Investigating the reaction between Potassium Permanganate - Oxalic Acid

Introduction

Often, the titration of oxalic acid ($H_2C_2O_4$) with potassium permanganate ($KMnO_4$) in acidic medium is a well know redox reaction which is performed by students at the higher secondary and undergraduate levels across the globe. The unknown concentration of one of the entities (that is, either $H_2C_2O_4$ or $KMnO_4$ in the supplied sample) can be determined by using this titration. Generally, $H_2C_2O_4$ solution is taken in flask to which about 10 mL - 15 mL of 2 M H_2SO_4 is added. The flask is heated and is titrated with $KMnO_4$ solution which is filled in burette.

Solid $KMnO_4$

For a glimpse of the titration between $KMnO_4$ and $H_2C_2O_4$ in acidic medium, the following youtube videos will be helpful.
https://youtu.be/aXsNaqY48hs, https://youtu.be/E6dGam2mEFQ
https://www.youtube.com/watch?v=HDUd4KqBKa8

Solid $H_2C_2O_4$

The current module presents opportunities to explore this reaction with respect to important reaction conditions. We hope such an investigation will help to develop insights about the reaction conditions.

Suggestions to implement the module

We strongly recommend that 2 students be grouped together for performing any given sub-part of the experimental module.

The current experimental module has two subparts. Depending of the availability of time, either all parts can be explored by all students or different subparts can be explored by different groups of students. At least 2 or 3 groups need to perform the same sub-parts of the experimental task to collect enough data points through multiple trials. The data points of all groups performing same subpart should be considered together for discussions.

For subpart 2, there are pre-lab questions so that students prepare themselves for the forthcoming task. It is important that students try to answer these questions before they begin their laboratory work. The role of the teachers in such situation is to facilitate discussions and not to provide answers. The lab task is then followed by post-lab questions.

Photo- credit
https://en.wikipedia.org/wiki/File:Potassium-permanganate-sample.jpg
https://en.wikipedia.org/wiki/File:Oxalic_acid_dihydrate.jpg

The subparts of the module are as follows-

1. Different oxidation states of Mn and their colors
2. To investigate effect of pH on reaction between $KMnO_4$ – $H_2C_2O_4$

1. Different oxidation states of Mn and their colors

Objective: Manganese (Mn, atomic number- 25) is a transition element which has several oxidation states and these oxidation states have different colors. Here, you will associate the oxidation states of Mn with the different colors in the solution.

In the current experiment, you will perform the tests described in the table below with $KMnO_4$ solution. Carefully observe the solution at the beginning prior to the test and also at the end of the test. Try to identify the ions that are likely to react and the likely state of Mn at the end of the reaction.

For teachers- Student will/should be able to correlate the colour of the manganese containing ions in the solution with the oxidation states and identify the predominant form of the manganese ion.

At your work bench

Test tubes	4	Measuring cylinder	2
Droppers	2		

Chemicals:

H_2SO_4 (2 M)		$NaHSO_3$ (0.02 M)	
$KMnO_4$ (0.01 M)		NaOH (0.1 M)	

Hazard symbols

 Corrosive to skin

 Harmful to skin

Write the colour of the solutions supplied to you:

$KMnO_4$ ---------- $NaHSO_3$ ---------- H_2SO_4 ---------- NaOH ----------

Observation Table-

Test	Colour observed after addition of $NaHSO_3$	Likely oxidation state of Mn based on colour
2 mL of 0.002 M $KMnO_4$ + 0.5 mL of 0.1 M NaOH + slowly add dropwise 0.02 M $NaHSO_3$ solution **Observe the color of the solution after addition of each drop, write your observations.**		

2 mL of 0.002 M $KMnO_4$ + 0.5 mL of 0.1 M NaOH + 1-2 mL 0.02 M $NaHSO_3$ solution		
2 mL of 0.002 M $KMnO_4$ + 1-2 mL 0.02 M $NaHSO_3$ solution		
2 mL of 0.002 M $KMnO_4$ + 0.5 ml of 0.05 M H_2SO_4 + 1-2 mL 0.02 M $NaHSO_3$ solution		

For teachers- This can also be just a demonstration of colors and perhaps the oxidation state of Mn can be given and students can be asked to write the corresponding half-cell and full equations.

