Chemical Kinetics: A Preview

Chemical kinetics is the study of the rates of chemical reactions, the factors that affect these rates, and the reaction mechanisms by which reactions occur.

Reaction rates vary greatly – some are **very fast** (e.g., combustion) and some are **very slow** (e.g., disintegration of a plastic bottle in sunlight).

SAFETY WARNING: CAUSTIC CORROSIVE TOXIC CHEMICALS & PRESENCE OF FLAME/HEAT.

1. **YOU MUST WEAR SAFETY GOGGLES ALL THE TIME.**
2. **MUST HANDLE THE CHEMICALS & HEATING EQUIPMENT VERY CAREFULLY, AVOID CONTACT WITH SKIN, RINSE WITH PLENTY OF WATER IMMEDIATELY UPON CONTACT.**
3. **MUST DISPOSE WASTE CHEMICALS AS DIRECTED & PLACE IN THE APPROVED WASTE CONTAINERS.**

4. YOU MUST OBEY ALL THE SAFETY RULES OR YOU MUST LEAVE THE LABORATORY IMMEDIATELY.

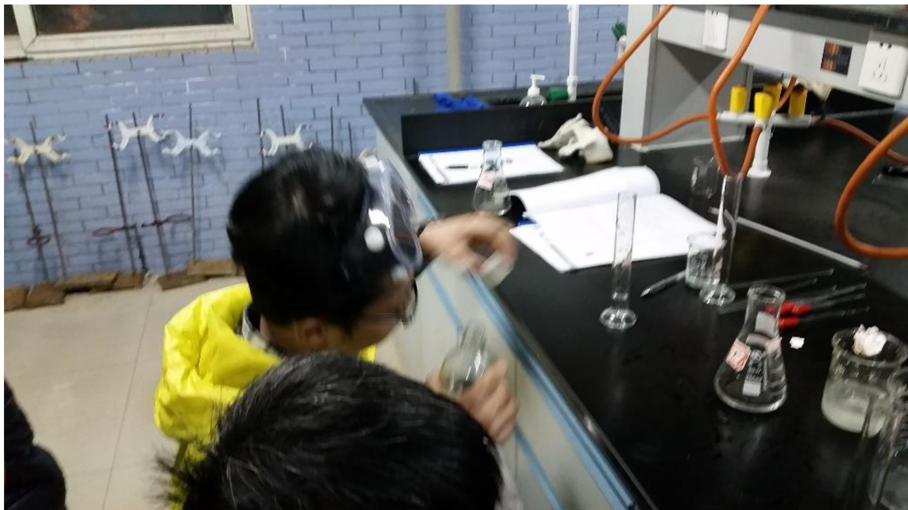
SAFETY HIGHLIGHTS

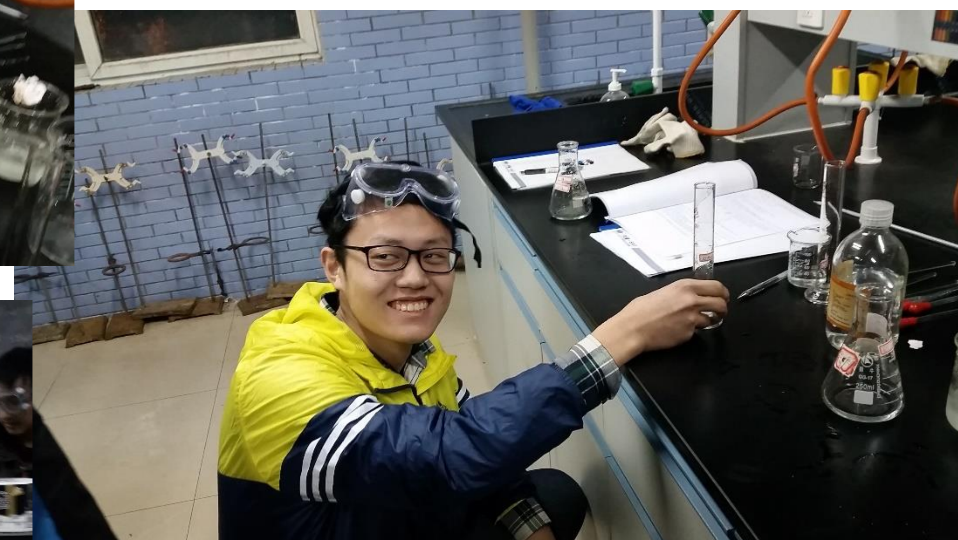
☐YOU ARE RESPONSIBLE FOR YOUR OWN SAFETY FIRST THEN OTHERS
☐BROKEN GLASS, PREVENTION& DISPOSAL ☐HOW TO WASH & RINSE GLASSWARE ☐WEAR GOGGLES & LAB COATS
☐KEEP GLASSWARE AT LEAST 20cm AWAY FROM EDGE OF BENCH
☐CLUTTER (MESS)
☐CHEMICAL WASTE & DISPOSAL (ORGANIC, INORGANIC &, CORROSIVES, & SOLIDS) ☐WASTING CHEMICALS BE CONSERVATIVE & PROTECT ENVIRONMENT☐IMMEDIATELY STORE AWAY STOCK CHEMICALS (COVER ON TIGHTENED & TOP BENCH)
☐SAFETY RUBBER GOLVES (CORROSIVE LIQUIDS RESISTANT & SOLVENTS RESISTANCE)
☐SAFETY CLOTH GLOVES & TONGUES: HEAT PROTECTION, HOT PLATES, & BURN PROTECTION ☐FIR HAZARDS & PROTECTION (EXTINGUISHERS) ☐SPATULAS ☐CHEMICAL TRANSPORTATION PROHIBITED, NOT EVEN ALLOWED TO TAKE OUTSIDE THE DOOR

HANDLE/DISPOSE BROKEN GLASS CAREFULLY & USE SAFETY GLOVES UNDER SUPERVISION OF THE INSTRUCTOR

BE CAUTIOUS WORKING IN WET AREAS & MOP/AVOID THAT AREA WHENEVER POSSIBLE

SAFETY VIOLATION: IMPROPER WEARING OF GOGGLES





*** DO NOT WASTE CHEMICALS.**
*** DO NOT REPEAT TRIALS MORE THAN INSTRUCTED.**
*** DO E4(I) EXPERIMENT FIRST, EACH TWO STUDENTS IN A GROUP MUST DO THE ENTIRE EXPERIMENT AS INSTRUCTED BY E4(I) & CANVAS.**
*** DO E4(II) EXPERIMENT NEXT AS INSTRUCTED BY E4(II) & CANVAS. EACH GROUP DO THE ENTIRE EXPERIMENT WHERE EACH INDIVIDUAL IN A GROUP MUST DO 1 SAMPLE REACTION REPEATED ONCE ONLY.**
*** SHARE RESULTS WITH YOUR GROUP AND COMPLETE INDIVIDUAL REPORTS.**

Predicting Reaction Rates

Variables of control are:

***Concentrations of reactants*: Reaction rates generally increase as the concentrations of the reactants are increased.**

***Temperature*: Reaction rates generally increase exponentialy as the temperature is increased.**

***Surface area*: For reactions that occur on a surface rather than in solution, the rate increases as the surface area is increased.**

Catalysts are substances that speed up a reaction but emerge unchanged by the reaction. How catalysts work is covered later in the chapter.

