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Physical Chemistry I Laboratory Manual

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Physical Chemistry I
Laboratory Manual

Department of
Physical and Earth Sciences
Arkansas Tech University
Fall 2022

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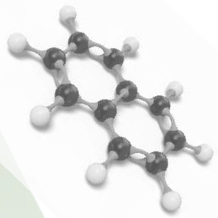

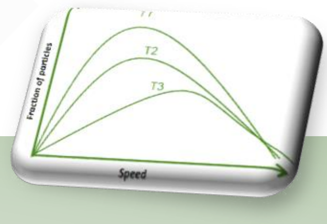

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January 2023

Prologue

Significance of a physical chemistry laboratory class

Undergraduate Physical Chemistry Laboratory is an enjoyable part of active learning as students are engaged in performing the experiments in a standard chemistry laboratory. Students get a chance to carry on experiments in small groups and discuss their observations, which incorporates a sense of inclusion and trusting environment. This triggers in revealing collective intelligence and strengthen teamwork.

Students are exposed to several state-of-the-art instrumentation, and standard techniques used by scientists in chemistry, biochemistry, food sciences, biotechnology, and pharmaceutical and chemical industries.

Students gain hands-on experience on setting up experiments and data acquisition while performing the experiments. They learn skills in appropriate analysis of data, preparing graphical representations along with proper error analysis.

In addition, students acquire hands-on experience with a few computational chemistry experiments by molecular modeling and excel workshops.

Every experiment is designed with an appropriate pre-lab discussion/quiz on the underlying theory and calculations.

Brief discussion on contemporary real-world applications of the instrumentation and their significance is presented to every experiment.

Experiments are completely aligned with lecture content, which in turn enhances student's understanding in the theoretical concepts.

In the bibliography and suggested reading section, students will find resources to read, to further their knowledge.

The author is thankful to Arkansas Tech University for providing the facilities and financial support to bring this curriculum into a reality.

Subha Pratihar

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Contents

Physical Chemistry Experiments

Safety in Chemistry Laboratory

Safety Guidelines

a. Personal Safety

1. Never work alone in the laboratory.
2. Approved splash-proof safety goggles must be always worn in the laboratory all the time.
3. Wearing contact lenses is especially hazardous around chemicals.
4. Appropriate clothing is mandatory while working inside the laboratory.

   Suitable clothing examples:

   - Clothing that protects the one's body from the '*neck to the ankles.'* No skin should be exposed from the waist down.
   - Cotton attire is the best choice for laboratory. Wearing a lab-coat is recommended.
   - Footwear that covers the entire foot.

   Inappropriate clothing examples:

   - Clothing items not covering the shoulders or abdominal areas or skintight and made from synthetic fabric are not suitable for working in laboratory. Examples include sleeveless shirts, tank-tops, leggings, tights etc.
   - Slippers, clogs, and sandals or other open-toed and open-heeled shoes are not suitable for working in laboratory.

5. Confine long hair securely when inside the laboratory.
6. Never bring food or drink inside the laboratory. (No chewing gum, or tobacco products)
7. Use of cosmetics (including lip balm) is prohibited inside the laboratory.

Special note:

SAFETY IS A SERIOUS ISSUE. Always protect your eyes. Unexpected accidents do happen, and eyes are your priceless possession.

You must always wear safety googles while in the laboratory.

b. Laboratory Safety

1. Each laboratory is equipped with a safety shower and eyewash.
2. A fire blanket in a red box, first aid box, SDS handbook, are located on the wall/rack near the entrance of the laboratory.
3. Fire extinguishers are located at the entrance, and on the wall inside the laboratory.
4. A telephone is located on the wall near the entrance.

c. Chemical/Experimental Safety

1. Adhere to accepted waste disposal procedures to prevent safety hazards and environmental contamination.
2. Mouth suction to pull up liquids into pipette is hazardous. Always use a pipette pump or bulb.
3. Check all electrical equipment carefully, make sure it is electrically grounded before touching.
4. Never use damaged, cracked, chipped, or broken glassware.
5. Wear gloves while working with strong acids or bases and corrosive liquids.
6. Wear laser safety goggles while working with lasers.
7. Determine the potential risks and check the appropriate safety practices for each experiment before performing them.
8. Discuss with the instructor if you have any doubt.

