EXPERIMENT E4(II)

Determining the Rate Law: A Kinetics Study of Iodination of Acetone

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(Modified version of Kristen Spotz and University of Michigan General Chemistry Laboratory Manual)

I. OBJECTIVES

- Gain a quantitative understanding of kinetics.
- Determine the rate of a reaction, the order of the reaction with respect to the reactants and the value of the rate constant.
- Predict reaction times using an experimentally determined rate law.

II. INTRODUCTION

One factor influencing the rate of the reaction is the concentration of the reactants. Typically, as the concentration of the reactants increases so does the rate of the reaction. The actual relationship, however, can be quite complicated. Sometimes, doubling the concentration of a reactant will result in a doubling of the rate. For other chemical reactions doubling the concentration of a reactant might have no effect on the rate or it might result in a four – fold increase in the rate. It can be useful for the scientist to have understanding of the relationship between the concentration of the reactants and the rate of the reaction. For example, for a quantitative knowledge of reaction rates, scientists are able to gain insight into reaction mechanisms and even predict the time frame of a reaction. Detailed study by 1995 Nobel laureates F. Sherwood Rowland and Mario Molina of the rates of hundreds of chemical reactions provided insight into the role of chlorofluorocarbons (CFCs) in the depletion of the ozone layer (Figure 1). So, how do scientists determine the relationship between concentration and reaction rate and how are the results expressed in a useful form?

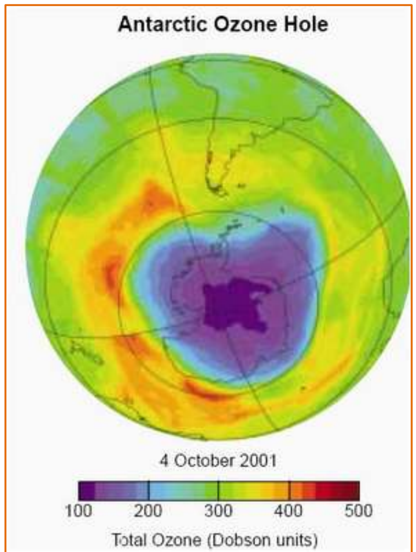


Figure 1:Earth's Ozone Layer Depletion.

III. BACKGROUND

A. The Rate Law

All the information needed to predict the rate of a given reaction is contained in the rate law, or the rate equation. Given the generic reaction in equation 1, the general form of the rate law would be given in Equation 2:

$$aA + bB \rightarrow cC + dD \qquad \text{Equation 1}$$

$$rate = k[A]^m[B]^n \qquad \text{Equation 2}$$

The rate constant, k, is specified for each reaction and is temperature dependent. The units for the k are dependent on the overall order of the reaction. The rate law also includes the concentrations of the reactants raised to the reaction orders, m and n. the values of m and n must be determined experimentally (as you will do in today’s experiment) and cannot be derived from the balanced chemical equation.

As an example, we will examine the reaction (equation3) and the experimental data (table 1) for the reaction of nitrogen monoxide and hydrogen gas to produce nitrogen gas and steam.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g) \qquad \text{Equation 3}$$

Exp #	$[NO]_{initial}$ M	$[H_2]_{initial}$ M	Initial rate M/s
1	0.1	0.1	1.23×10^{-3}
2	0.1	0.2	2.46×10^{-3}
3	0.2	0.1	4.92×10^{-3}

The first step in determining the rate law is to follow the example in equation 2 and write the general form of the rate law for the reaction (Equation 4)

$$Rate = k[NO]^m[H_2]^n \qquad \text{Equation 4}$$

The next step is to find the order for each reactant. In order to find the order with respect to hydrogen gas, experiment #1 and #2 are compared

$$\frac{Rate2}{Rate1} = \frac{2.46\times10^{-3}}{1.23\times10^{-3}} = \frac{k[0.10]^m[0.2]^n}{k[0.10]^m[0.1.]^n} \qquad \text{Equation 5}$$

The rate constants, k, and the concentrations of nitrite will cancel (along with the unknown m) leaving equation 6:

$$2 = 2^n \qquad \text{Equation6}$$

Mathematically, n=1. In terms of kinetics, this is interpreted to mean that the reaction is first order with respect to hydrogen gas. This result makes sense if we look back at table 1. Comparing experiment 1 and 2, if the concentration of nitrogen monoxide is held constant and we double the concentration of hydrogen, the rate of the reaction doubles.