Introduction to Kinetics:
Factors That Affect the Rate of Reaction
Determining the Rate Law:
A Kinetics Study of the Iodination of Acetone

Objectives:

1. Be able to list and rationalize the factors that affect the rate of reaction.
2. Explain various scenarios using the factors that affect reaction kinetics.
3. Gain a quantitative understanding of kinetics.
4. Determine the rate of a reaction, the order of the reaction with respect to the reactants and the value of the rate constant.
5. Predict reaction times using an experimentally results of the rate law.

Introduction to Kinetics:
Factors That Affect the Rate of Reaction

Career	Application	Fast or slow
Biologist	Preservation or decomposition of specimens	
Chemical Engineer	Production rates & cost analysis	
Civil Engineer	Concrete and asphalt curing rates	
Doctor	Medication or toxics effecting the body	
Museum Curator	Dating, restoration, preservation of artifacts	
Restaurant Owner	Food spoilage, safety, & preservation (via cooling)	
Computer Engineer	Speed of calculation (GHz etc.)	

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

The Rate Law for RXN: $aA + bB \rightarrow cC + dD$

Rate of Disappearance of A = Reaction Rate =

$$-R_A = d[A]/dt = v = k[A]^m[B]^n$$

Where m and n are determined experimentally.

k = Reaction Rate Constant (its units depends on reaction).

Arrhenius Equation: $k = f\, e^{-Ea/RT}$

Where f is frequency factor, Ea is activation energy, R is gas constant, and T is the absolute temperature

Rate Laws

The *values of the exponents* in a rate law establish the **order of a reaction**

For reactant A,

Rate = $k[A]^m[B]^n$

if $m = 1$, reaction is first order in A

if $m = 2$, reaction is second order in A

- The proportionality constant, ***k*, is the rate constant** and its value depends on the reaction, the temperature, and the presence or absence of a catalyst.

EOS

- Reaction rate constant exponentially proportional to temperature (Arrhenius Equation).

Introduction to Kinetics:
Factors That Affect the Rate of Reaction

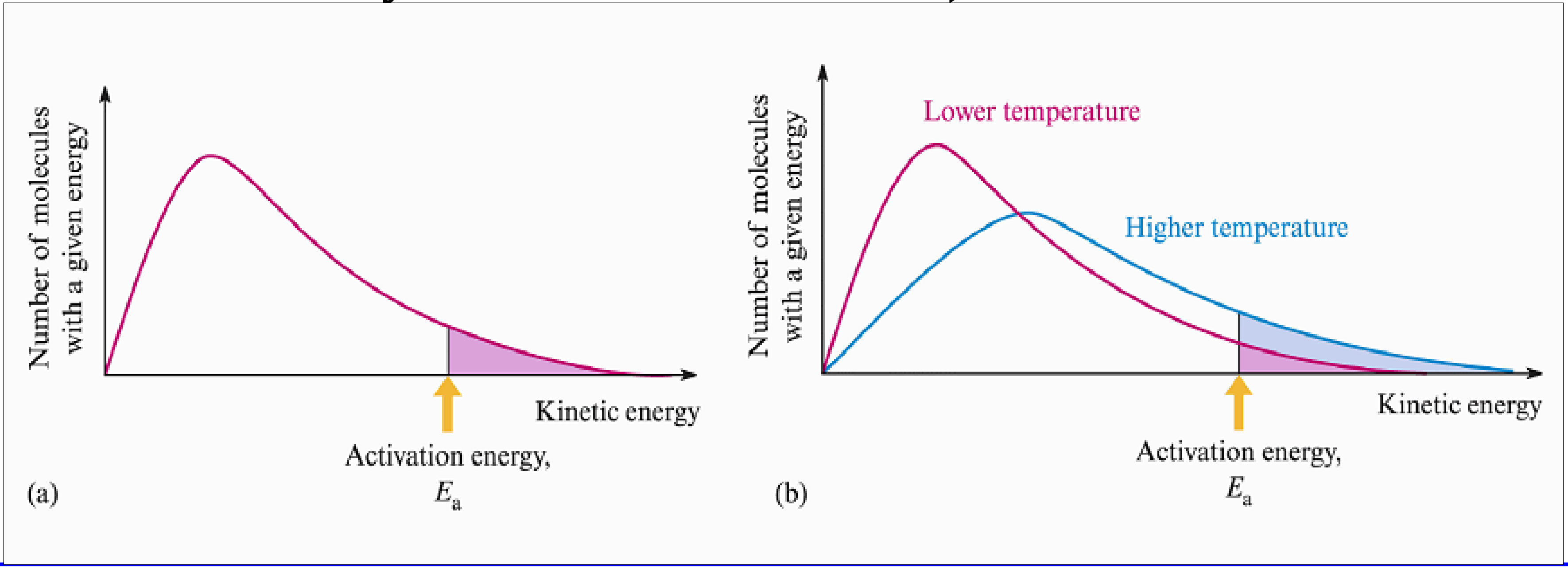
A. Effect of Changing the Concentration of Reactants:

Solid:	**Effect of Changing the Surface Area**
Gas:	**Pressure of the Gas**
Liquid:	**----------**
Solution:	**Concentration of the Reactant**

