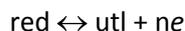


Classical qualitative analysis. 5. Analysis of non-metallic ions - anions

During qualitative analysis of non-metallic ions (anions) mixture majority of identification reactions are oxidation-reduction (redox) ones. The course of these reactions depends on the difference in values of standard redox potentials of half reactions. Redox potential is determined by oxidant and reducer properties and their concentrations in the solution. Assuming that half reaction:



is reversible, redox potential can be expressed by Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{utl}}}{a_{\text{red}}}$$

where E^0 represents standard redox potential, R – gas constant, T – absolute temperature (K), n – number of electrons involved in reaction, F – Faraday's constant, a_{oxid} and a_{red} – activities of oxidized and reduced forms. Substituting values of constants and transforming natural logarithms into base-10 logarithm the Nernst formula at 25°C is presented as:

$$E = E^0 + \frac{0.059}{n} \log \frac{a_{\text{utl}}}{a_{\text{red}}}$$

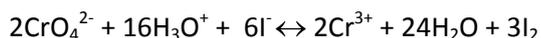
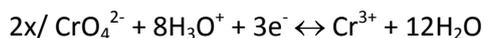
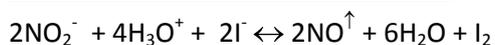
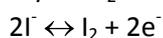
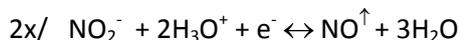
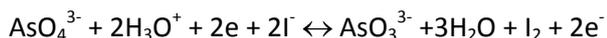
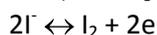
Potential is expressed in volts. Assuming $a_{\text{oxid}}=a_{\text{red}}$, than $E=E^0$ and system reaches **standard potential**. Value of standard potential is constant and characteristic for a particular system.

Factors affecting value of the potential:

- 1) change in concentration: increase of reduced form concentration, fraction value is smaller, then log value is smaller, so potential value is lower
- 2) pH
- 3) complexation
- 4) precipitation

Reactions – redox test (tests for oxidizing and reducing agents)

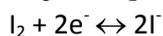
Oxidizing anions, e.g. NO_2^- , AsO_4^{3-} , CrO_4^{2-} ($\text{Cr}_2\text{O}_7^{2-}$), - positive reaction with **KI** solution (in the presence of diluted H_2SO_4 and starch solution), at room temperature. Starch solution is stained navy blue owing iodine secretion (I_2) that is oxidation of iodide ions into iodine proceeds: $2\text{I}^- \leftrightarrow \text{I}_2 + 2\text{e}^-$. Reactions:

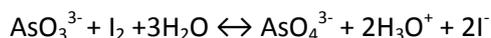
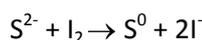
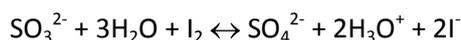


Reducing anions:

Strong reducing anions, e.g. S^{2-} , SO_3^{2-} , AsO_3^{3-} positive reaction with **iodine** solution (I_2) (I_2 in $\text{KI} - \text{I}_3^-$) in the presence of starch solution – discoloration from navy blue to stainless that is reduction of iodine into iodide ion:

$\text{I}_2 + 2\text{e}^- \leftrightarrow 2\text{I}^-$. Reactions:





Moderate reducing anions: Br^- , I^- , NO_2^- - positive reaction with diluted solution of potassium permanganate KMnO_4 (in the presence of H_2SO_4 , **without heating**) – discoloration of solution from pink to stainless that is reduction of MnO_4^- to Mn^{2+} ion:



Reactions:

$10\text{Br}^- + 2\text{MnO}_4^- + 16\text{H}_3\text{O}^+ \leftrightarrow 2\text{Mn}^{2+} + 5\text{Br}_2 + 24\text{H}_2\text{O}$ (final result – yellow stained solution, yellow colour comes from bromine);

$10\text{I}^- + 2\text{MnO}_4^- + 16\text{H}_3\text{O}^+ \leftrightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 24\text{H}_2\text{O}$ (final result – yellow stained solution from iodine);

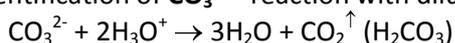
$5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}_3\text{O}^+ \leftrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 9\text{H}_2\text{O}$ (final result – stainless solution - Mn^{2+} ions)

Positive reaction also for all strong reducers, that were not formerly oxidized or eliminated.

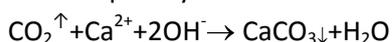
NO_2^- amphoteric redox properties – oxidant and reducer.

Neutral anions with reference to redox properties: CO_3^{2-} , SO_4^{2-} , Cl^- , PO_4^{3-} . Identification reactions:

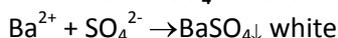
a) Identification of CO_3^{2-} - reaction with diluted non-oxidizing acid (HCl)



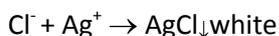
and subsequently identification of evolved CO_2 by reaction with calcium hydroxide $\text{Ca}(\text{OH})_2$:



b) Identification of SO_4^{2-} - reaction with solution of Ba^{2+} ions (BaCl_2) in acidic solution:

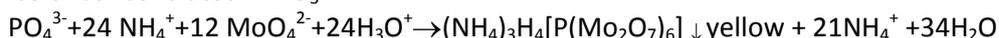


c) Identification of Cl^- - reaction with AgNO_3 solution in 2M/l HNO_3 medium:



With time the white precipitate gets dark in the light – photochemical reaction – metallic silver is precipitated: $2\text{AgCl} \rightarrow 2\text{Ag}^0 + \text{Cl}_2$

d) Identification of PO_4^{3-} - reaction with ammonium molybdate/ammonium orthomolybdate in the presence of concentrated HNO_3



Experimental procedure

1. Pour 0.5 cm^3 of NO_2^- ions solution into a glass test tube. Perform the test for oxidizing anion .
2. Pour 0.5 cm^3 of AsO_3^{3-} ions solution into a glass test tube. Perform the test for moderately reducing anions.
3. Pour 0.5 cm^3 of NO_2^- ions solution into a glass test tube. Perform the test for strongly reducing anions.
4. Pour 0.5 cm^3 of each neutral ions solution (with reference to redox properties) respectively into 4 test tubes: CO_3^{2-} , SO_4^{2-} , Cl^- , PO_4^{3-} . Perform the test for their identification.

Unknown analysis:

Each student receives a solution containing a mixture of unknown anions. Using redox tests the student is obliged to detect group of anions present in the solution- oxidizing, strong or moderate reducing. Additionally using previously known identification reactions detect the presence of one from four ions: CO_3^{2-} , SO_4^{2-} , Cl^- , PO_4^{3-} . Describe the performed analysis of anions with appropriate reaction equations.