The same process (Equation 5) is taken to determine the order with respect to nitrogen monoxide. From setting up the ration of experiments 1 and 3, the order with respect to nitrogen monoxide is determined to be second order. This means that if the concentration of hydrogen is held constant while doubling the concentration of nitrogen monoxide, the rate of the overall reaction quadruples. The overall order of the reaction (n+m) is 3.

Now that we know the order of the reaction, the next step is to know the value of the rate constant, k. the units for the k are dependent on the overall order of the reaction. Data from any experiment given in the table may be used to determine the rate constant. For example, using the data from experiment #1 results in Equation 7.

$$1.23\times10^{-3} M/s = k[0.10M][0.1.M]^2 \qquad \text{Equation 7}$$

Solving for the rate constant, the value is equal to $1.23M^{-2}s^{-1}$. The final rate law includes the value for both the rate constant and the orders of the reaction.

$$Rate = 1.23M^{-2}s^{-1}[H_2][NO]^2 \qquad \text{Equation 8}$$

Using equation 8 above, any initial concentration of hydrogen gas and nitrogen monoxide can be inserted into the rate law in order to predict the rate of the reaction.

In another similar example, the method involves a series of experiments in which the initial concentrations of some reactants are held constant and others are varied in convenient multiples in order to determine the rate law for that reaction. The following is the data for the gaseous reaction: 2NO(g) + Cl_2(g) = 2NOCl (g)

Experiment	Initial [NO]	Initial [Cl_2]	Initial Rate, M s^{-1}
1	0.0125 M	0.0255 M	2.27×10^{-5}
2	0.0125 M	0.0510 M	4.55×10^{-5}
3	0.0250 M	0.0255 M	9.08×10^{-5}

Show that the following rate expression applies: Rate = k $[NO]^2$ $[Cl_2]$
In general, set Rate = k $[NO]^m$ $[Cl_2]^n$ use data above to find m, n, & k.
$2.27x10^{-5}$= k $(0.0125)^m(0.0255)^n$ …………Eq.1
$4.55x10^{-5}$= k $(0.0125)^m$ $(0.0510)^n$ …………Eq.2
$9.08x10^{-5}$= k $(0.025)^m$ $(0.0255)^n$ ………..…Eq.3
Eq.2/Eq.1: 2 = 2^n , then n = 1
Eq.3/Eq.1: 4 = 2^m, then m = 2

The overall order of reaction = m + n = 3, first order with respect to Cl_2 gas & second order with respect to NO gas.
Using any of the equations, then k is solved:

k = 5.70 M^{-2} s^{-1}

Rate = 5.70 M^{-2} s^{-1} $[NO]^2$ $[Cl_2]$

B. The Iodination of Acetone

In today's experiment, you will be studying the kinetics of the reaction between acetone and iodine to form iodoacetone and iodide (Equation 9).

$$CH_3COCH_3(aq) + I_2(aq)(yellow) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)(colorless) \qquad \text{Equation 9}$$

The rate law will be determined by varying the concentration of acetone and iodine. To study reaction rates it is necessary to measure the concentration of reactants as a function of time at the start of the reaction (the "initial rate" in table 1), making kinetics studies typically difficult. In this particular experiment, however, the amount of acetone will be kept in vast excess with respect to the amount of iodine so that the concentration of acetone does not change appreciably during the course of the reaction. As a result, the rate of the reaction remains relatively constant throughout the course of the reaction. In other words, the "initial rate" that we need in order to determine the rate law will be equated with the average rate of the reaction. The equation used to find the average rate of reaction (equation 10) is found by measuring the change in iodine concentration divided by the time needed to react.

$$Rate = -\frac{-\Delta[I_2]}{\Delta t} = \frac{-([I_2]_{final} - [I_2]_{initial})}{\Delta t} \qquad \text{Equatin10}$$

The study of the reaction for the iodination of acetone is also made easy due to the color ranges of the solution. Iodine (I_2) is a pale yellow whereas the iodide ion (I^-) is colorless.---acid, which is introduced to the reactant solution as a catalyst, is also colorless. Therefore, changes in iodine concentration can easily be visualized. The time at which the pale yellow color of the initial solution turns clear indicates that the reaction is completed and that $[I_2]_{initial}$ =0 M.