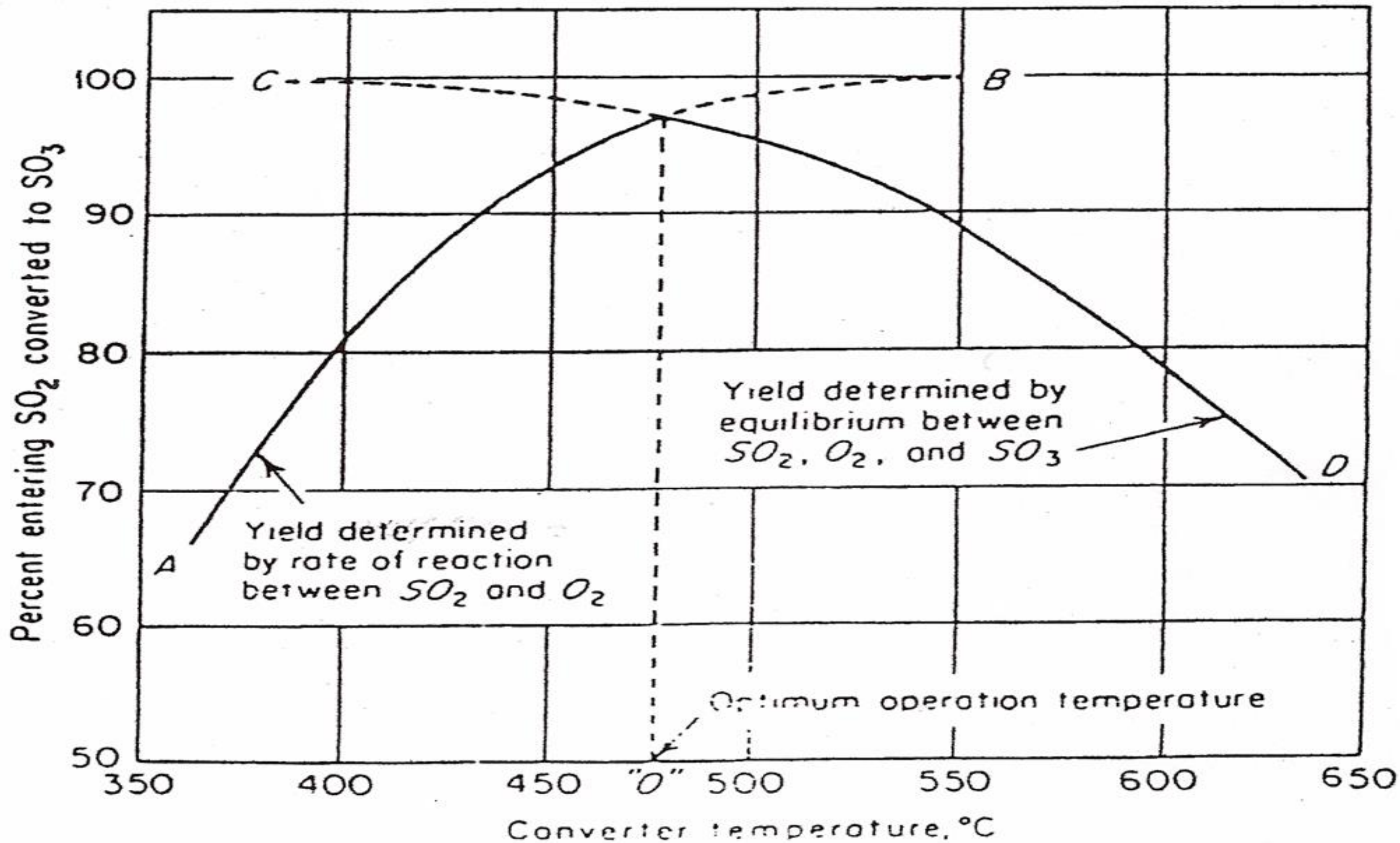
Introduction to Kinetics:
Factors That Affect the Rate of Reaction

B. Effect of Changing the Temperature:

(According to thermodynamics for reactions at equilibrium, K_{equil} decreases with increased temperature so the rate of reaction from thermodynamics view decreases). See next slide.



AUTOMOBILE CATALYTIC CONVERTER OPTIMUM DESIGN

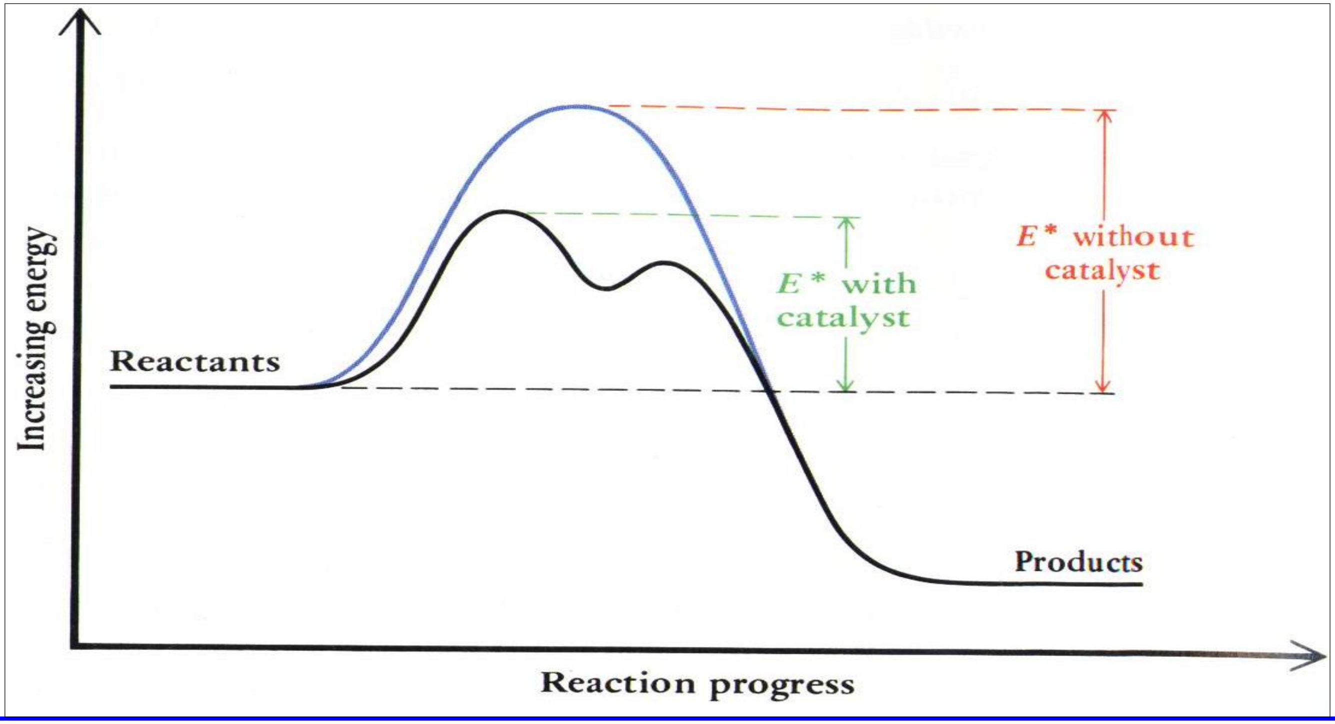


Determination of optimum operation temperature in sulfur dioxide converter.

