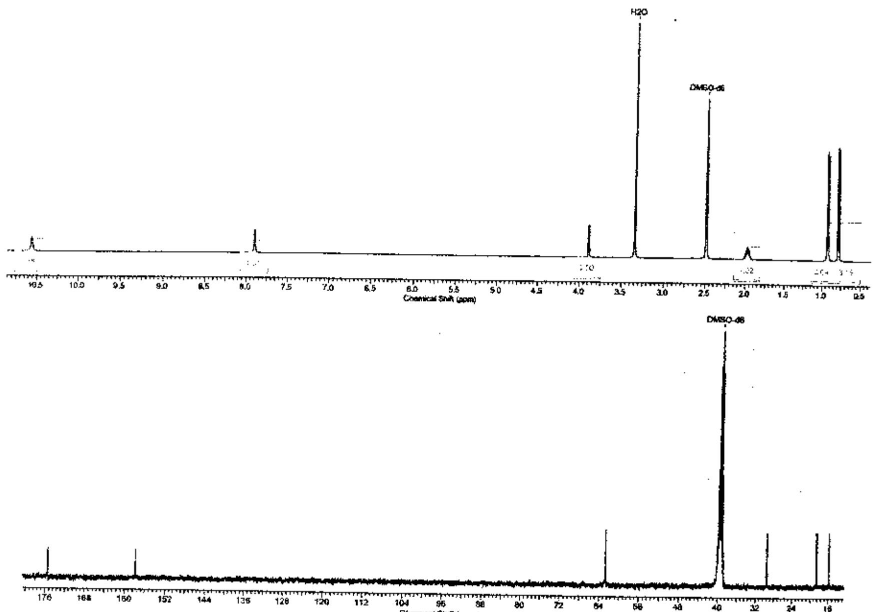
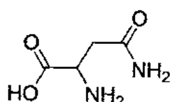


Fig. 4/2012. [1]H- and [13]C-NMR-spectra of hydantoins.

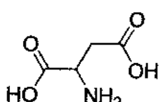
9. What natural biomolecules (proteins, nucleic acids, oligosaccharides, lipids, enzymes, glycoproteins, and vitamines) amino acid residues can be found in?

10. Give the symbols of chemical elements found in amino acids incorporated in proteins during translation.

11. Suppose you are given Asparagine (Asn) and Aspartic acid (Asp):



Asn



Asp

How many dipeptides can be formed from these amino acids? All possible dipeptides have been mixed and then heated for a long period of time in the presence of concentrated hydrochloric acid. Draw the structural formulae of all the reaction products.

–CH_2SH group is found as a side substituent in cystein. Draw Fischer jection of D- and L-isomers of cysteine and attribute the absolute configuration he stereo centers according to the R/S-nomenclature.

. Write down the equation of hydrolysis of an amino acid hydantoin.

The 47th Mendeleev Olympiad (2013)

Decomposition of hydrogen peroxide

(author – Chulkin P.V.)

Hydrogen peroxide is used as an oxidizing or weak reducing agent in organic and analytical chemistry as well as a disinfectant in medicine. When stored, hydrogen peroxide spontaneously decomposes, the process being significantly accelerated in the presence of various ions such as iodide. In this task, you will study the kinetics of catalytic decomposition of hydrogen peroxide.

The general plan

1. Standardization of $KMnO_4$ solution.

2. Determination of the decomposition reaction order in H_2O_2: investigation of the dependence of peroxide concentration on time by titrimetry and determination of the reaction order from the obtained plot.

3. Calculation of the rate constant of H_2O_2 decomposition: plotting the concentration dependence on time in appropriate coordinates.

4. Calculation of the reaction order with respect to iodide ion and derivation of the kinetic equation in the differential form.

5. Determination of KI concentration in an unknown solution by the kinetic method: investigation of the concentration dependence on time (based on the results of 8 titrations) followed by the calculation of the rate constant from the dependence revealed above and the kinetic equation derived above.

