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:

red ↔ utl + n*e*

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

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

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 25^0C is presented as:

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

Potential is expressed in volts. Assuming $a_{oxid}=a_{red}$, 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)

<u>Oxidizing anions</u>, e.g. NO_2^- , AsO_4^{3-} , CrO_4^{2-} ($Cr_2O_7^{2-}$), - 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: $2I^- \leftrightarrow I_2 + 2e$. Reactions:

$AsO_4^{3-} + 2H_3O^+ + 2e \leftrightarrow AsO_3^{3-} + 3H_2O$
$2I^- \leftrightarrow I_2 + 2e$

$AsO_4^{3-} + 2H_3O^+ + 2e + 2I^- \leftrightarrow AsO_3^{3-} + 3H_2O + I_2 + 2e^-$
$AsO_4^{3-} + 2H_3O^+ + 2I^- \leftrightarrow AsO_3^{3-} + 3H_2O + I_2$

2x/ $NO_2^- + 2H_3O^+ + e^- \leftrightarrow NO\uparrow + 3H_2O$
$2I^- \leftrightarrow I_2 + 2e^-$

$2NO_2^- + 4H_3O^+ + 2I^- \leftrightarrow 2NO\uparrow + 6H_2O + I_2$

2x/ $CrO_4^{2-} + 8H_3O^+ + 3e^- \leftrightarrow Cr^{3+} + 12H_2O$
3x/ $2I^- \leftrightarrow I_2 + 2e^-$

$2CrO_4^{2-} + 16H_3O^+ + 6I^- \leftrightarrow 2Cr^{3+} + 24H_2O + 3I_2$

<u>Reducing anions</u>:

Strong reducing anions , e.g. S^{2-}, SO_3^{2-}, AsO_3^{3-} positive reaction with **iodine** solution (I_2) (I_2 in KI - I_3^-) in the presence of starch solution – discoloration from navy blue to stainless that is reduction of iodine into iodide ion:

$I_2 + 2e \leftrightarrow 2I^-$. Reactions:

$SO_3^{2-} + 3H_2O \leftrightarrow SO_4^{2-} + 2H_3O^+ + 2e^-$
$I_2 + 2e^- \leftrightarrow 2I^-$

$SO_3^{2-} + 3H_2O + I_2 \leftrightarrow SO_4^{2-} + 2H_3O^+ + 2I^-$

$S^{2-} + I_2 \rightarrow S^0 + 2I^-$

$AsO_3^{3-} + I_2 + 3H_2O \leftrightarrow AsO_4^{3-} + 2H_3O^+ + 2I^-$

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:

$$MnO_4^- + 8H_3O^+ + 5e \leftrightarrow Mn^{2+} + 12H_2O.$$

Reactions:

$10Br^- + 2MnO_4^- + 16H_3O^+ \leftrightarrow 2Mn^{2+} + 5Br_2 + 24H_2O$ (final result – yellow stained solution, yellow colour comes from bromine);

$10I^- + 2MnO_4^- + 16H_3O^+ \leftrightarrow 2Mn^{2+} + 5I_2 + 24H_2O$ (final result – yellow stained solution from iodine);

$5NO_2^- + 2MnO_4^- + 6H_3O^+ \leftrightarrow 2Mn^{2+} + 5NO_3^- + 9H_2O$ (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)

$$CO_3^{2-} + 2H_3O^+ \rightarrow 3H_2O + CO_2\uparrow (H_2CO_3)$$

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

$$CO_2\uparrow + Ca^{2+} + 2OH^- \rightarrow CaCO_3\downarrow + H_2O$$

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

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow \text{ white}$$

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

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow \text{white}$$

With time the white precipitate gets dark in the light – photochemical reaction – metallic silver is precipitated: $2AgCl \rightarrow 2Ag^0 + Cl_2$

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

$$PO_4^{3-} + 24\,NH_4^+ + 12\,MoO_4^{2-} + 24H_3O^+ \rightarrow (NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow \text{yellow} + 21NH_4^+ + 34H_2O$$

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 oblige 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.