IV OVERVIEW

Follow the overview carefully and summarize in 1-2 sentences in your report.

Results of Experiment E4(II) are mostly quantitative so you need to be precise in conducting the experiment and collecting the data. This is a group experiment but you must submit individual report along with the ALR of Experiment E4(I). Do not forget that the individual pre-lab exercises (PLE) due at start of this experiment.

<u>Safety Warning:</u> Safety rules & chemical waste disposal guidelines must be followed in order to prevent personal injury and to protect yourself, others & the environment. If you are unable to observe the rules then you are at risk of been dismissed from the lab.

<u>Caution:</u>
- Do not dump any of the reagents down the sink!
- Discard the waste in an appropriate waste container under the supervision of your instructor!
- Do not allow solutions to come in contact with your skin! Wear gloves & goggles!

(Silver ion, Ag^+, will color your skin. Some ions are TOXIC).
- Separate chemical waste of: Acetone, HCl, solutions of ($CuSO_4$, I_2, MnO_2), H_2O_2, & solids to recycle Fe & Zn.
- <u>Do not waste chemicals and repeat trials not required.</u>

--- following a procedure for the preparation of solution 1, you will devise your own experimental protocol for creating solution 2,3 and 4 in order to determine the order with respect to acetone and iodine, the value of the rate constant, and predictions concerning reaction rate. Remember for Step 6 in the procedure decide with your partner by proposing to the TA how to change the concentrations of each of the reactants by varying the volume of each in a manner to yield easily the values of the reaction orders m & n, as illustrated by the example in the manual for this experiment. Have your TA approve the proposal before proceeding. The uncompleted data table shown in this procedure is a guideline table that you may use to propose your work for this part of the experiment and then complete the table. **The data table at the end of the procedure must be completed as part of the PLE & PLQ, but ahead of the lab session. Then your TA inspects the table and if approved you can proceed with this experiment.**

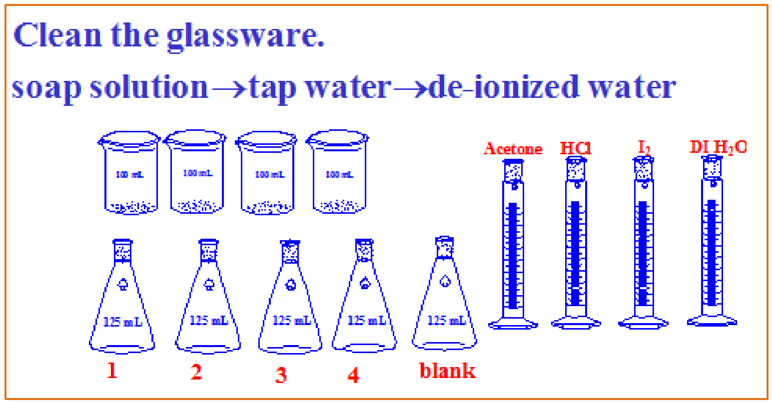
V. EXPERIMENTAL PROCEDURE

"Students work in pairs / Copy & complete the data table in this section under Calculations & Data Recording, as part of your PLE & also PLQ (show calculations & record the data in the table before starting the experiment). Each student must complete one design reaction.

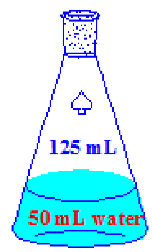
Chemicals used	Materials used
4 M Acetone (100 mL)	50 mL graduated cylinders (4)
1M HCl (100 mL)	100 mL Beakers (4)
0.00118 M Iodine (100 mL)	125 mL Erlenmeyer flasks (5)
De-ionized water (DI H_2O)	Plastic pipet (4)
	Stop – watch
	Stir – plate and stir bar (optional)

"Make sure you take photos of your favorite lab work for use in your final PPT presentation assigned by your TA about one of the experiments E1-E5"