SAFETY COMES FIRST

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AGREEMENT WITH ARKANSAS TECH UNIVERSITY

(Fill out, Sign, and Return to the Instructor)

I, the undersigned, have received a copy of safety procedures/guidelines for the course stated below.

I agree to:

1. Follow all the safety instructions, procedures and guidelines laid down by the instructor
2. Properly use all safety equipment provided or required for my use as part of this course
3. Not bringing children or individuals not enrolled for this class inside this laboratory at any point of time
4. Not working alone in the laboratory
5. Wear proper clothing and covered shoes
6. Not be under the influence of illegal drug or alcohol while participating in course activities
7. Ask the lab instructor or teaching assistant (TA) if I have any questions

---

Student’s printed name

Course name & number

Instructor’s name

____ ____________________________

STUDENT’S SIGNATURE DATE

Laboratory Ethics

1. Maintain a prudent, professional attitude. Always maintain a learning environment inside the laboratory.
2. You may benefit by discussion with your laboratory co-workers, or instructor, but do not copy from them while preparing the experimental report.
3. Prepare yourself for each laboratory experiment by studying the objectives and completing the pre-laboratory assignments.
4. Maintain a lab-notebook. Record experimental data and submit a copy of recorded data to the instructor after completing an experiment.

Report Preparation

Your priceless possession is your integrity. Be conscientious in your effort to observe, record, and interpret experimental data.

Each experimental report should begin on a new page.

Include the following information on the cover sheet:

a. The title of experiment, date of experiment done, and date of report submission
b. Co-worker/lab-partner for the experiment
c. Report the most fundamental result obtained from your experiment and the absolute and relative errors by comparing with literature value.
d. Use reliable resources for literature value [Example: CRC Handbook for Chemistry and Physics, NIST Database, Resources from Physical Chemistry by Atkins]

The elaborated report should have the following:

e. The purpose/objective of the experiment
f. Flow chart of the experimental method
g. Brief narrative and sketch of apparatus/instrumentation (as applicable)
h. A section for recorded data
i. A section for data analysis: Must include representative calculations, error analysis, and graphical analysis
j. A section for results and discussion: Answer all the questions in the calculations and discussions section for each experiment. You may use reliable literature available to improve your answers to the discussion questions. Literature review is a great practice, but do not plagiarize.

k. A section for bibliography (report the resources/journal articles/textbooks you have used to get literature values, and other crucial information to prepare the report)

The specific instruction that are unique to an experiment will be discussed during the lab by the instructor.

Special note:

PLAGIARIZM IS A SERIOUS ISSUE.

Do not to copy from your lab-partners.

Keep a list of resources you have used to collect necessary information to prepare your report, and mention in the bibliography section.

Final report must be written in your own words. Signature on the cover sheet of every lab-report is mandatory, to acknowledge submission of your original work.

ACT LIKE A SCIENTIST

PHYSICAL CHEMISTRY LAB REPORT (COVER SHEET)

NAME:

CO-WORKERS:

EXPERIMENT COMPLETION DATE:

REPORT SBMISSION DATE:

TITLE OF EXPERIMENT:

RESULTS: (Most fundamental result)

Experimental value:	**Theoretical or Literature values (resources used):**
(Round uncertainties to two significant figures)	
Percent relative error:	**Percent absolute error:**

I am submitting my original work for assessment.

Signature: ______________________________

SAMPLE RUBRIC FOR LAB EXPERIMENT GRADING

Performance in Lab	**Maximum Points**
Expectations	
Showing up on time in proper clothing	
Pre-lab quiz	**15 points**
Performing experiment	
Following safety procedure	
Data collections, and submission (LAB DAILY)	**05 points**
Schematics of the apparatus	
Tables (recorded data and units)	
Lab Report: (Plagiarism unaccepted)	
Expectations	
Cover sheet	**10 points**
Flow chart of experimental procedure	**10 points**
Schematics of experimental setup with brief description	**10 points**
Recorded data (charts, tables, units)	**10 points**
Representative hand calculation Error analysis Graphs (labels on the axes, units, fitting of data showing the equation, and R^2 value)	**20 points**
Result and discussion Answer to all the questions asked in calculations, and discussion part Bibliography Report all resources/journal articles/textbooks/scientific databases used to prepare the report	**20 points**

Experiment 1:

Error Analysis and Use of Spreadsheet

Objective: In this guided note-taking exercise, the methods of data collection and quantitative analysis will be discussed. Students will study and apply statistics and regression for efficient data processing and error analysis. Students will learn the use of spreadsheet for preparing graphical representation and fitting of data, to obtain mathematical relationship between different physical quantities.

