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Redox Reactions

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Kharkiv, 2026

1 Definitions

Oxidation state

- There are 2 groups of reactions based on changes in a formal parameter, the *oxidation state*
  - ✓ $2HCl + K_2O = 2KCl + H_2O$ – exchange reaction
  - ✓ $4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O$ – Redox reaction
- *Oxidation state* (or oxidation number) is the hypothetical charge of an atom, calculated assuming the ionic structure of the compound
- Rules for determining the oxidation state (we use it in the given order):
  - ✓ the sum of the ox. numbers of all atoms in a particle is equal to its charge
  - ✓ Li, Na, K, Rb, Cs: $+1$
  - ✓ $Be, Mg, Ca, Sr, Ba, Zn, Cd$: $+2$
  - ✓ $F: -1$
  - ✓ H: $+1$ with **non-metals** and -1 with **metals**
  - ✓ Cl, Br, I: -1 in binary compounds with metals
  - ✓ $O: -2$ in most compounds; exceptions are easily detected ($\overset{+1}{K}\overset{-1/3}{O}_3, \overset{+1}{H}_2\overset{-1}{O}_2$)
- Examples: $\overset{+1}{K}_2\overset{+6}{Cr}_2\overset{-2}{O}_7, \overset{+1}{H}_2\overset{+6}{S}\overset{-2}{O}_4, \overset{+3}{Fe}_2(\overset{+6}{S}\overset{-2}{O}_4)_3$

Reactions with changes in oxidation state

- Oxidation is the *loss* of electrons
- Reduction is the *gain* electrons
- Electrons are taken by the oxidizing agent, and lost by the reducing agent
- *The oxidizing agent is reduced, the reducing agent is oxidized*
  $16\underbrace{H\overset{-1}{Cl}}_{\text{reductant}} + 2\underbrace{K\overset{+7}{Mn}O_4}_{\text{oxidizer}} = 2\overset{+2}{Mn}Cl_2 + 5\overset{0}{Cl}_2 + 8H_2O + 2KCl$
- Broad sense of the term "oxidizing agent":
  particle $KMnO_4$, ion MnO_4^-, atom Mn $(+7)$
- There are three Redox reactions groups:

✓ intermolecular: $2SO_2 + O_2 = 2SO_3$

✓ disproportionation: $2KOH + \overset{0}{Cl}_2 = K\overset{-1}{Cl} + K\overset{+1}{Cl}O + H_2O$

✓ comproportionation: $\overset{-3}{N}H_4\overset{+5}{N}O_3 = \overset{+1}{N}_2O + 2H_2O$

- *Cannizzaro reaction* – disproportionation of aldehyde:

$$2R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H} \quad + \quad NaOH = R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow ONa} \quad + \quad R-CH\genfrac{}{}{0pt}{}{\nearrow H}{\searrow OH}$$

1.1 Oxidizing agents and reducing agents

- Oxidation corresponds to an increase in the oxidation state of a certain atom, and reduction corresponds to a decrease
- An atom in the highest oxidation state can only be an oxidizing agent, and in a lower state - only a reducing agent
- *The highest oxidation state* of an element is the same as *total number of valence electrons*

  ✓ examples: $S(3s^23p^4) : +6$, $P(3s^23p^3) : +5$, $Mn(3d^54s^2) : +7$

  ✓ exceptions: $F\ (0), O\ (+2), Fe\ (+6), Co\ (+3), Ni\ (+3)$

- *Lowest oxidation state*:

  ✓ 0 for metals

  ✓ (total number of valence electrons) minus 8 for non-metals

  ✓ examples: $Co\ (0), F\ (-1), K\ (0), P\ (-3)$

  ✓ exceptions: $B\ (-3)$, noble gases

- We are talking only about the *possibility* of manifesting certain properties: $P\ (+5)$ *can only be an oxidizing agent*, but almost does not exhibit these properties

1.2 The most important reducing agents

Commonly used reducing agents include:

- active metals (Al, Mg, Ca, Na, Zn)
  $Cr_2O_3 + 2\overset{0}{Al} = 2Cr + \overset{+3}{Al}_2O_3$ – aluminothermy
- compounds of some metals in low oxidation states ($FeSO_4$, $SnCl_2$, $CrSO_4$)
  $\overset{+2}{Sn}Cl_2 + 2HNO_2 + 2HCl = 2NO + 2H_2O + \overset{+4}{Sn}Cl_4$

- series of nonmetals (H_2, C) and their compounds (CO, Na_2SO_3)
$CuO + \overset{0}{H}_2 = Cu + \overset{+1}{H}_2O$
$Na_2\overset{+4}{S}O_3 + H_2O_2 = Na_2\overset{+6}{S}O_4 + H_2O$

1.3 The most important oxidizing agents

The main oxidizing agents include:

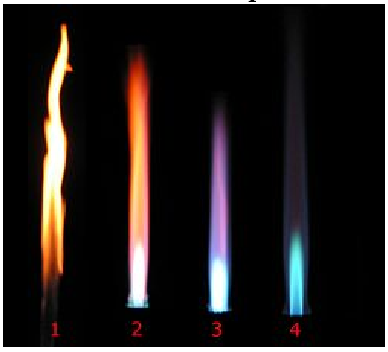
- nonmetals (F_2, Cl_2, Br_2, I_2, O_2, S) and their derivatives (O_3, SO_2Cl_2)
$2CuS + 3\overset{0}{O}_2 = 2Cu\overset{-2}{O} + 2S\overset{-2}{O}_2$

- compounds of some metals in higher oxidation states ($KMnO_4$, $K_2Cr_2O_7$, PbO_2)
$\overset{+4}{Pb}O_2 + 4HCl = \overset{+2}{Pb}Cl_2 + Cl_2 + 2H_2O$

- the so-called non-oxidizing acids are oxidizers due to H^+, and oxidizing acids due to the acid residue
$2\overset{+1}{H}Cl + Zn = ZnCl_2 + \overset{0}{H}_2$, $H_2SO_4 + Fe = FeSO_4 + H_2$
$4H\overset{+5}{N}O_3 + Cu = Cu(NO_3)_2 + 2\overset{+4}{N}O_2 + 2H_2O$, $2H_2SO_{4(conc)} + Cu = CuSO_4 + SO_2 + 2H_2O$

1.4 Combustion

- *Combustion* – a special type of Redox reaction:
  - ✓ a lot of heat is released in the reaction;
  - ✓ with intense combustion a flame is observed
- Up to 90% of energy humanity receives from burning various fuels
- Combustion requires both fuel and oxidizer



Combustion of natural gas in a burner:
1, 2 - lack of oxidizing agent (O_2)
3 - best ratio of components
4 - excess oxidizing agent

If the oxidizer is mixed with fuel in advance and then set on fire, an explosion is possible!

- To start combustion, the mixture must be heated to a certain temperature, the so-called *autoignition temperature*

2 Balansing the Redox equations

Redox balancing: general ideas

- Determining coefficients in Redox can be a difficult task
- The general idea is simple: the numbers of electrons donated by the reducing agent and accepted by the oxidizing agent are the same
- To assign coefficients in the Redox equation, 2 methods are used
  - ✓ ox. numbers change method for a ready-made reaction scheme (all reactantsproducts are known)
  - ✓ the ion-electron (half-reaction) method is suitable for any reaction in solution
- The first method is easy to learn, the second is more effective to apply

2.1 Oxidation number change method

- Find elements that change the oxidation state
  $H\overset{-1}{Cl} + K\overset{+7}{Mn}O_4 = \overset{+2}{Mn}Cl_2 + \overset{0}{Cl}_2 + H_2O + K\overset{-1}{Cl}$
- Write down diagrams of oxidation and reduction processes
  $$\begin{array}{l|l} \overset{+7}{Mn} + 5e = \overset{+2}{Mn} & 2 \\ 2\overset{-1}{Cl} - 2e = \overset{0}{Cl}_2 & 5 \end{array}$$
- Set the balance by the number of electrons
- The resulting factors are transferred to the equation
  $HCl + 2KMnO_4 = 2MnCl_2 + 5Cl_2 + H_2O + KCl$
- Place other coefficients (if necessary) before
  - ✓ metal atoms (K)
  - ✓ ions of acidic residues (Cl^-)
  - ✓ hydrogen atoms
- $16HCl + 2KMnO_4 = 2MnCl_2 + 5Cl_2 + 8H_2O + 2KCl$