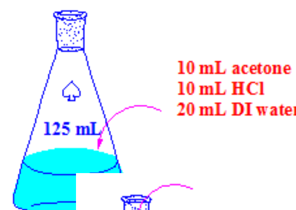
1. Thoroughly clean four 100-mL beakers, four 50-mL graduated cylinders [one cylinder for each acetone (reactant B), HCl solution (acts as catalyst only), I_2 (iodine reactant A), & de-ionized water (for dilution)], and five 125-mL Erlenmeyer flasks (for 4 samples & 1 blank) with soap and water. Rinse all the glassware with deionized water and allow drying. Label one of each beaker and graduated cylinder with the following: "Acetone", "HCl", "I_2", "DI H_2O". Label four of Erlenmeyer flasks with number 1 – 4 and label the flask "blank" (see figure below). Rinse each beaker/graduated cylinder with 2 – 3 mLs of the solution named on the label. Pour approximately 50 mL of the appropriate solution into the labeled 100-mL beakers.



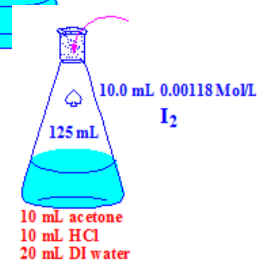
2. Prepare a blank that you will use for a color comparison. The blank should consist of 50 mL of water in a 125-mL Erlenmeyer flask. The changes in the clarity of the solution colors during reactions for samples 1 – 4 will be compared to the clarity of this blank DI H_2O sample. To view colors clearly, place each flask during the reactions over white paper.



3. With the appropriately labeled 50 mL graduated cylinders, add 10.0 mL of acetone, 10.0 mL of HCl and 20.0 mL of deionized water into a clean 125 mL Erlenmeyer flask (labeled solution #1).



4. Get your stop watch ready, measure 10.0 mL of 0.00118 M iodine into the clean "I_2" graduated cylinder. Place the Erlenmeyer flask (solution #1) onto the stir – plate and drop carefully a stir bar into the solution. Set a stir plate to a medium setting. Get the stop watch started as soon as you quickly pour all the iodine solution into the Erlenmeyer flask. Immediately being timing the reaction as soon as all the iodine has been transferred to solution #1. The solution will appear yellow due to the presence of iodine. The color will fade as the iodine react with the acetone. Record the time when the color of iodine just disappears by comparison with the blank. Record the volumes of acetone, HCl, iodine and H_2O for solution #1 in the data table at the end of this section. Do not use the heating mode on the stir plate (do not heat sample).



5. Repeat steps 3 and 4 only once, using same amount of chemicals. Calculate the percent difference (of times to complete the reactions) between the trials. When you careful, the percent difference is less than 5%. Unfortunately, to reduce chemical waste you cannot do more than 2 trials total for each of the 4 samples, so work diligently.

6. With your partner, decide how to alter the composition of solution #1 to determine the order with respect to iodine (solution #2) and the order with respect to acetone (solution #3). The only requirement is that you must maintain a total volume of 50 mL and the volume of HCl must be 10 mL. After showing your proposal to your instructor, carry out the reactions for solutions #2 and #3 exactly as described for solution #1. If you are careful then no need to repeat trials to 95% accuracy.

7. For your final reaction, devise solution #4 using reactant volumes that you have not previously used. Remember, the total volume must remain 50 mL and that 10 mL of the total volume must be 1 M HCl. Record the time of the reaction.

8. Summarize all your data by completing the attached table in the next section. Using the data to determine the reaction rate order (m) with respect to I_2, the reaction rate order (n) with respect to acetone, and the rate constant (k). Then write the final equation for the rate expression.

Calculations & Data Recording: Every group/student must complete data below as part of the pre-lab & before the start of the lab session. Then show that to your ta's for his approval before proceeding with the experiment. Include this section in both PLE & PLQ.

$$I_2(aq) + CH_3COCH_3(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

$$aA\ (aq) + bB\ (aq) \rightarrow cC\ (aq) + dD\ (aq) + eE\ (aq)$$

$$R_A = -\Delta[I_2] / \Delta t = -([I_2]_{final} - [I_2]_{initial}) / (t_2 - t_1)$$

Or in general: $R_A = k\,[A]^m\,[B]^n$

where [A] & [B] are initial conc. of I_2 & acetone consecutively at time -0- seconds.