Introduction to Kinetics:
Factors That Affect the Rate of Reaction

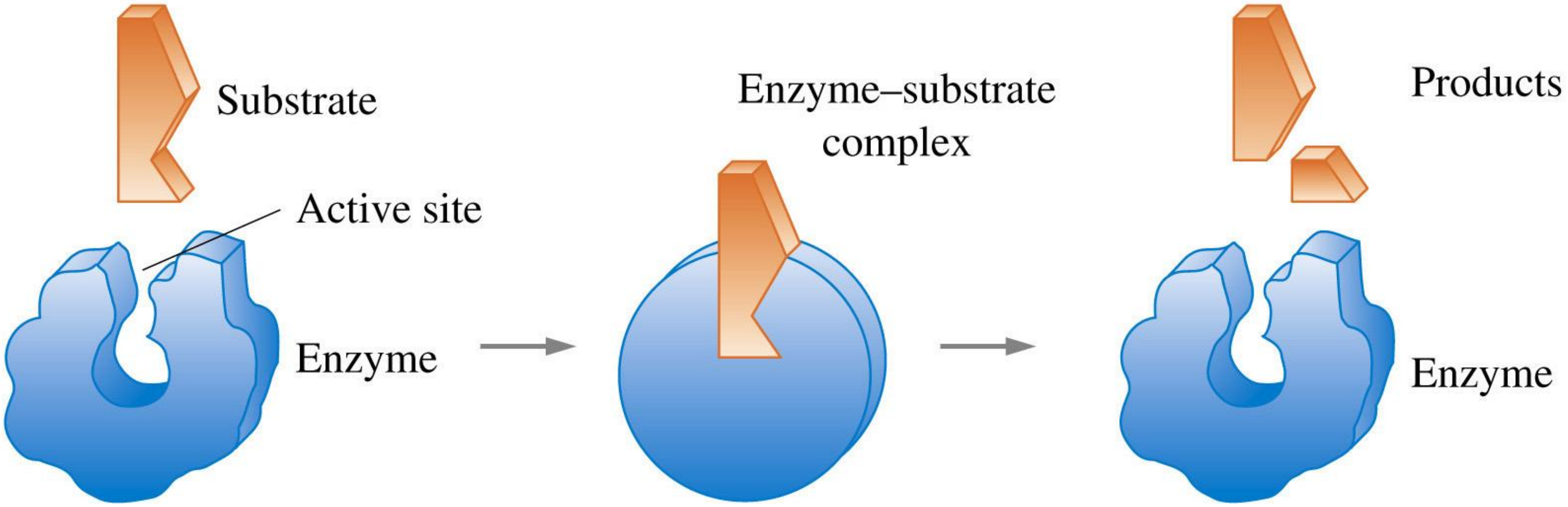
C. Effect of Adding a Catalyst:

Catalyst does not get consumed by the reaction but it donates or absorbs electrons, hydrogen ions or hydroxide ions (see Laboratory Manual, experiment E4(I))



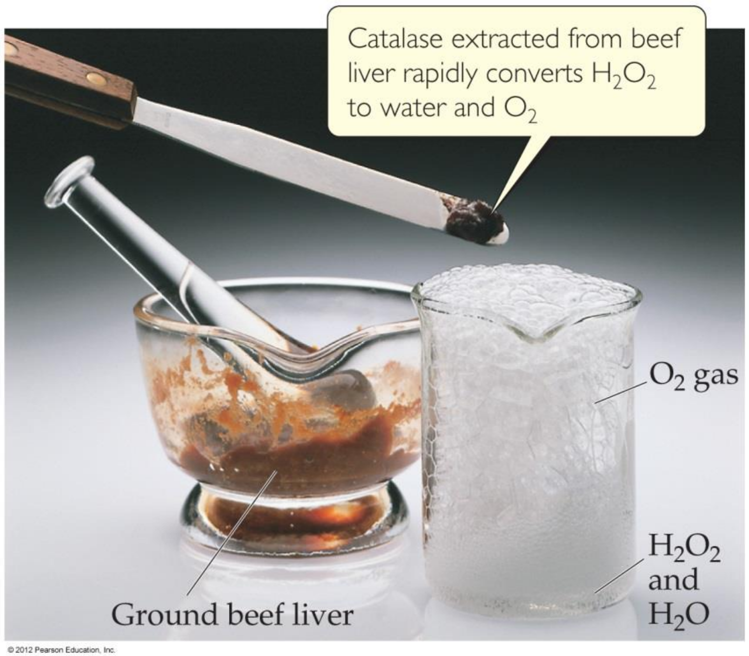
Enzyme Catalysis

Enzymes are high-molecular-mass proteins that usually catalyze one specific reaction—or a set of quite similar reactions—but no others

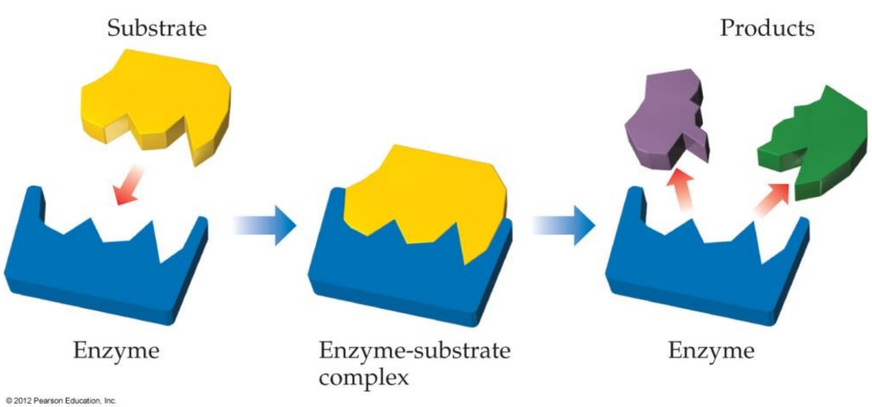


Enzymes are catalysts not consumed during reaction

Enzymes



- Enzymes are catalysts in biological systems.
- The substrate fits into the active site of the enzyme much like a key fits into a lock.



VC211 EXPERIMENT E4(I) DATASHEET: KINETICS FACTORS AFFECTING REACTION RATES

	SECTION: ________			TA: ______________			EACH 2 STUDENTS COMPLETE ENTIRE E4(I) EXPERIMENT			
			GROUP EXPERIMENT BUT EACH TWO STUDENTS DO ENTIRE EXPERIMENT. SUBMIT INDIVIDUAL REPORT							
	PROCEDURE PARTS →		A	A	B	B	C	C	E	E
			CONCENTRATION EFFECT		SURFACE AREA EFFECT		TEMPERATURE EFFECT		ADDING CATALYST EFFECT	
GRP	NAME	ID	EGGSHELL RXNS		COLOR CHANGE $CuSO_4$ @ 80^0C		COLOR CHANGE $CuSO_4$ & 0.05g Zn		10mL 6% H_2O_2 & 0.05g MnO_2 POWDER	
#	Chinese		1M HCl	6M HCl	0.2g Fe Wire	0.2g Fe Powder	Ice Cold	Hot @ 80^0C	80^0C, in 30-40s	10mL ICE AFTER 30-40s
	NOTES →		Add no more than 10 drops		Use available cylinder to measure 5.0 mL and the available hot water bath		Use available cylinder to measure 5.0 mL and the available hot water bath		To avoid back flash avoid direct view and place the sample small beaker inside larger beaker	
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- **IMPORTANT NOTES**
- **Each two students will do entire E4(I)**
- **Clean all glassware and rinse with distilled water**
- **Use 5mL $CuSO_4$ and hold beaker down with hand while wearing cloth gloves**
- **Use hot water bath for heating to 80^0C**
- **Handle hot beakers with tong or cloth glove**
- **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 containers, while disposing E4(II) waste into another beaker then remove stirring rod and place on top of stirrer machine pan then dispose the solution in organic waste container**