Reagents, glassware and equipment

Item	*Quantity*	*Label*
For each participant		
Laboratory stand	1 pc.	
Clamp	2 pcs.	
Volumetric flask	1 pc.	
Burette (for $KMnO_4$ and $FeSO_4$)	2 pcs.	
5 mL pipette (for H_2O_2)	1 pc.	
10 mL graduated pipette (for KI)	1 pc.	
25–50 mL beaker (for preparation of H_2O_2 solutions and filling the burettes with titrants)	3 pcs.	

300 mL bottle	5 pcs.	$KMnO_4$, H_2SO_4, KI, $FeSO_4$, $NaHCO_3$
Funnel (for the burettes)	2 pcs.	
Conical flask for titration	2 pcs.	
10 mL measuring cylinder (for H_2SO_4)	1 pc.	
Wash bottle with distilled water	1 pc.	
Rubber bulb	1 pc.	
Spatula	1 pc.	
Scaled paper (A4)	1 pc.	
$KMnO_4$ 0.050 M	200 mL	$KMnO_4$
$FeSO_4$ 0.10 M	200 mL	$FeSO_4$
H_2SO_4 (~10 %)	200 mL	H_2SO_4
$NaHCO_3$ (0.10 M)	300 mL	$NaHCO_3$
KI (0.10 M)	100 mL	KI
The solution of **X** (x M KI + 0.10 M $NaHCO_3$)	100 mL	X
H_2O_2 as "Hydroperite" tablet (complex of urea and H_2O_2)	2 tablets, 1.5 g each	H_2O_2

Procedure

a) Fill in the burettes with $KMnO_4$ and $FeSO_4$ solutions. Transfer a 5.00 aliquot of $FeSO_4$ solution into the titration flask. Add 5 mL of H_2SO_4 using the cylinder. Titrate with $KMnO_4$ solution until the mixture stops decolorizing (fig. 1/2013).

1. Write down the equation of reaction proceeding upon standardization. Calculate the precise concentration of $KMnO_4$.

b) Preparation of the working solution. Hydrogen peroxide oxidizes iodide in an acidic medium, thus the experiment should be conducted in an alkaline solution. Dissolve one "Hydroperite" tablet in $NaHCO_3$ buffer solution (one tablet contains about 0.6 g of H_2O_2). Transfer the solution in the 100 mL volumetric flask. Add KI solution in a quantity providing its concentration in the final solution of 0.001, 0.003, 0.005, 0.007, or 0.009 M (choose any of these values). Bring up to the mark with $NaHCO_3$ solution. Write down the KI concentration in the resultant solution.

Record the time when the working solution was ready with an accuracy of 1 min (use your own watch or laboratory clock).

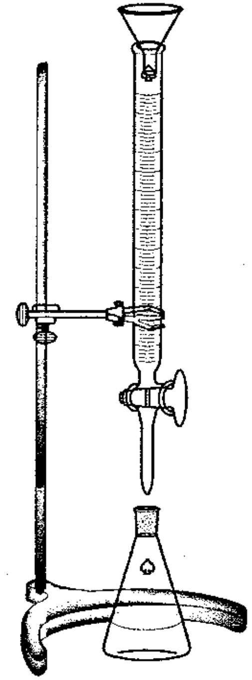


Fig. 1/2013. A typical titration setup.

c) The kinetic experiment is based on back titration of the reaction mixture aliquots removed after definite periods of time. First, an excess of the acidified permanganate solution is added to the titration flask. The unreacted permanganate is further titrated with the iron sulfate solution.

2. Write down the equations of all the reactions occurring upon addition of $KMnO_4$ to the aliquot. Calculate the amount of $KMnO_4$ needed for complete oxidation of H_2O_2 in a 5.00 mL aliquot. Write down the corresponding solution volume as V_{theor}.

Using the pipette, place $KMnO_4$ solution into the beaker (V_{theor} and extra 0.50 mL) and add 10 mL of 10 % H_2SO_4. Using the pipette, remove a 5.00 mL aliquot of H_2O_2 solution and put it into the titration flask. Rapidly add the $KMnO_4$ solutio from the beaker to the titration flask. Record the time with an accuracy of 10 Mix the flask contents and wait until the gas evolution is over.

Note. Gas evolution accompanies the H_2O_2 aliquot removal. Thus, H_2O_2 decomposes faster, the phenomenon making only marginal effect on the obtained results, which can be neglected.