$R_A = k\,[A]^m\,[B]^n$ …….. Eq.1, but in dilution $C_{conc} . V_{conc} = C_{dil} . V_{dil}$ ……….. Eq.2

or $C_{dil} = C_{conc} . V_{conc} / V_{dil}$ ………… Eq.2

but $R_{A1} = k_1\,[C_{A1}/V_{A1}]^m\,[C_{B1}/V_{B1}]^n$ or

$R_{A2} / R_{A1} = (k_2/k_1)\,[C_{A2}/V_{A2}]^m\,[C_{B2}/V_{B2}]^n / ([C_{A1}/V_1]^m\,[C_{B1}/V_{B1}]^n)$ ……….. Eq.3

Using Eq.2 into Eq.3 and applying the equations above at constant temperature ($k=k_1=k_2$) to data of Sample #1, #2 & 3, to get the reaction order m, n & the reaction rate constant k.

Remember $V_1 = V_2 = V_3 = V_4 = V_{dil} = 50mL$, while V_{conc} is the proposed design volumes X_i or Z_i in the table below so the distilled water volume is $Y_i = 50 - X_i - Z_i - 10mL$, and the starting concentrations C_{conc} are given below for each solution.

DATA TABLE: **Proposed lab work to determine the reaction rate orders m & n and the reaction rate constant k.**

SAMPLE #	**4M Acetone mL**	**H_2O mL**	**1M HCl mL**	**0.00118 M I_2 mL**	**Total Vol. mL**	**Initial M Acetone in 50mL Moles/L**	**Initial M I_2 in 50mL Moles/L**	**Trial 1 Rxn time s**	**Trial2 Rxn time s**	**Avg. Rxn time s**
1	10.0	20.0	10.0	10.0	50.0	?	?	?	?	?
2	X1	Y1	10.0	Z1	50.0	?	?	?	?	?
3	X2	Y2	10.0	Z2	50.0	?	?	?	?	?
4	X3	Y3	10.0	Z3	50.0	?	?	?	?	?
BLANK	0	50.0	0	0	50.0	Compare sample solution color to water sample transparent color				

Notes:

► The total volume should be 50.0mL, so Y values should be the difference between 50.0mL and what you proposed for the other solutions.

► Initial concentrations are shown at time 0s inside the 50.0mL solution and not the starting concentrated stock solution. Use $V_1 x C_1 = V_2 x C_2$ to get C_2

► The initial concentration. HCl acts as a catalyst and will not appear in the reaction rate expression.

► Sample #4 is to be used for the last part of the Step 7.

► At the end do not forget to write into the **PLQ** the complete reaction rate with values of m, n & k in the rate expression. It is OK to copy and complete the above table into **PLE or PLQ** to get the instructor's approval prior to starting the experiment, then enter the results on the same table after completing the experiment.

►When experiment is complete, remove the stir bar from the reaction flask using the metal side of a wire brush and do not discard the stir bar in waste containers or sink. If you do then you will remain in lab until you recover the stir bar and give to instructor or you will receive no credit for the experiment.

ALSO, RECORD YOUR RESULTS ON THE DATASHEET FOR THIS EXPERIMENT

E4(II): Determining the rate law: a kinetics study of the iodination of acetone

Name:	**Lab instructor:**
Date:	**Lab section:**

VI. PRE-LABORATORY EXERCISES (PLE)

1. According to your text book, what are the four factors that affect the rate of a chemical reaction? Which of these factors will be studied in this experiment?

2. Distinguish among the following terms: initial rate, average rate, and instantaneous rate.

   Which of these rates would you expect to have the largest value? Explain.

   Which of the rates are typically used to determine the rate law for a reaction?

   Which of these rates will we use to determine the rate law for a reaction?

3. Use equation 9 to predict the initial rate if $[NO]_{initial}$=0.30 M and $[H_2]_{initial}$=0.15 M.

   What would happen to the initial rate of the reaction if $[NO]_{initial}$ =0.60 M and $[H2]_{initial}$=0.15 M instead. Does your result make sense in terms of the order of the reaction?

4. Assuming that concentrations are expressed in moles per liter and time in seconds, what are the units of the rate constant, k, for an overall first order rate law? Show your work.