2.2 Ion-electron method

- The method is based on the assumption: redution patterns are determined by the medium and reaction partner

- In the reference book, you can find *reduction half-reactions* for different chemical species
  $MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \quad E^\circ = 1.51$ V
  $Cl_2 + 2e = 2Cl^- \quad E^\circ = 1.36$ V

- *Half-reaction having less E° occurs as oxidation!*

- Condition for the occurrence of a redox reaction: $E_{ox} > E_{red}$

- The balance is established according to a well-known scheme

$$\begin{array}{l|l} MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O & 2 \\ 2Cl^- - 2e = Cl_2 & 5 \\ \hline \multicolumn{2}{l}{2MnO_4^- + 16H^+ + 10Cl^- = 2Mn^{2+} + 8H_2O + 5Cl_2} \end{array}$$

- Other coefficients are found arithmetically
  $16HCl + 2KMnO_4 = 2MnCl_2 + 5Cl_2 + 8H_2O + 2KCl$

3 Algorithm for writing the Redox equation

- Assignment: for known reaction participants you need to write the redox equation
  $MnO_2 + HCl \to \ldots$

- The solution algorithm can be like this

  ✓ find an oxidizing agent and a reducing agent

  ✓ write down schemes for converting them into a product

  ✓ complete the half-reactions of transformations

  ✓ take into account the balance of electrons

  ✓ write the molecular equation of the reaction finally

3.1 Conversion schemes

- Writing transformation schemes requires knowledge of inorganic chemistry

- For example, MnO_4^- reducing goes like this

  ✓ $MnO_4^- \to Mn^{2+}$ at pH < 7 (acidic medium)

- ✓ $MnO_4^- \to MnO_2$ at $pH = 7$ (neutral medium)
- ✓ $MnO_4^- \to MnO_4^{2-}$ at $pH > 7$ (alkaline medium)

- Another example is HNO_3
  - ✓ concentrated acid is reduced to NO_2
  - ✓ diluted acid is reduced to NO
  - ✓ strong reducing agents can reduce diluted acid up to NH_4^+

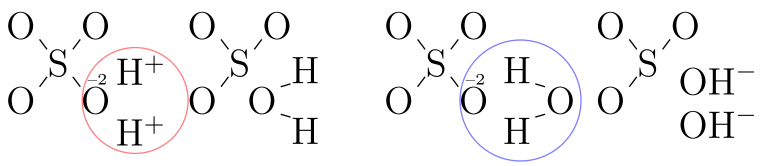
- To write an oxidation or reduction scheme, it is enough to know:
  - ✓ two particles with an element that changes the oxidation state
  - ✓ nature of the medium (acidic, neutral or alkaline)

3.2 Change in chemical species composition

- The number of atoms of an element that changes the oxidation state is balanced by multipliers
  - ✓ $Cl_2 \to 2Cl^-$
  - ✓ $Cr_2O_7^{2-} \to 2Cr^{3+}$

- Oxygen atoms number changes with H^+, OH^- or H_2O depending on the pH of the medium

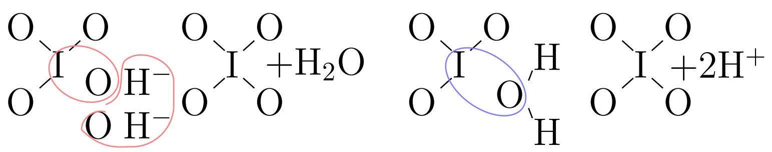
- Reducing the number of O atoms



$O^{2-} + 2H^+ = H_2O$, $pH < 7$ $(SO_4^{2-} + 2H^+ \to SO_3^{2-} + H_2O)$
$O^{2-} + H_2O = 2OH^-$, $pH \geqslant 7$ $(SO_4^{2-} + H_2O \to SO_3^{2-} + 2OH^-)$