Titrate the excess of $KMnO_4$ with the $FeSO_4$ solution. Write down the titrant volume consumed.

3. Calculate the H_2O_2 concentration in the aliquot used.

Repeat the procedure with at least 8 aliquots of H_2O_2 solution withdrawn after different periods of time. Always record the time with an accuracy of 10 s. Write down the results.

Note. Time intervals between the titrations of consecutively withdrawn aliquots should be within the range of 4 to 10 min.

4. Determine the reaction order of hydrogen peroxide decomposition on H_2O_2. If needed, plot the dependence of H_2O_2 concentration on time. Propose coordinates affording linear dependence of H_2O_2 concentration on time. Draw the plot in these coordinates on the graph-paper (Plot #1). Draw the straight line fitting the experimental points in the best possible way. You can skip the points looking as outliers (it is your decision!). Use the plot to evaluate the rate constant k' of H_2O_2 decomposition following the kinetic equation $w = k'[H_2O_2]^x$.

d) At concentration $[I^-]$ = 0.010 M, the rate constant k' in the equation $w = k'[H_2O_2]^x$ equals 6.9×10^{-4}. The dependence of the rate constant k' on I^- concentration is linear. Parameters of the complete kinetic equation of H_2O_2 decomposition can be determined if two values of the rate constant corresponding to two concentrations c(KI) are known. Write down the kinetic equation in the differential form with all the parameters as numeric values.

e) Wash the volumetric flask when finished with the above experiment. Dissolve the other H_2O_2 tablet in $NaHCO_3$ solution and transfer the obtained solution into the volumetric flask. Transfer the KI solution of the unknown concentration quantitatively into the same flask and bring it up to the mark with $NaHCO_3$ solution. Titrate as described in item *b* and the plot the results in coordinates providing for linear dependence of $c(H_2O_2)$ on time (Plot #2). Using the complete kinetic equation and Plot #2, calculate the amount of KI in the analyzed solution.

Answer the questions

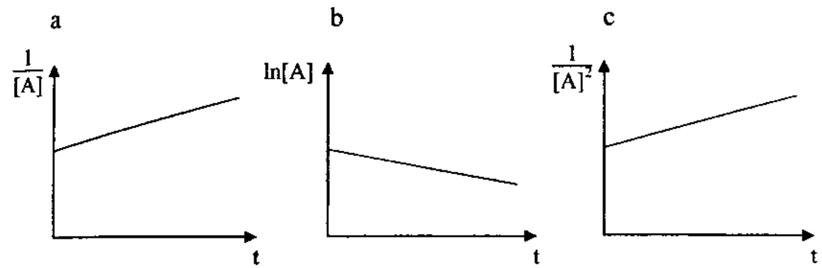
5. The reaction of catalytic decomposition of peroxide is carried out in weakly alkaline medium. When analyzing H_2O_2, the reagents ($KMnO_4$ and H_2SO_4) are added in an excess, simultaneously and rapidly. What side reactions can occur if:

5.1. an aliquot of H_2O_2 is directly titrated with the acidified $KMnO_4$ solution?

5.2. $KMnO_4$ solution is added first, which is followed by H_2SO_4?

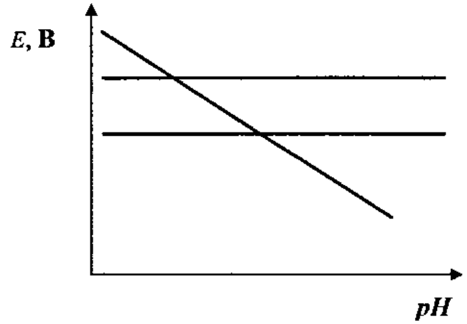
.3. $NaHCO_3$ is not added to the initial solution?

. Determine the reaction order on the substance A for each of the plots (a, b, c):



7. On the following graph, label each line (E *vs.* pH) with one of the following numbers:

1 – $E(MnO_4^-/Mn^{2+})$, *2* – $E(I_2/I^-)$, *3* – $E(Cl_2/Cl^-)$:



Is it possible to selectively oxidize I^- with $KMnO_4$ in the presence of Cl^-? If so, encircle the corresponding pH range.