   What are the units of k for an overall second order rate law? Show your work

   Using these two rate constants as examples, write a general rule to explain how the units of the rate constant depend on the overall order of the rate law.

5. Write the general form of the rate law for the reaction in Equation 9.

E4(II): Determining the rate law: a kinetics study of the iodination of acetone

Name:	Lab instructor:
Date:	Lab section:

VII. RESULTS AND POST-LABORATORY QUESTIONS (PLQ)

"Use the following tables or the table at the end of the procedure to record your calculations and data." Also, the students of each group must record their experimental raw data on one datasheet of page 11, then copy it (photocopies ok) and include it with this PLQ. In addition, students must complete all the sections on this PLQ.

	Solution #1	Solution #2	Solution #3	Solution #4
Volume, 4.0 M acetone				
Volume, 1 M HCl				
Volume, 0.00118 M iodine				
Reaction time, trial 1				
Reaction time, trial 2				
Average reaction time				

For solution #1, only record the times for the two trials within 5%.

Summarize your results as in table 1 in the background:

Solution	$[\text{Acetone}]_{\text{initial}}$ (M)	$[\text{iodine}]_{\text{initial}}$ (M)	Initial rate (M/s)
1			
2			
3			
4			

" be sure to account for your dilution to 50 mL.
" use Equation 10 in Background.

1. Determine the rate law (including the values for the orders of the reaction and the value for the rate constant with units) for the reaction studied in this experiment. Show all your work.

2. Use the rate law to make a prediction for theoretical initial rate of the reaction for solution #4. How does it compare to the experimental initial rate for solution #4?

3. Why is it important to keep the total volume of solutions #1-4 at 50 mLs? If more water had been introduced to one of the solutions (giving a total volume of 60 mLs), would you expect the reaction rate to increase or decrease? Explain.

4. The following reaction occurs without a change in the color. $2A(g)+B_2(g)\rightarrow 2AB(g)$

   a. How could you monitor the concentration of the reactants and products?

   b. How would you determine the reaction orders?

   c. How would you find the rate constant and the units for the rate constants?

SAMPLE DATASHEET FOR A LAB SECTION

Print this datasheet and bring it with your ALR report, record your raw experimental data on it, then attach it to your individual PLQ.

VC211 EXPERIMENT E4(II) DATASHEET: DETERMINING THE RATE LAW

TA: ____________ LAB ROOM: ______

$I_2(aq) + CH_3COCH_3(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$

$aA + bB \rightarrow cC + dD + eE$ *Rate = k [A]^m[B]^n*

Procedure Part ----------→ GROUP EXPERIMENT BUT EACH STUDENT MUST DESIGN, PREPARE & TEST ONE SAMPLE. SUBMIT INDIVIDUAL REPORTS

Compare color to clarity of blank 50 mL DI H_2O

GROUP #	NAME Chinese	ID	SAMPLE #	1M HCl mL	4M Acetone X mL	D-I Water Y mL	0.00118M Iodine Z mL	INT. M Acetone Moles/L	INT. M Iodine Moles/L	TRI. 1 RXN. Time t1 (s)	TRI. 2 RXN. Time t2 (s)	AVG. RXN. Time t_{avg} (s)	RATE CALCULATIONS m	n	k
			EXAMPLE	10	10	20	10								
1			1												
1			2												
1			3												
1			4												
2			1												
2			2												
2			3												
2			4												
3			1												
3			2												
3			3												
3			4												
4			1												
4			2												
4			3												
4			4												
5			1												
5			2												
5			3												

IMPORTANT NOTES:

- **Each student must do one reaction of entire E4(II)**
- **Clean all glassware and rinse with distilled water**
- **Use graduated cylinders to measure volumes directly**

From stock solutions, do not use beakers

- **Must stir reaction without heating & splashing starting low setting**
- **Compare reaction color change to blank water sample – glassware over white paper**
- **Must not dispose stirrer rod in sink or waste container**

  You will be penalized heavily if you do not follow
- **Work safely & dispose chemicals in waste container**
- **Must follow chemical disposal instructions: E4(I) waste in one large beaker (no rinse water), then remove solids into its own waste container, then drain solution into inorganic waste container, while E4(II) waste in another beaker then remove stirring rod and place on top of stirrer machine pan then dispose the solution in organic waste container**