

CONCURSUL STUDENTESC DE CHIMIE ANALITICĂ ȘI CHIMIE COORDINATIVĂ "PETRU SPACU"

6 Mai 2017

FACULTATEA DE CHIMIE APLICATĂ ȘI ȘTIINȚA MATERIALELOR
UNIVERSITATEA POLITEHNICA DIN BUCUREȘTI



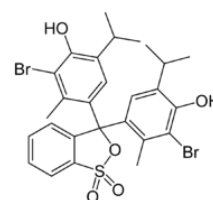
Subjects

1. 15 p

The amount of protein in a cheese sample is determined by Kjeldahl analysis for nitrogen. After digesting a 0.9814 g sample of cheese, the nitrogen is oxidized to NH_4^+ , and then is distilled into a collection flask containing 50.00 mL of 0.1047 M HCl (standardized solution). The HCl excess is back titrated with a NaOH solution of 0.1142 M requiring 22.84 mL to reach the bromothymol blue equivalence point (0.1% ethanol solution with change in color from yellow to blue). The NaOH solution was standardized against 0.1234 g oxalic acid for which titration in phenolphthalein presence it have been used 18.70 mL of NaOH 0.1142 M.

Given data: $M_{\text{HCl}} = 36.5 \text{ g/mol}$; $M_{\text{NaOH}} = 40 \text{ g/mol}$; $M_{\text{NH}_3} = 17 \text{ g/mol}$; $A_{\text{N}} = 14 \text{ g/mol}$; $M_{\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}} = 126.066 \text{ g/mol}$.

- 2p** Determine the exact concentration of NaOH used to titrate the HCl excess.
- 6p** Calculate the titration curve for titrating the 0.1047 M HCl with the NaOH solution having the exact concentration previously calculated. (*It is recommended to use the titration degree.*)
- 2p** Plot the titration curve which was calculated previously.
- 3p** Calculate the titration error when using the bromothymol blue for determining the equivalence point, if the indicator exponent, $pT = 6.8$, and its indicator range is between $\text{pH} = 6.0$ and $\text{pH} = 7.6$.
- 2p** Report the protein mass content (%) in the cheese sample assuming that there are 6.38 g protein for every gram of nitrogen in most dairy products.



Bromothymol blue

2. 15p

For antimony determination from an emetic compound, the antimony and potassium basic tartrate with molecular formula $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$, it is titrated in acidic media with a potassium bromate solution. Into a conical flask it was introduced a volume from 0.1 N emetic solution further diluted with 25 mL H_2O distilled, then 15 mL HCl concentrated solution (reaction media) and 1.5 mL of methyl red as indicator were added. The obtained solution has been titrated with 11.1 mL standardized potassium bromate 0.1 N solution till the solution discoloration.

The involved reaction in the titration process is:

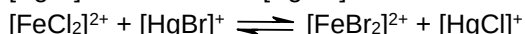
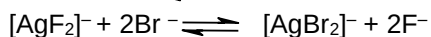


Given data: $A_{\text{Sb}} = 121,76 \text{ g/mol}$; $A_{\text{Br}} = 79,91 \text{ g/mol}$; $E_{\text{Sb}^{5+}/\text{Sb}^{3+}}^0 = 0,746 \text{ V}$, $E_{\text{Br}^{5+}/\text{Br}^{-1}}^0 = 1,440 \text{ V}$ at $\text{pH} = 1$.

- 2p** Establish the redox coefficients for reaction (1).
- 2p** Determine the amount of emetic present in sample.
- 8p** Calculate the titration curve for titrating 10 mL of emetic 0.1 N, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$, in HCl media with the KBrO_3 0.1 N standardized solution.
- 3p** Plot the titration curve previously calculated and mark the titration specific points.

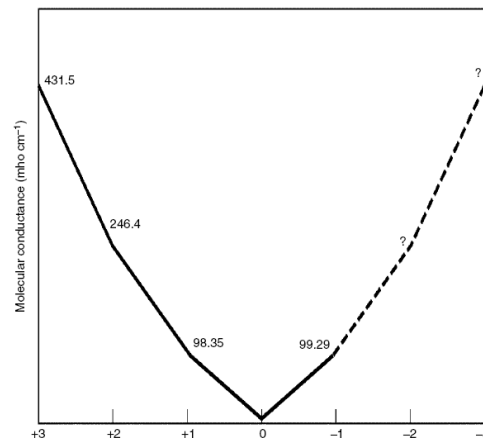
3. 15p Based on HSAB principle (*Hard and Soft (Lewis) Acids and Bases - Pearson theory*):