Brief Description:

Experimental Data Collection and Reporting

I. Data Recording:

Record all data as they are being collected. Be sure to use appropriate units following each numerical entry.

Record data in the lab notebook directly in permanent ink. All quantitative data that are collected must reflect the reliability of the equipment/instrument. All necessary calibration data must be recorded. Record data to appropriate number of significant figures.

II. Data Analysis

Data analysis must always incorporate proper treatment of error. Error analysis is one of the most important aspects of experimental science. We need methods of estimating the uncertainty in each measurement.

Statistical Treatment of Errors:

Error is a general term for deviations in experimental data.

Absolute error is experimental value as compared to "true value". This determines the accuracy of the data.

Absolute % error = ……….

Random error is the bounds of reliability of measured quantities. This is also known as relative error, or uncertainty or precision.

Sources of Uncertainty in Collected Data

Experimental data always may have some error. We will first study the several sources of error in data collection, and subsequently learn different methods of statistical estimation of errors.

1. Systematic error: No matter how many times a measurement is repeated, a systematic error cannot be minimized or removed. An experienced experimenter can consistently detect systemic error and avoid or rectify them, by taking trained actions.
   Examples: Calibration error in the instrument, incorrect graduation, or configuration of an instrumental scale, flawed electrical circuits, etc. Faulty theoretical treatment, perhaps a faulty approximation is also considered as systematic error.
   Systematic errors are difficult to eradicate.

2. Random errors: Random errors are produced by many uncertain and undetermined changes in the experimental condition. They can result from small errors in judgement in part of the experimenter or can be temperature fluctuation, small mechanical vibration of the equipment etc. Statistical methods can be applied to deal with random error.

3. Erratic error or Mistakes: Mistakes in recording numbers or in arithmetic calculations. Please BE CAREFUL while performing any experiment to eliminate this type of error.

   If a measurement has <u>small systematic error</u>, then the data is **extremely accurate**.
   If a measurement has <u>small random error</u>, then the data is **extremely precise**.

Propagation of Error

1. **Statistical method of determining uncertainty:**
   As a method of best practice, make several independent measurements of a quantity as possible.

   To report an experimental value, take the average, and its uncertainty as some multiple (t) of the standard deviation σ. Experimental value = Average ± t σ

   Average = ……….

   and

   Standard deviation = ……….

The best practice is to report a value to 95% confidence level, *i.e.*, Average ± 2σ (t =2)

A measured quantity can be reported to 68% confidence level by reporting Average ± σ (t =1)

For very small sample standard deviation can be calculated as

σ = ……….

Percent relative error: Expression of precision of an experimentally determined quantity relative to its magnitude.

% Relative error = ……….

Outliers: Rejection of data by Q Test:

Q = ……….

Compare Q with Q_c, if $Q \geq Q_c$, then the data can be rejected.

Discordant data rejection can be done at 90 % confidence level, by using the critical Q values (Q_c) as listed below:

N (number of data points)	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Q_c								

Propagation of uncertainty:

1. Addition /Subtraction: ……….

2. Multiplication by constant: ……….

3. General form $(A \pm \Delta A)^m (B \pm \Delta B)^n$ ……….

4. Logarithm functions: ……….

2. Computer generated plots:

Scientists and experimenters use the advantages of the data handling capability of excel spreadsheet to produce charts and plots.

Take note of the following:

1. Decide the minimum and maximum values of x and y in such a way that all the points fit inside the available area for plotting.
2. Label the axes, use reasonable scales.
3. Use proper units for data being plotted. Report the units on each axis.
4. Use distinctive symbols to denote separate runs. Add error bar to each point.
5. Add legends.
6. Consider the graphed values ($x_i \pm \Delta x_i$, $y_j \pm \Delta y_j$) with error bars. Best fit can be determined by computer. Always report fitting function for the best fitted line, and the R^2 value to prove the reliability of the fitting.
7. Uncertainty in slope must be calculated for straight line fits.

