermite burning (*e.g.* $Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$)

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Red-ac and ox-bas reactions

- Potassium permanganate (purple/magenta, it is colorless or pale pinkish in acids), reaction occurs fully in water, so no need to write (aq) at each reagent:

$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \rightarrow 2MnSO_4 + 5KNO_3 + K_2SO_4$

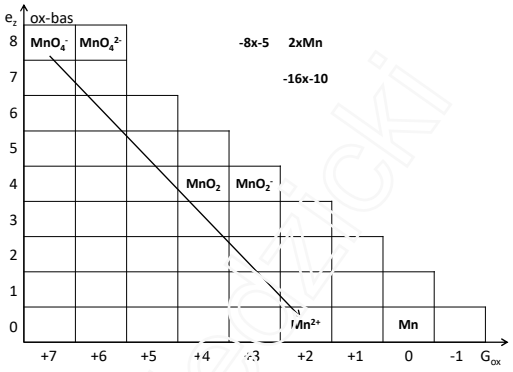
$(8H_3O^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 12H_2O)$ /·2

$(NO_2^- + 3H_2O \rightarrow NO_3^- + 2H_3O^+ + 2e^-)$ /·5

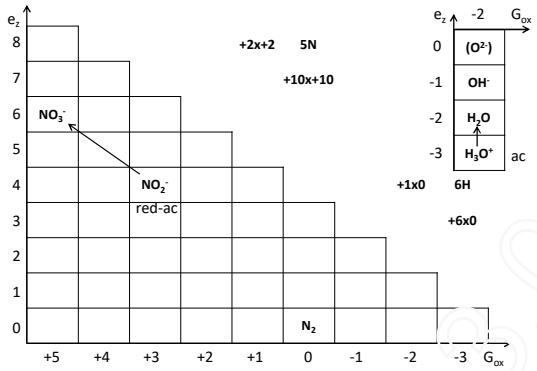
$(16H_3O^+ + 2MnO_4^- + 10e^- \rightarrow 2Mn^{2+} + 24H_2O)$

$(5NO_2^- + 15H_2O \rightarrow 5NO_3^- + 10H_3O^+ + 10e^-)$

Red-ac and ox-bas reactions



Red-ac and ox-bas reactions



Reaction occurrence and pH

Presence of H_3O^+ or OH^- in the adequate concentration can be treated as the presence of any other chemical. Thus, if the reaction needs protons to occur, (H^+ ions) or hydroxide ions (OH^-), then the reactions is dependent on pH (presence of adequate ions).

An example of the reaction which proceeds in different directions depending on pH value is reaction of $KMnO_4$ and KNO_2.

Reaction occurrence and pH

$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \rightarrow$

$\rightarrow 2MnSO_4 + 5KNO_3 + K_2SO_4 + 3H_2O$

$8H_3O^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 12H_2O$ /·2

$NO_2^- + 3H_2O \rightarrow NO_3^- + 2H_3O^+ + 2e^-$ /·5

(low pH is requires and during the reaction pH is increasing – more basic)

$2KMnO_4 + 3KNO_2 + H_2O \rightarrow 2MnO_2 + 3KNO_3 + 2KOH$

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ /·2

$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e^-$ /·3

(more-less neutral pH is required; during the reaction OH^- ions are formed, so the pH increases)

Reaction occurrence and pH

$2KMnO_4 + KNO_2 + 2KOH \rightarrow$

$\rightarrow 2K_2MnO_4 + KNO_3 + H_2O$

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$ /·2

$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e^-$

(high pH value is required and during the reaction it decreases towards the neutral value - 7)

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Acids, bases, oxidants, reductant

- Acid can accept the oxide anion (O^{2-}, in water solutions usually in OH^- form) or donate proton (H^+, in water solutions in H_3O^+ form).
- Base can donate oxide anion or accept proton.
- Oxidant oxidates other atoms (it reduces itself). Oxidant accepts electrons (take away from other atoms).
- Reductant reduces other atoms (it oxidizes itself). Reductant donates its electrons to other atoms.

Complex redox reactions

$Zn_{(s)} + NH_4Cl_{(aq)} + MnO_{2(s)} \rightarrow$

$\rightarrow Zn(NH_3)_2Cl_{2(aq)} + MnOOH_{(s)}$

$Zn \rightarrow Zn^{2+} + 2e^-$

$MnO_2 + e^- + H^+ \rightarrow MnOOH$ /·2

$NH_4Cl \rightarrow NH_3 + Cl^- + H^+$ /·2

$Zn_{(s)} + 2NH_4Cl_{(aq)} + 2MnO_{2(s)} \rightarrow Zn(NH_3)_2Cl_{2(aq)} + 2MnOOH_{(s)}$

Complex redox reactions

$NiOOH_{(s)} + Cd_{(s)} + H_2O_{(l)} \rightarrow Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$

$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ /·2

$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

$2NiOOH_{(s)} + Cd_{(s)} + 2H_2O_{(l)} \rightarrow$

$\rightarrow 2Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$

Complex redox reactions

$NiOOH_{(s)} + H_{2(g)} \rightarrow Ni(OH)_{2(s)}$

$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ /·2

$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

$2NiOOH_{(s)} + H_{2(g)} \rightarrow 2Ni(OH)_{2(s)}$

Complex redox reactions

$SO_{2(l)} + Li_{(s)} \rightarrow Li_2S_2O_{4(s)}$

$Li_{(s)} \rightarrow Li^+_{(solution)} + e^-$ /·2

$2SO_{2(l)} + 2Li^+_{(solution)} + 2e^- \rightarrow Li_2S_2O_{4(s)}$

$2SO_{2(l)} + 2Li_{(s)} \rightarrow Li_2S_2O_{4(s)}$

Complex redox reactions

$2SOCl_{2(l)} + 4Li_{(s)} \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(l)}$

$Li_{(s)} \rightarrow Li^+_{(solution)} + e^-$ /·4

$2SOCl_{2(l)} + 4Li^+_{(solution)} + 4e^- \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(l)}$

$2SOCl_{2(l)} + 4Li_{(s)} \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(l)}$

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