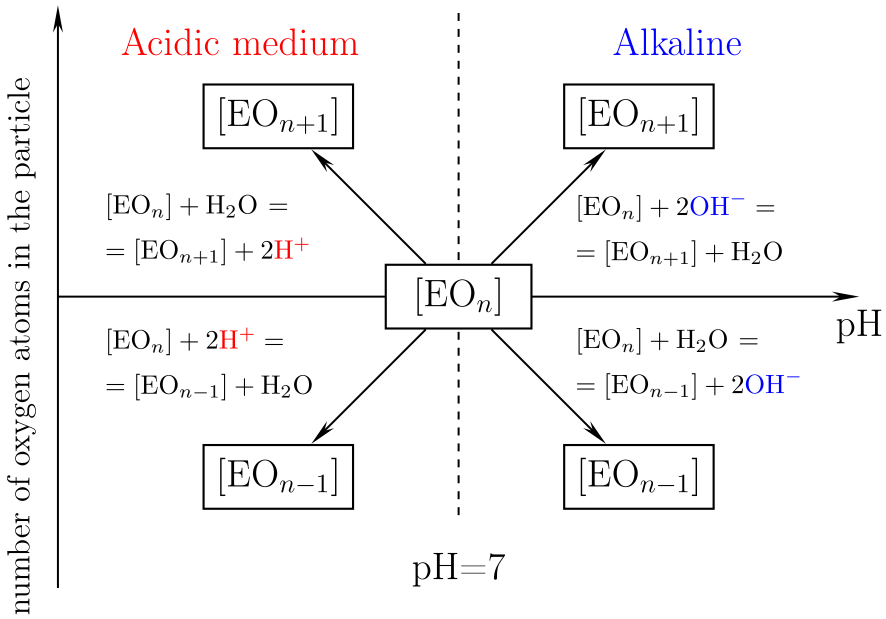
- Conclusion: in an acidic medium, O atoms are subtracted using H^+, and in a neutral or alkaline medium – using H_2O

- Increase in the number of atoms O



$2OH^- = O^{2-} + H_2O$, pH > 7 ($IO_3^- + 2OH^- \rightarrow IO_4^- + H_2O$)
$H_2O = O^{2-} + 2H^+$, pH ⩽ 7 ($IO_3^- + H_2O \rightarrow IO_4^- + 2H^+$)

- Conclusion: in an alkaline medium, O atoms are added using OH^-, and in a neutral or acidic medium – using H_2O
- Sometimes a similar scheme works for *other atoms*:
  $\underbrace{2NH_3}_{6H} + 2OH^- - 2e \rightarrow \underbrace{N_2H_4}_{4H} + 2H_2O$ (pH > 7)
  $2NH_3 - 2e \rightarrow N_2H_4 + 2H^+$ (pH ⩽ 7)
- In a non-aqueous medium, other particles are used, for example: $ClO^- + CO_3^{2-} - 2e = ClO_2^- + CO_2$



3.3 Half-reactions

- Based on the oxidation or reduction scheme, a half-reaction (oxidation or reduction) is built
- Balance consists of 3 stages
  - ✓ for element that changes the oxidation state
  - ✓ for oxygen atoms
  - ✓ for electrons
- Reduction example: $MnO_4^- \rightarrow Mn^{2+}$, pH < 7
  - ✓ $1MnO_4^- \rightarrow 1Mn^{2+}$
  - ✓ $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

✓ $MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$

- Example with oxidation: $Cr^{3+} \rightarrow Cr_2O_7^{2-}$, pH < 7

  ✓ $2Cr^{3+} \rightarrow Cr_2O_7^{2-}$

  ✓ $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

  ✓ $2Cr^{3+} + 7H_2O - 6e = Cr_2O_7^{2-} + 14H^+$

3.4 Composition of half-reactions

- Two half-reactions must be composed to obtain the ORR equation in ion-molecular form

- Key requirement: formal reduction of electrons according to the reaction equation

- For example

$$\begin{array}{l|l} MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O & 2 \\ NO_2^- + H_2O - 2e = NO_3^- + 2H^+ & 5 \\ \hline \end{array}$$

$$2MnO_4^- + 16H^+ + 5NO_2^- + 5H_2O = 2Mn^{2+} + 8H_2O + 5NO_3^- + 10H^+$$

- Identical particles are reduced:
  $2MnO_4^- + 6H^+ + 5NO_2^- = 2Mn^{2+} + 3H_2O + 5NO_3^-$

- The abbreviation can also be as follows: $H^+ + OH^- = H_2O$

3.5 Molecular form of redox equation

- The ion-molecular equation describes the essence of the process

$$2MnO_4^- + 6H^+ + 5NO_2^- = 2Mn^{2+} + 3H_2O + 5NO_3^-$$

  Permanganate ion in an acidic medium oxidizes nitrate (III) ion to nitrate ion.