Probably the link to a related video can be given- (The following videos were accessed on April 28, 2022)
https://www.youtube.com/watch?v=6UGrixD3yiQ
https://www.youtube.com/watch?v=jR0rO_ZpSXE
https://www.youtube.com/watch?v=u_R-aBlyCdw

2. To investigate the effect of pH on the reaction between $KMnO_4$ and $H_2C_2O_4$

In the current subpart, you will investigate whether you are able to perform titration between oxalic acid and potassium permanganate if the acidity of oxalic acid solution taken in flask is changed by adding different amounts of acid or base. In other words, you are changing pH of the system.

Instruction for students:
You will be working as pair for this subpart. Your teacher will form the pairs. Initially it is important to understand what you are investigating. Before you start your lab work, take 30 minutes to go through the pre-lab questions and try to answer them after discussing with another person in your group. If you are not able to answer all questions – please do not worry. However, try to answer most of these questions as it will help to think about the experiment in detail.

At your work bench

Pipette (10 mL)	1	Burette	1
Burette Stand	1	Conical Flask (100/50 mL)	1
pH Paper strips	1	Stop watch (least count)	1
Thermometer	1	Pipette Bulb	1
pH paper Strips			

Chemicals:

H_2SO_4 (2 M) 

Oxalic Acid (0.02 M) 

$KMnO_4$ (0.01 M) 

NaOH (0.1 M) 

Hazard symbols

 Corrosive to skin

 Harmful to skin

Pre-Lab Questions

1. Write all the equilibria corresponding to deprotonation of oxalic acid ($H_2C_2O_4$) in aqueous solution. (Oxalic acid pKa_1= 1.2 and pKa_2 =4.2). Also write equation for auto-protolysis of water.

2. Based on the equilibrium equations written by you in question 1,

   a) the prominent specie(s) of oxalic acid that will be present in aqueous solution is/are

   b) If the above aqueous solution is made highly acidic, the species(s) that will be predominantly present is/are

   c) If the above solution is made basic the species(s) that will be predominantly present is/are

3. Estimate the approximate pH of a 0.02 M aqueous oxalic acid solution. You need to use the information of the two pK_a's to estimate this pH. Explain your answer in brief. State the assumption, if any, needed to obtain the answer.

4. If you add 5 mL H_2SO_4 to 10 mL 0.02 M aqueous solution of oxalic acid, will the pH of the resultant solution be same or different from your estimate in question 3? (Also refer to your answer in question 2 (b)). Explain your answer in brief. State the assumptions, if any, needed to obtain the answer. (for sulphuric acid – first pKa is less than 1 (~ –3) and second pKa is 1.9)

5. Based on your answers for questions 3 and 4 explain, in brief why generally a large amount (excess) of sulphuric acid is added when we perform the $H_2C_2O_4$ - $KMnO_4$ titration?

6. Write the two half-cell equations and overall balanced equation for the redox reaction between $H_2C_2O_4$ and $KMnO_4$ in acidic medium.

7. Based on the stoichiometry of $KMnO_4$ – $H_2C_2O_4$ reaction under strongly acidic conditions (your answer in question 6), estimate the minimum volume of 2 M H_2SO_4 needed for complete reaction of 10 mL of 0.02 M oxalic acid with $KMnO_4$?

Laboratory task

1) Prepare six different flasks as indicated to you in the following table. Note the amount of oxalic acid taken ion each flask is same that is 10 mL.