Quiz
Error analysis and use of spreadsheets

1. Measurement of the area of a rectangular box was done. The accepted area of this box is **3.85 in^2**.
   An experimenter made two repetitions of the height and width measurements as follows:

Height	**Width**	
0.721 in	5.80 in	(high bound)
0.614 in	5.18 in	(low bound)

a. **(3 pts)** Calculate the standard deviation in area measurement. Report the measured area with 95% confidence limit.

b. **(1 pts)** Calculate the % relative error in area measured by the student.

c. **(1 pts)** Calculate the % absolute error in area measured by the student.

2. **(5 pts)** An experimenter collected five set of % absorbance data from a spectrometer at a static wavelength as follows: 32.0, 38.0, 21.0, 35.0, and 34.0. Is 21.0 a discordant data?

3. **(5 pts)** An experimenter performed acid/base titration six times, and recorded the following values for the titrant:

Volume of titrant (mL)
10.12
9.89
11.64
10.40
10.36
10.55

a. Calculate the standard deviation in the data.

b. Report the volume of titrant within 68% and 95% confidence limit.

Practice using computer generated plot: (submit full-page plots)

4. **(10 pts)** An experimenter determined viscosity of a pure liquid substance in centipoise (cP) units, under constant pressure of 1 atm, at eight distinct temperatures. Following is the data.

t (ºC)	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0
Viscosity (cP)	1.779	1.449	1.168	0.979	0.831	0.709	0.601	0.489

a. Prepare a plot using these data and draw a smooth curve. What is the temperature coefficient of viscosity at 25.5ºC from the plot?

b. Use least square fitting for these data and report the least square fitting function. Calculate the temperature coefficient of viscosity at 25.5ºC applying the least-square fitting function.

Sample Error Analysis Problem:

An experimenter dispenses **0.2000 M** HCl aqueous solution from a burette at **25ºC**. The recorded initial and final readings in mL units are as follows:

Initial reading (mL)	6.79	6.78	6.79	6.77	6.76	6.78
Final reading (mL)	28.02	28.03	28.01	28.02	28.02	28.03

Calculate the standard deviations for the initial and final volumes.

Determine "*n*", the number of moles of HCl in the solution dispensed. Determine the error in "*n*" within 95% confidence limit.

KEY:

Average of initial volume $V_{initial}$ = 6.778… mL
Standard deviation of initial volume $V_{initial}$ = 0.01169… mL

Average of final volume V_{final} = 28.0166… mL
Standard deviation of final volume V_{final} = 0.0075277… mL

$\boldsymbol{V_{dispersed} = V_{final} - V_{initial}}$

$= (28.02 \pm 0.007528) - (6.78 \pm 0.0117)$ mL

$= (28.02 - 6.78) \pm (0.007528^2 + 0.0117^2)^{1/2}$ mL

$= 21.24 \pm 0.00194$ mL

0.2000 M HCl:

1000 mL of HCl has 0.2000 moles of HCl

21.24 ± 0.00194 mL of HCl has $2.0 \times 10^{-4} \times (21.24 \pm 2\times 0.00194) = 0.004248 \pm 7.76 \times 10^{-7}$ moles of HCl within **95%** confidence limit.

Experiment 2:

Heat Capacity Ratios of Gases: Acoustic Interferometry

Objective: In this experiment the ratio of constant-pressure to constant-volume heat capacities, $\gamma = C_p/C_v$, will be determined by the acoustic interferometry method. Three gases will be studied: Dry air, N_2 and He. The experimental values will be compared to the calculated values from the equipartition theorem, perfect gas assumptions, and van der Waals gas equation.

Real World Applications:

1. Acoustic Interferometry is widely used for precise measurements of temperature, pressure, gas concentrations, characterization of fluids etc.

2. Swept-Frequency Acoustic Interferometry (SFAI), was developed at the Los Alamos National Lab, NM, USA for chemical weapons treaty verification. It is a noninvasive and nondestructive fluid characterization technique. [D. N. Sinha et. el., *Applications of swept-frequency acoustic interferometry technique in chemical diagnostics*, Conference: High performance capillary electrophoresis annual conference, Orlando, FL (1996)]

Brief Introduction: The heat capacity of a substance is one of the most fundamental properties.

The amount of heat required to raise the temperature of one mole of the substance through 1°C at constant volume or pressure, is known as the molar heat capacity.