- During the transition to the molecular form, cations and anions must contact each other

- Additional particles may appear in the molecular equation that are not formally involved in oxidation or reduction

$$2KMnO_4 + 3H_2SO_4 + 5KNO_2 = 2MnSO_4 + 3H_2O + 5KNO_3 + K_2SO_4$$

3.6 Examples

- $NaBr + NaBrO_3 + H_2SO_4 =$
- Reduction scheme:
  - ✓ $BrO_3^- \rightarrow Br_2$
  - ✓ $2BrO_3^- + 12H^+ + 10e = Br_2 + 6H_2O$
- Oxidation scheme:
  - ✓ $2Br^- \rightarrow Br_2$
  - ✓ $2Br^- - 2e = Br_2$
- Compilation of half-reactions

$$\begin{array}{l|l} 2BrO_3^- + 12H^+ + 10e = Br_2 + 6H_2O & 1 \\ 2Br^- - 2e = Br_2 & 5 \\ \hline \end{array}$$
$$2BrO_3^- + 12H^+ + 10Br^- = Br_2 + 6H_2O + 5Br_2$$

- Reducing the equation
  $BrO_3^- + 6H^+ + 5Br^- = 3Br_2 + 3H_2O$
- Writing an equation in molecular form
  $5NaBr + NaBrO_3 + 3H_2SO_4 = 3Br_2 + 3H_2O + 3Na_2SO_4$

$NH_3 + SeO_2 =$

- Reduction scheme:
  - ✓ $SeO_2 \rightarrow Se$
  - ✓ $SeO_2 + 2H_2O \rightarrow Se + 4OH^-$
  - ✓ $SeO_2 + 2H_2O + 4e = Se + 4OH^-$
- Oxidation scheme:
  - ✓ $NH_3 \rightarrow N_2$
  - ✓ $2NH_3 \rightarrow N_2 + 6H^+$
  - ✓ $2NH_3 - 6e = N_2 + 6H^+$
- Compilation of half-reactions

$$\begin{array}{l|l} SeO_2 + 2H_2O + 4e = Se + 4OH^- & 3 \\ 2NH_3 - 6e = N_2 + 6H^+ & 2 \\ \hline \end{array}$$
$$3SeO_2 + 6H_2O + 4NH_3 = 3Se + 12OH^- + 2N_2 + 12H^+$$

- Reducing the equation
  $3SeO_2 + 4NH_3 = 3Se + 2N_2 + 6H_2O$

- The equation obtained after reduction is molecular

$Sb_2O_3 + Br_2 + KOH =$

- Reduction scheme:

  ✓ $Br_2 \to Br^-$

  ✓ $Br_2 \to 2Br^-$

  ✓ $Br_2 + 2e = 2Br^-$

- Oxidation scheme:

  ✓ $Sb_2O_3 \to SbO_3^-$

  ✓ $Sb_2O_3 + 6OH^- \to 2SbO_3^- + 3H_2O$

  ✓ $Sb_2O_3 + 6OH^- - 4e = 2SbO_3^- + 3H_2O$

- Compilation of half-reactions

$$\begin{array}{l|l} Br_2 + 2e = 2Br^- & 2 \\ Sb_2O_3 + 6OH^- - 4e = 2SbO_3^- + 3H_2O & 1 \\ \hline \end{array}$$

$$2Br_2 + Sb_2O_3 + 6OH^- = 4Br^- + 2SbO_3^- + 3H_2O$$

- Writing an equation in molecular form
  $Sb_2O_3 + 2Br_2 + 6KOH = 4KBr + 2KSbO_3 + 3H_2O$