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

TA: ______________ LAB ROOM: ________

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

$$aA + bB \rightarrow cC + dD + eE \qquad \textit{Rate} = k\,[A]^m[B]^n$$

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												
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- **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

PART A: Introduction to Kinetics:
Factors That Affect the Rate of Reaction

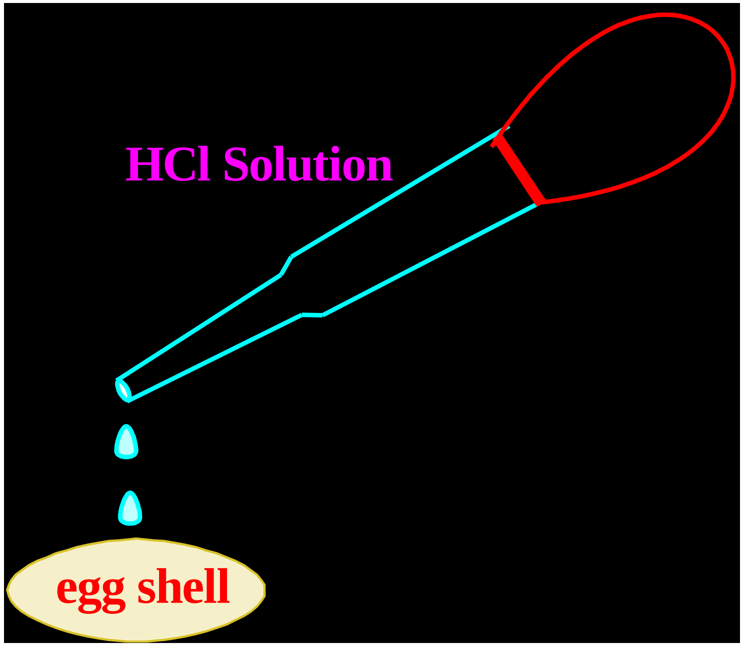
Procedure: DO NOT USE MORE THAN 10 DROPS

ALWAYS HANDLE HOT BEAKERS WITH CLOTH GLOVES

Part A: Effect of Changing the Concentration of Reactants

1M HCl

6M HCl

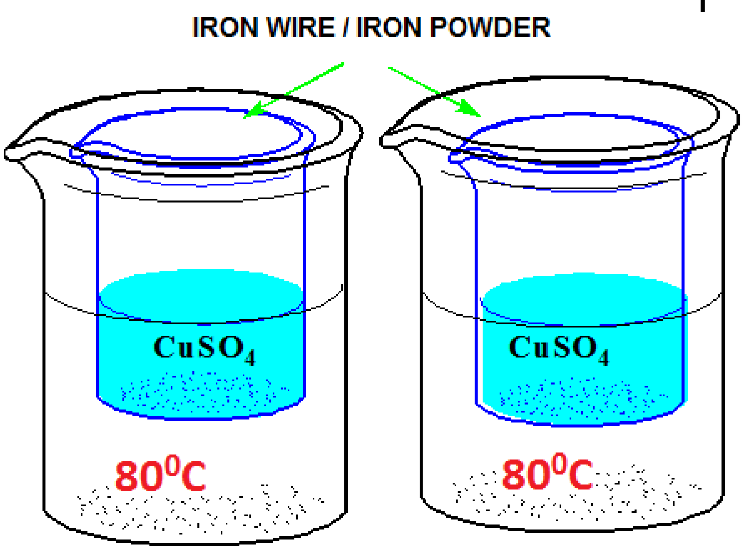


PART B: Introduction to Kinetics:
Factors That Affect the Rate of Reaction

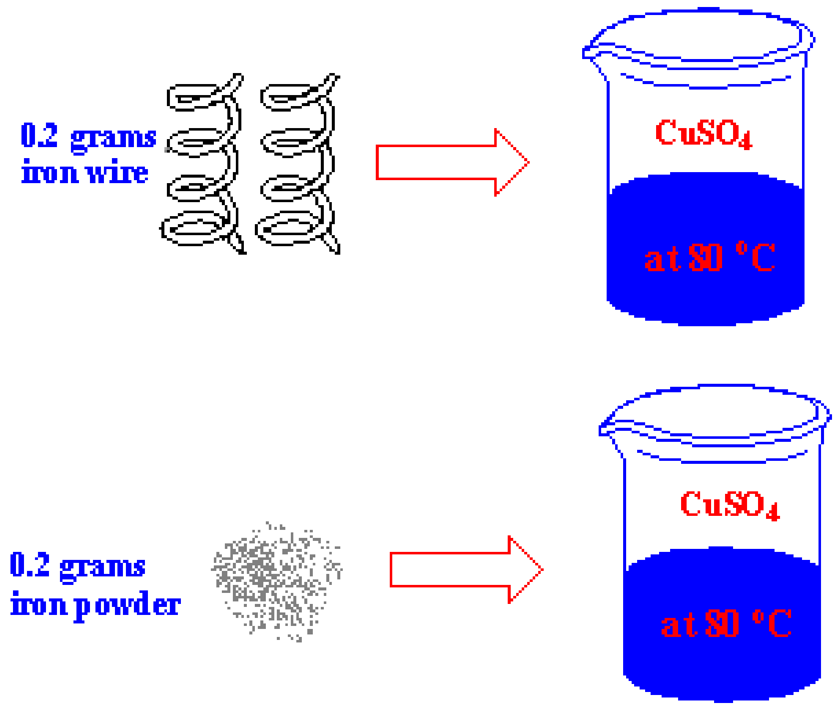
Procedure: For heating, use the hot water bath