The two heat capacities are defined as follows:

$$\boldsymbol{C_v = \left(\frac{\partial U}{\partial T}\right)_v} \qquad \text{(Constant volume molar heat capacity)} \qquad 2.\,1$$

$$\boldsymbol{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \qquad \text{(Constant pressure molar heat capacity)} \qquad 2.\,2$$

For small temperature changes, the heat absorbed are given by the following:

$$\boldsymbol{q_v = nC_v\Delta T} \qquad \text{(Constant volume, n = no of moles)} \qquad 2.\,3$$

and

$$\boldsymbol{q_p = nC_p\Delta T} \qquad \text{(Constant pressure, n = no of moles)} \qquad 2.\,4$$

The ratio of constant-pressure to constant-volume heat capacities, $\gamma = C_p/C_v$, is a property of a gas and can be measured.

We will apply acoustic interferometry for measurement of speed of sound waves in different gases. Sound propagates through a gaseous medium by *longitudinal waves*, where pressure variations are along the direction of propagation as shown in figure 2.1

Figure 2. 1 Schematics of a longitudinal wave, showing compression and rarefaction and wavelength (λ_s)

The speed of sound wave of frequency υ_s is determined as follows:

$$\boldsymbol{c_s = \lambda_s . \upsilon_s} \qquad \text{(Speed of sound wave)} \qquad 2.\ 5$$

Perfect gas:

Considering sound wave propagation as a reversible adiabatic process in perfect gas, the speed of sound is related to the heat capacity ratio as follows:

$$\boldsymbol{c_s = \sqrt{\frac{\gamma RT}{M}}} \text{ ms}^{-1} \qquad 2.\ 6$$

where, T = temperature in K, M = molar mass of gas in kg mol^{-1}, R = 8.314 $\text{JK}^{-1}\ \text{mol}^{-1}$

The speed of sound through a gas is less than the average speed of gas molecules, as sound wave propagates via the collisions between molecules. With increase in temperature, the average speed of gas molecules increases, which results in a higher speed of sound.

The speed of sound in air is 331.3 m s^{-1} at 0°C and 1 atm pressure. The temperature correction to speed of sound in air is given by equation 2. 7.

$$\boldsymbol{c_s(air) = \left(331.3 \times \sqrt{1 + \frac{Temperature\ in\ {}^{o}C}{273.15}}\right)} \textbf{ m s}^{-1} \qquad 2.\ 7$$

At a particular temperature, pressure has no effect on the speed of sound.

Speed of sound in different gases at 20 ^{o}C is as follows:

Gas	*c_s (m s^{-1})*
Dry air	343.2
Nitrogen	349.0
Methane	446.0
Hydrogen	1270.0
Helium	1007.0

From equation 2. 6, we see that sound travels faster in low molecular weight gases with large values of γ, at high temperature.

Rearranging equation 2. 6 we get γ as follows:

$$\gamma = \frac{M{c_s}^2}{RT} \qquad 2.\ 8$$

This is the key equation in this experiment.

Heat Capacity and Molecular Structure:

The value of γ is usually found between 1 to 1.7 depending on the complexity of the three-dimensional molecular structure.

The heat capacity of monatomic gas, linear and non-linear polyatomic molecules depend on the degrees of freedom (*df*) for *translational, rotational,* and *vibrational* motion.

According to the *equipartition theorem* of classical statistical mechanics, the degrees of freedom and contribution to heat capacity are as follows (within the perfect gas approximation):

Molecule Type	***Translational df***	***Rotational df***	***Vibrational df***	***C_v***	***C_p***	***γ***
Monatomic	*3*	-	-	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$
Polyatomic (N = number of atoms)						
Linear	*3*	*2*	*3N-5*	*(6N-5)/2R*	*(6N-3)/2R*	$\frac{6N-3}{6N-5}$
Non-linear	*3*	*3*	*3N-6*	*(3N-3)R*	*(3N-2)R*	$\frac{3N-2}{3N-3}$

van der Waals Gas:

For van der Waals gas, the relation between speed of sound and heat capacity ratio is given by equation 2. 9. [$\tilde{V}$ is molar volume]

$$c_s^2 = \gamma \frac{RT}{M}\left(1 - \frac{2a}{p\tilde{V}^2} + \frac{2b}{\tilde{V}}\right) \qquad 2.\ 9$$

This leads to γ for van der Waals gas as shown in equation 2. 10.

$$\gamma = 1 + \frac{R}{C_v}\left(1 + \frac{2a}{pV^2}\right) \qquad 2.\ 10$$

Experimental Setup:

Apparatus and Chemicals:

Acoustical tube, audio frequency generator, oscilloscope, Acoustic tube, speaker, piston with movable microphone, scale, thermometer and barometer, dry air, helium, and nitrogen gas cylinder.