	Volume of Oxalic Acid Solution (mL)	Other reagent to be added	
I	10	10 mL of 2 M H_2SO_4	
II	10	1 mL of 2 M H_2SO_4	
III	10	0.2 mL of 2 M H_2SO_4	
IV	10	0.0 mL of 2 M H_2SO_4	
V	10	add NaOH dropwise, shake the flask and continue adding NaOH till you observe pH ~ 7	Volume of NaOH used =
VI	10	add NaOH dropwise, shake the flask and continue adding NaOH till you observe pH ~ 12	Volume of NaOH used =

- For any titration use maximum 20 mL of $KMnO_4$.
- During course of titration, observe each flask carefully for the changes in colours / appearance of turbidity or formation of precipitate or any other changes during the titration. You should take photos of the flask at the time when you observe the change in the flask. These photos will help you recall the observations post experiment while answering the questions given as part of experiments and also as post lab questions.
- You are allowed to repeat each titration two times.

2) Using a pH paper, check the pH of each solution prepared initially before titration and also after you finish your titration. Note your observations in the observation table given below.
3) Heat each solution to 60-70 °C on a hot plate when you want to titrate it.
4) Add $KMnO_4$ solution dropwise manner. The titration will be considered to be complete only when you see a stable pink colour that persists for more than 2 minutes. You may face a situation where you may not get the pink color.

Observation Tables

flask	I	II	III	IV	V	VI
Initial pH						
Approximate $[H^+]$ concentration						
Final pH						
Approximate $[H^+]$ concentration						

flask	Changes in solution during the titration (in brief) w.r.t. to colour/appearance of turbidity/ formation of ppt	Volume of $KMnO_4$ solution (for stable pink colour as end point)	Approximate time taken for titration (mins.)
I			
II			
III			
IV			
V			
VI			

After you finish above tasks you need to answer the post laboratory questions given below. Discuss in your own group before you write the answers to these questions. Suppose there are three pairs who were allocated two of the above combinations then all these three pairs will sit together and discuss their answers.

Post Lab Questions

1. Copy the pH once gain in the following table. Based on the video or qualitative tests and the colours observed by you while performing the titration, write the likely state of manganese for the final pH

flask	I	II	III	IV	V	VI
Final pH						
Likely specie of Manganese						

2. You have identified the likely species of manganese at the final stage. You also know that initially that in $KMnO_4$ the oxidation state of Mn is…… (calculate and fill in the blank). You know various other entities present in the reaction flask. Write the corresponding balanced chemical equations explaining the observed color change and reaction that has happened in each flask. Often these reactions are going to be ionic reactions.

Flask	Chemical Equation(s)
I	
II	
III	
IV	
V	
VI	

3. In your opinion, the quantitative titration $H_2C_2O_4$ - $KMnO_4$ can be performed at which of the above pH ranges? Also state the pH ranges where this titration cannot be performed.

4. Based on your titration results obtained by you,
   a) state the minimum volume of 2 M H_2SO_4 which can be used for titration of 0.02 M $H_2C_2O_4$ with $KMnO_4$ solution.
   b) Compare this value to the value you wrote in pre-lab section (Q7). Do both values match or are these different? Explain your answer in brief.

5. $KMnO_4$ is commonly used as a disinfectant for skin infections in humans and animals, where it acts as an oxidizing agent. Here, normally a ten times diluted solution of 0.1 % $KMnO_4$ is used (solution should be light pink in color). In these biological systems, what pH conditions are prevalent? Using the observations made in this experiment, what colour change is expected on treatment of $KMnO_4$ with skin? What are the Mn-containing products formed in these conditions on $KMnO_4$ application?

Note: The following questions should be answered after a group discussion with the class after all students discuss their results.

6. From the above experiment can you list the variables that determine the outcomes (results/end point) in $KMnO_4$ – $H_2C_2O_4$ titration?

7. Based on the above experiment, list one or two other aspects of the $KMnO_4$ – $H_2C_2O_4$ reaction that you would like to investigate.

8. Can you suggest a small experiment that can be done to explore one of the aspects stated in Q7 above using the $KMnO_4$ – $H_2C_2O_4$ titration setup?