- 6p** Predict whether the equilibrium constants for the following reactions should be greater than 1 or less than 1. Explain:



- b) **6p** The thiocyanate ion, SCN^- offers either a N atom (M-NSC, N-isomer) or a S atom (NCS-M, S-isomer) to metal ions. Indicate for the complex ions: $[\text{Co}(\text{CNS})(\text{NH}_3)_5]^{2+}$, $[\text{Rh}(\text{CNS})_6]^{3-}$, $[\text{Fe}(\text{CNS})_3(\text{OH}_2)_3]^{2+}$ the coordination mode of this ambidentate ligand SCN^- (*here noted CNS*)
- c) **3p** The ambidentate ligand: SCN^- is bound to Cu^{2+} through S atom in $[\text{Cu}(\underline{\text{SCN}})_2(\text{NH}_3)_4]$ and through N atom in $[\text{Cu}(\underline{\text{NCS}})_2(\text{py})_4]$. Taking into account that pyridine acts as a σ -donor, π -acceptor ligand whereas ammonia ($:\text{NH}_3$) acts only as σ -donor ligand, explain this coordination behaviour. (*A π -acceptor ligand is a ligand that has empty π orbitals that are available for occupation*)

4. 15p In $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ complex, the neutral ammonia ($:\text{NH}_3$) ligands are successively replaced by NO_2^- anionic ligands (from NaNO_2). The molecular conductances of the whole series of newly formed complexes are plotted against the charges of the complex ions.



a) **3p** For each value on x-axis, write the corresponding formula of the complex.

b) **12p** Draw all possible isomers of the complexes and name, for each complex, the type of isomerism.

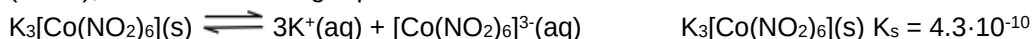
5. 30p The complex - $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ is formed upon addition of NaNO_2 to a slightly acidic (CH_3COOH) solution of CoCl_2 and it is used in qualitative analysis as a precipitating reagent and identifying test for K^+ , NH_4^+ , Ti^+ , Cs^+ ions. For $\text{CN}=6$, $r_i(\text{Na}^+) = 1.02\text{\AA}$, $r_i(\text{K}^+) = 1.38\text{\AA}$, $r_i(\text{NH}_4^+) = 1.48\text{\AA}$, $r_i(\text{Ti}^+) = 1.50\text{\AA}$, $r_i(\text{Cs}^+) = 1.67\text{\AA}$. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ is very soluble in water (720 g/L at 20°C).

5.1. 3p Give the equation for the formation of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$.

5.2. 3p Determine the oxidation state and hybridization of central metal ion in $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (*the complex is diamagnetic*).

5.3.

- a) **1p** the analogous complex compound: $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ has a solubility product (K_s) of $4.3 \cdot 10^{-10}$. Based on ionic radii given for monovalent cations: Na^+ , K^+ , NH_4^+ , Ti^+ , Cs^+ , estimate if K^+ ion can be identified by precipitation in presence of any other cation.
- b) **3p** determine the solubility of $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ (g/L) and calculate the molar concentration of $[\text{Co}(\text{NO}_2)_6]^{3-}$ (mol/L), when the following equilibrium is established..



5.4.

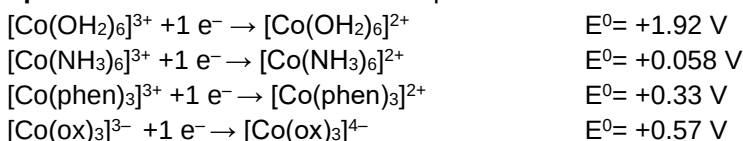
- a) **6p** Use the information in the Latimer* diagrams (both in acidic and basic solutions) for cobalt to construct the Frost** diagram ($n \cdot E^0 = f(\text{oxidation states})$) for cobalt in acidic/basic solution.