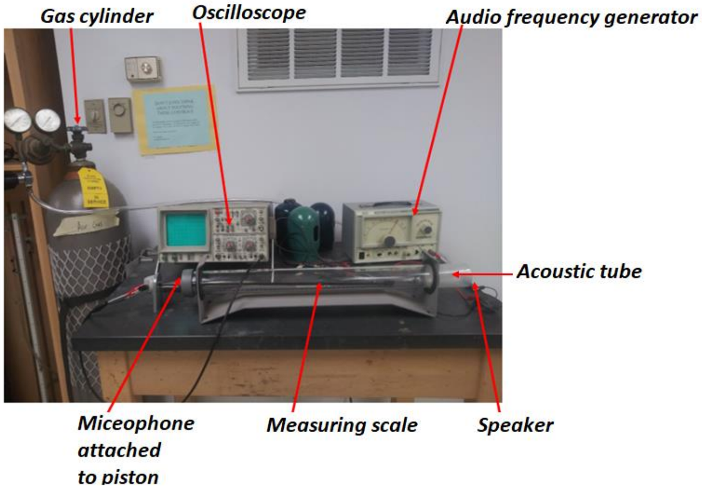


Figure 2. 2 Experimental setup of Kundt tube, and associated acoustical and electronic components

Experimental Procedure:

1. Check the following connections:
   a. The speaker is connected to the audio frequency generator
   b. Microphone attached to the movable piston is connected to the oscilloscope
   c. Oscilloscope and audio frequency generator are connected to appropriately grounded main electrical outlet.
2. Move the microphone outwards (away from the speaker) close to the far end of its travel.
3. Open the gas valve to allow passage of gas across the acoustic tube for about 10 minutes. This is to remove the air inside the tube.
4. Decrease the gas flow to a steady gentle stream only to block air from dispersing back inside the tube.
5. Record the ambient temperature, and pressure.
6. Set the audio frequency generator to the preferred frequency (1kHz for dry air and N_2) and turn on the oscilloscope. Record the frequency.
7. Check the height of the signal waveform on the oscilloscope.
8. Slowly move the microphone towards the speaker until the height of the wave is zero. This is a nodal point.

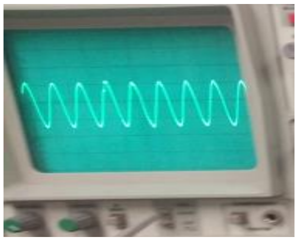


Figure 2. 3 Oscilloscope with sound wave displayed (Height of wave – amplitude)

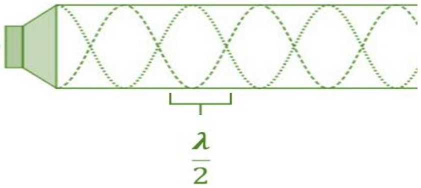


Figure 2. 4 Schematic of a standing wave inside the Kundt tube. A zero amplitude represents the node.

9. Record the position of the microphone. Move the microphone inward again until another nodal point has been reached and record the position. We are attempting to measure the distance between 2 nodes.
10. Keep on recording such readings to find an acceptable pattern. Determine as many nodal positions as possible.
11. Repeat steps 2-10 for nitrogen gas. Record positions of nodal points.
12. Repeat steps 2-10 for helium gas. Change the audio generator to the desired frequency within 2 to 2.5 kHz for helium gas.

Calculations: (Show one representative calculation by hand)

1. Calculate the speed of sound c_s in each gas using average values of $\lambda/2$, distance between adjacent nodes and the frequency υ_s.
2. Use equation 2. 8 to calculate γ , within perfect gas limit.
3. Using the van der Walls constants for nitrogen (N_2), recalculate γ using equation 2. 10. [Assume, perfect gas molar volume, V ~ RT/p].
4. Determine approximate values for the molar constant-volume heat capacity C_v for He, and N_2 within perfect gas assumptions, [$C_p = C_v + R$].

Discussion:

1. Compare experimental heat capacity ratios with the theoretical values for dry air, N_2, and He gases.
2. For carbon dioxide (CO_2) and sulfur dioxide (SO_2) calculate the theoretical heat capacity ratios using equipartition theorem.
3. Could you determine the three-dimensional molecular structures of these gases from the heat capacity ratios?