Part B: Effect of Changing the Surface Area---------I

$CuSO_4$ 5.0 ml



$CuSO_4$ 5 ml



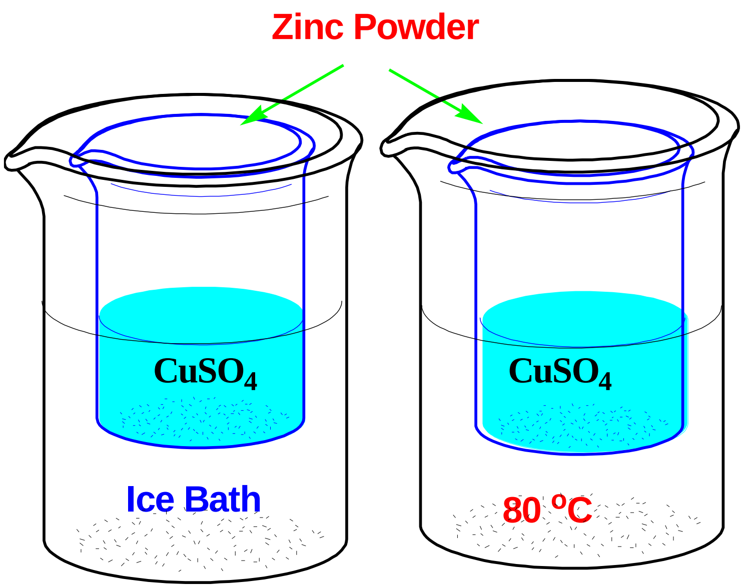
PART C: Introduction to Kinetics: Factors That Affect the Rate of Reaction

Procedure: add 0.05 g Zn granular to $CuSO_4$ solution

For heating, use the hot water bath

Part C: Effect of Changing the Temperature-------II

ALWAYS HANDLE HOT BEAKERS WITH CLOTH GLOVES



$CuSO_4$ 5 ml

Introduction to Kinetics:
Factors That Affect the Rate of Reaction

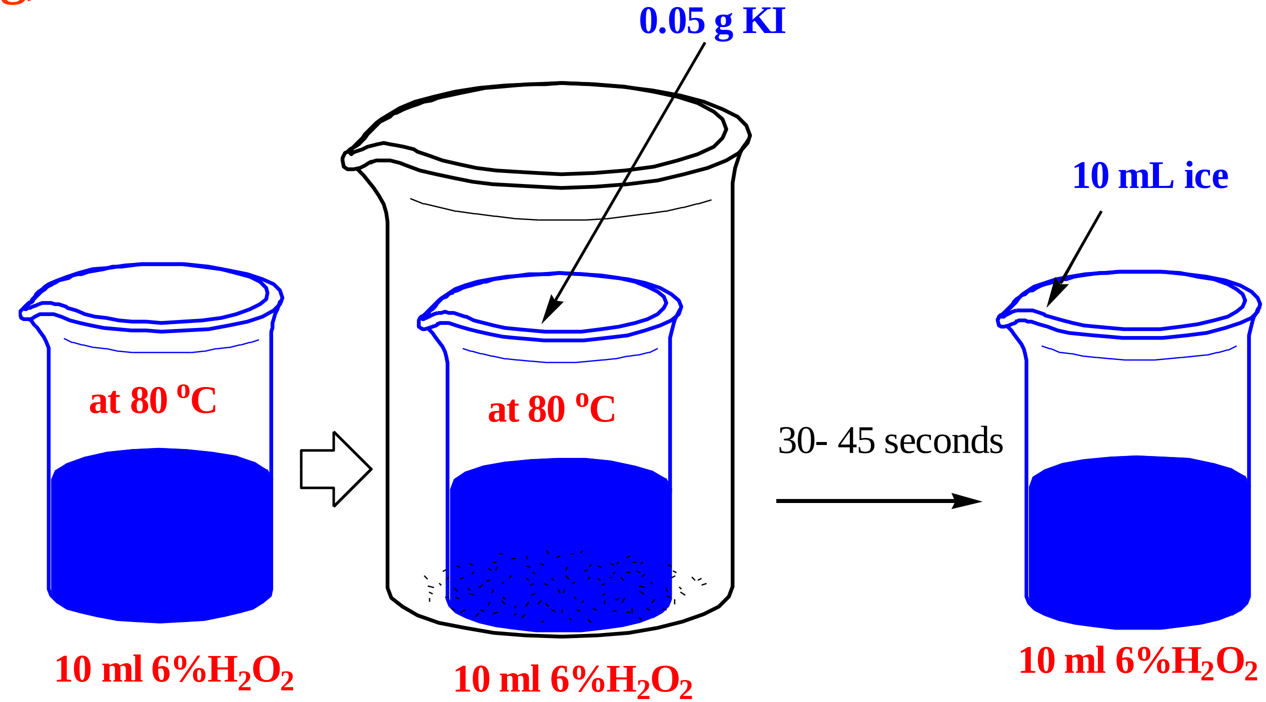
Part D: Effect of Adding a Catalyst----- Decomposition of H_2O_2

Procedure: ADD 0.050g MnO_2 INSTEAD OF 0.05g KI

Reaction is splashy (& violent when more than 0.05 g solid is added).

Avoid observing directly from top when solid is added.

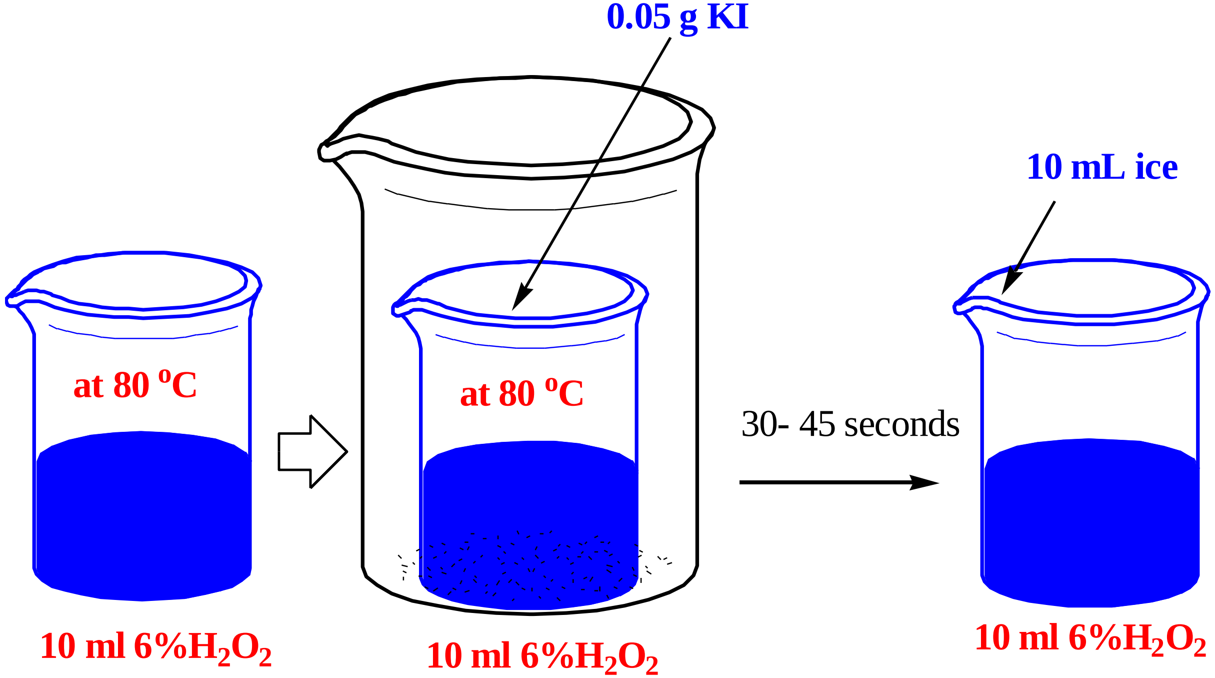
For heating, use the hot water bath



Introduction to Kinetics:
Factors That Affect the Rate of Reaction

Effect of Adding a Catalyst. Catalyst does not get consumed by the reaction but it donates or absorbs electrons, hydrogen ions or hydroxide ions (see Experiment E4(I) of lab manual)