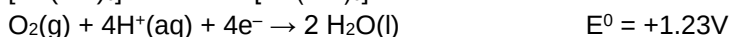
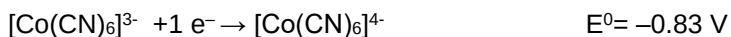
pH = 0		pH = 14
$\begin{array}{ccccccc} +4 & & +3 & & +2 & & 0 \\ \text{CoO}_2 & \xrightarrow{+1.4\text{V}} & \text{Co}^{3+} & \xrightarrow{+1.92\text{V}} & \text{Co}^{2+} & \xrightarrow{-0.282\text{V}} & \text{Co} \end{array}$		$\begin{array}{ccccccc} +4 & & +3 & & +2 & & 0 \\ \text{CoO}_2 & \xrightarrow{+0.7\text{V}} & \text{CoO}(\text{OH}) & \xrightarrow{-0.22\text{V}} & \text{Co}(\text{OH})_2 & \xrightarrow{-0.873\text{V}} & \text{Co} \end{array}$

- b) **2p** Consider the Latimer diagram for cobalt in acidic solution and find the potential for the disproportionation of Co^{3+} .



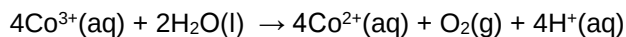
- c) **4p** Consider the standard reduction potentials of cobalt in the following complex ions:



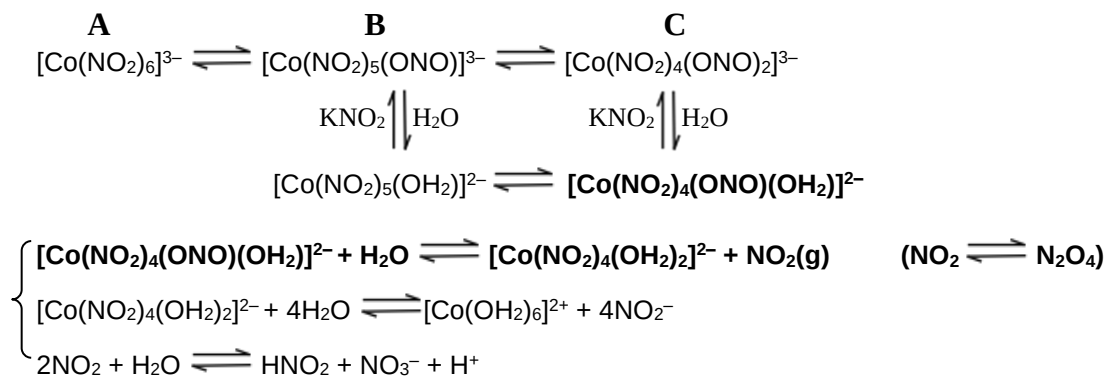


and indicate:

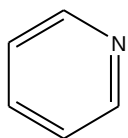
- 1.5p the complex ions that are reduced by water, $\text{H}_2\text{O}(\text{l})$
- 1.5p the complex ions that are oxidized by atmospheric oxygen, $\text{O}_2(\text{g})$
- 1p discuss the stability (with respect to reduction) of $\text{Co}^{3+}(\text{aq})$ when coordinated with these ligands.



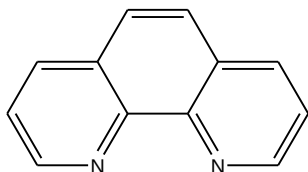
5.5. 8p In diluted aqueous solutions, $[\text{Co}(\text{NO}_2)_6]^{3-}$ ion is unstable (the solutions cannot be kept for long time). The $[\text{Co}(\text{NO}_2)_6]^{3-}$ ion decomposes by aquation of one ONO^- ligand, followed by a slower redox reaction between Co^{3+} and ONO^- to give NO_2 (more accurately as N_2O_4) and Co^{2+} .



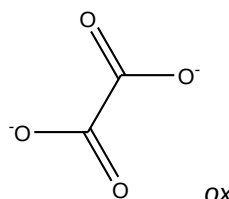
- 4p For **A-C** complexes, indicate the type of isomerism.
- 4p Use the information in the Frost diagrams (acidic/basic solutions) to determine the reactions between $[\text{Co}(\text{NO}_2)_6]^{3-}$ and strong acids/strong bases.



pyridine, py



phen



ox

Given data: $A_{\text{Co}} = 59$, $A_{\text{K}} = 39$, $A_{\text{O}} = 16$

*In a **Latimer diagram** (also known as a *reduction potential diagram*) for an element, the numerical value of the standard potential (in volts) is written over a horizontal line (or arrow) connecting species with the element in different oxidation states. The most highly oxidized form of the element is on the left, and in species to the right the element is in successively lower oxidation states.

** A **Frost diagram** (also known as an *oxidation state diagram*) of an element X is a plot of nE° for the couple $\text{X}(N)/\text{X}(0)$ against the oxidation number, N , of the element.