For heating, use the hot water bath, handle hot beakers with cloth gloves



Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

The Rate Law:

$$aA + bB \rightarrow cC + dD$$

Reaction Rate:

$$R_A = k[A]^m[B]^n = -\,d[A]/dt = -\Delta[A]/\Delta t$$

m and n are determined by the experiments.

Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

The Iodination of Acetone:

yellow **colorless**

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow[\text{HCl catalyst}]{} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

$$R_a = \frac{-\Delta[I_2]}{\Delta t} = \frac{-([I_2]_{final} - [I_2]_{initial})}{\Delta t}$$

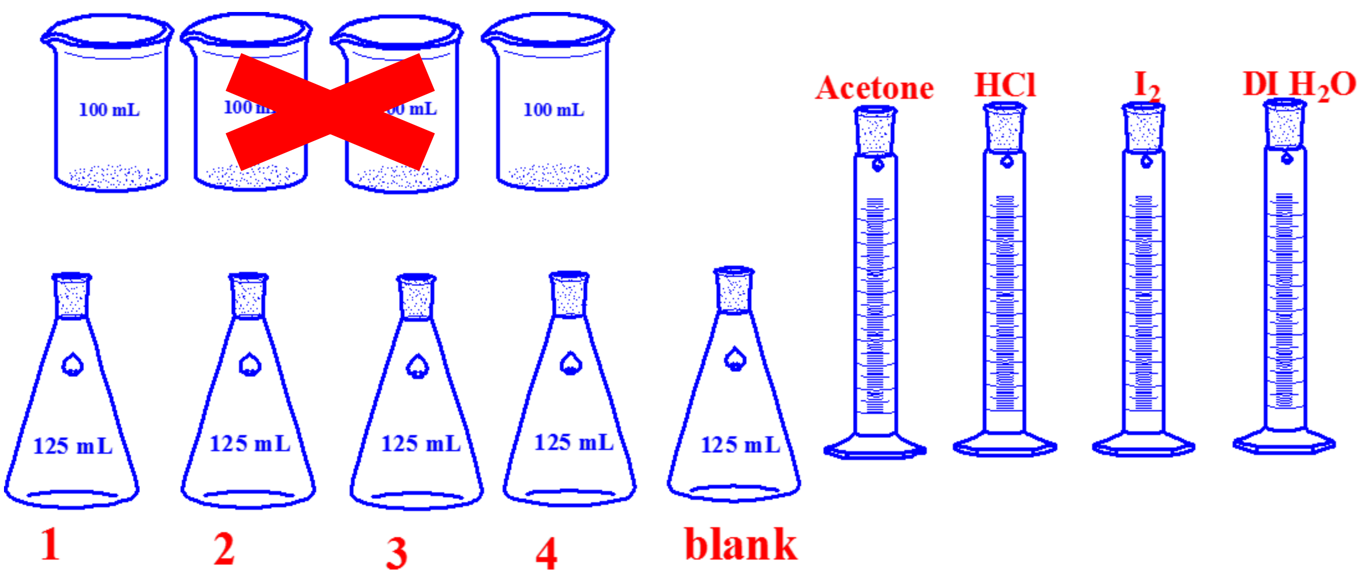
Note: Upon completion of the reaction $[I_2]_{initial}$ yellow color changes to colorless, then at that point $[I_2]_{final}$ = 0 M, and Δt is the total time it takes for such change

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

Procedure:

1. Clean the glassware, use only Erlenmeyer flasks to carry the reactions & not the beakers (to minimize splashing effect due to stirring).

soap solution → tap water → de-ionized water



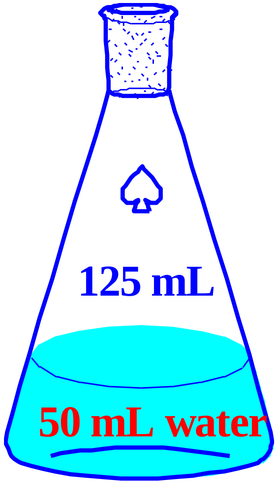
Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

Procedure: **Flasks shown are 125-mL but use 250-mL or suitable Erlenmeyer flasks if not available.**

2. Prepare a blank: Place over white background paper

50 mL of water in 250-mL Erlenmeyer flask



- **Design your reactants & catalyst volumes so you are able to determine the reaction order and the reaction rate constant easily**

- **Have your TA approve the table of your design volumes (see example in next slide)**

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

$$R_a = \frac{-\Delta[I_2]}{\Delta t} = \frac{-([I_2]_{final} - [I_2]_{initial})}{\Delta t}$$

$$R_a = k[A]^m[B]^n = -\Delta([I_2]_{final} - [I_2]_{init}) / \Delta t$$

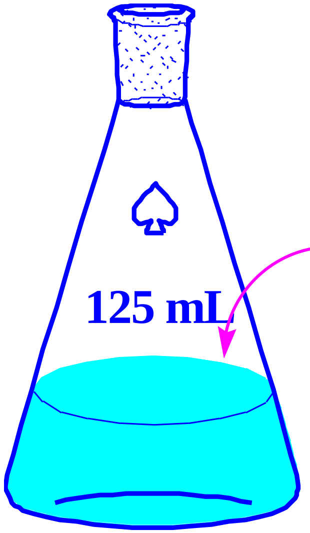
	4 M acetone mL	H_2O mL	1 M HCl mL	0.00118 M I_2 mL	Total Volume mL
1	10.0	20.0	10.0	10.0	50.0
2	x1	y1	10.0	z1	50.0
3	x2	y2	10.0	z2	50.0
4	x3 (not used above)	y3	10.0	z3 (not used above)	50.0

HCl acts as catalyst (remains unchanged at end of reaction)

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

Procedure:

3. Prepare a mixture without I_2.



Example:

10 mL acetone
10 mL HCl
20 mL DI water

HCl acts as a catalyst

Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

Procedure: Place the white stirring rod inside flask

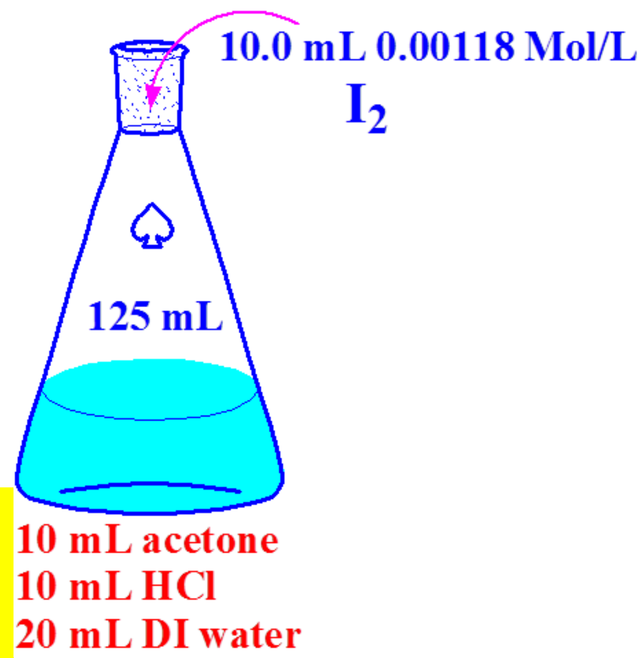
4. Add I_2 and start the timer.

Example:

a. I_2 is added quickly with stirring

b. Record the time when the color of the solution changed from yellow to colorless

c. Record the volumes of all chemicals



Use white paper as background to compare REACTION color with the blank transparent water color

Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

Procedure:

5. Repeat steps 3 and 4 .

1 time for 1 formula

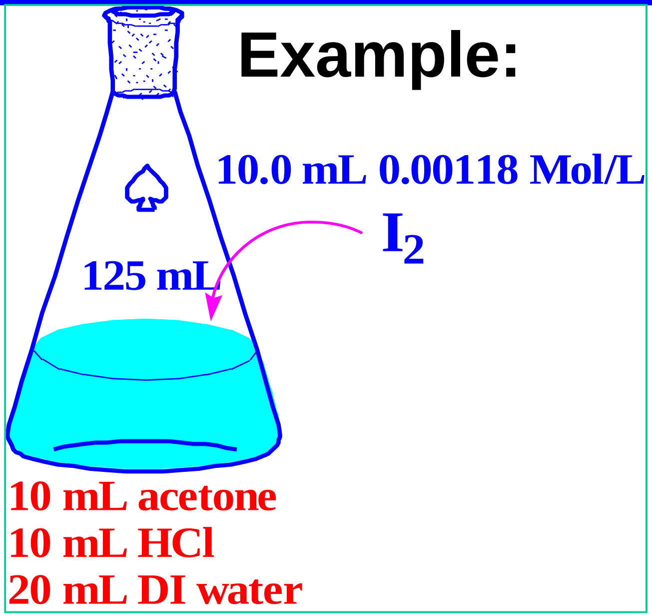
(not 2 times)

a. Calculate the percent difference between two trials.

b. It is suggested to repeat until the percent difference is less than 5%, but groups do not have enough time. Therefore work diligently, do not repeat the second trial, and report whatever data you have.

HCl acts as a catalyst

Example:



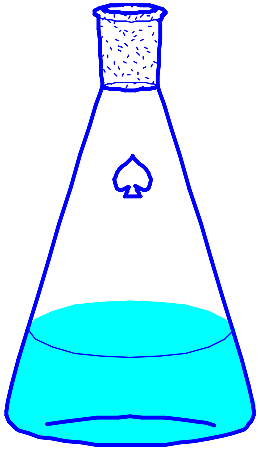
Determining the Rate Law:

A Kinetics Study of the Iodination of Acetone

Procedure:

6. How to determine the order with respect to *Acetone* .

Make your proposal, and show it to your instructor.



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

$$R_a = \frac{-\Delta[I_2]}{\Delta t} = \frac{-([I_2]_{final} - [I_2]_{initial})}{\Delta t}$$

$$R_a = k[A]^m[B]^n = -\Delta([I_2]_{final} - [I_2]_{init}) / \Delta t$$

	4 M acetone mL	H_2O mL	1 M HCl mL	0.00118 M I_2 mL	Total Volume mL
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 (not used above)	y3	10.0	z3 (not used above)	50.0

HCl acts as catalyst (remains unchanged at end of reaction)

Where [A] & [B] are initial conc. of I_2 & Acetone at -0- seconds. Note $[I_2]$final = 0 when color change

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

$$aA + bB \rightarrow cC + dD$$

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

$$R_A = k[A]^m[B]^n$$

STUDENTS TO COMPLETE X, Y, Z VALUES INTO TABLE AHEAD OF LAB WORK & GET TA APPROVAL

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	0.00118M 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	Trial 2 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	?	?	?	?	?

$$R_A = k[A]^m[B]^n$$

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

$R_{A2} / R_{A1} = (k2/k1)[C_{A2}/V_{A2}]^m [C_{B2}/V_{B2}]^n /([C_{A1}/V_1]^m [C_{B1}/V_{B1}]^n)$ ………. 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.

Method of Initial Rates

(different example than manual but same analysis)

$$2NO(g) + Cl_2(g) = 2NOCl\ (g)$$

The **method of initial rates** 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

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}

$$\text{Rate} = k\,[NO]^2\,[Cl_2]$$

EOS

Using data for reaction of NO & Cl_2 we can now calculate m, n, & k

$2NO(g) + Cl_2(g) = 2NOCl\ (g)$

Then: $-R_a = k\,[NO]^m\,[Cl_2]^n$

From data in previous table:

$2.27\times10^{-5} = k\,(0.0125)^m\,(0.0255)^n$ …………Eq.1

$4.55\times10^{-5} = k\,(0.0125)^m\,(0.0510)^n$ …………Eq.2

$9.08\times10^{-5} = k\,(0.025)^m\,(0.0255)^n$ …………..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 wrt Cl_2 gas & second order wrt NO gas.

Using any of the equations, then k is solved:

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

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

Example 2: REACTION ORDER

$$H_2O_2\,(aq.) + I^-\,(aq.) + H^+\,(aq.) \rightarrow I_2\,(aq.) + H_2O\,(l)$$

The rate law expression for the reaction:
Rate of disappearance of reactants = - Rate of appearance of products.
I_2 was easily observed for color change. Then the rate of production of I_2 :

$$R_{I2} = v = k\,[H_2O_2]^m\,[I^-]^n\,[H^+]^p$$

Note: Using enough experimental data we can easily determine m, n, p & k

GO OVER E5 LAB MANUAL POSTED ON CANVAS & GIVE BRIEF REVIEW THIS WEEK