Pre-Lab Quiz

1. Draw the Lewis structures of the following molecules: CO_2, SO_2 and CH_4. What are the 3-dimensional geometry of these molecules from VSEPR theory?

2. What are the values of $\boldsymbol{\gamma}$ for these gases, by applying equipartition theorem?

3. Calculate the value of $\boldsymbol{\gamma}$ for methane, and nitrogen at 20°C applying perfect gas using gas limit. [Hint: Equation 2. 8]

4. Using the van der Waals constants for both methane and nitrogen, calculate the corrected values of $\boldsymbol{\gamma}$ [Hint: Equation 2. 9]

Gas	***a (atm L^2 mol^{-2})***	***b (L/mol)***
Methane	2.2678	0.04301
Nitrogen	1.3508	0.03870

5. Comment on the nature on intermolecular forces (IMF) in methane and nitrogen gases by comparing the $\boldsymbol{\gamma}$ values calculated in question 3 and 4.

Experiment 3:

Excel Spreadsheet Workshop on the Maxwell-Boltzmann Distribution Function

Objective: In this exercise Excel spreadsheet will be utilized to generate Maxwell-Boltzmann speed distribution. The effect of two parameters, *i.e.*, molecular weight and temperature will be determined. Next, an energy distribution calculation will be performed.

Real World Applications:

Excel spreadsheet has wide application in data processing, simple computational solutions, statistical analysis of big data and graphical methods for data analysis.

Brief Introduction: Kinetic theory of gases was developed by Scottish physicist James C. Maxwell in the nineteenth century. The probability distribution of speed is based on statistics. His finding was further generalized by Austrian physicist Ludwig Boltzmann.

Assumptions: The system has a large number of non-interacting classical gas particles. These particles are distinguishable. The initial positions and speed of the particles are random. The collisions between gas particles are completely elastic. Diameters of the particles are much smaller compared to the distances between them. Gas particles move in straight line without interacting at a constant speed in between collisions.

Based on these assumptions, a purely statistical probability distribution of speed can be obtained as follows:

$$\boldsymbol{f(v) = 4\pi(\frac{M}{2\pi RT})^{3/2}\, v^2\, e^{(-\frac{Mv^2}{2RT})}} \qquad 3.1$$

where $f(v)$ is called the distribution of speed, M = molecular weight of the gas, T = temperature in Kelvin, v = speed of molecules, and R = perfect gas constant.

The fraction of molecules that have speed in the range v to $v+dv$ is proportional to the area under the curve in the range, given by $f(v)dv$.

Procedure to Create the Speed Distribution Function:

The speed distribution function can be written as the following

$$f(v) = Coef \times v^2 \times exp \qquad 3.\ 2$$

where,

$$Coef = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \qquad 3.\ 3$$

$$exp = e^{-\left(\frac{Mv^2}{2RT}\right)} \qquad 3.\ 4$$

It will be simpler to create a spreadsheet for calculating the speed distribution when you split the function in this way.

1. Use SI units for the calculations. For example, molecular weight (M) is kg mol^{-1}, R = 8.314 J K^{-1}mol^{-1}, and speed in ms^{-1}

2. Consider oxygen gas and two different temperatures (298.15 K and 1192.6 K).

3. Create a spreadsheet named “speed distribution”.

4. Create columns ***R, MW, Temp1, Temp2, Coef1, Coef2, Increment, Speed, Sq_term, exp1, fv(1), exp2, fv(2)***

5. Make the following entries: R = 8.314, MW = 0.032, Temp1 = 298.15, Temp2 = 1192.6.

6. Calculate *Coef1* and *Coef2* based on equation 3.3. [= $4\pi\left(\frac{MW}{2\pi\times R\times Temp}\right)^{3/2}$]

6. An increment of speed can be chosen to be 50 ms^{-1}.

7. In the speed column, make the first entry as 0. Next point will be *0 + increment*, the next *0 + 2 × increment*, and so on. Create **200** data points.

8. In *Sq_term* column, calculate square of the speed (v^2).

9. In *exp1* column, calculate the exponential term for Temp1 using equation 3. 4.

10. In the *f(v)1* column, calculate the value of distribution for MW, and Temp1 using equation 3. 2.

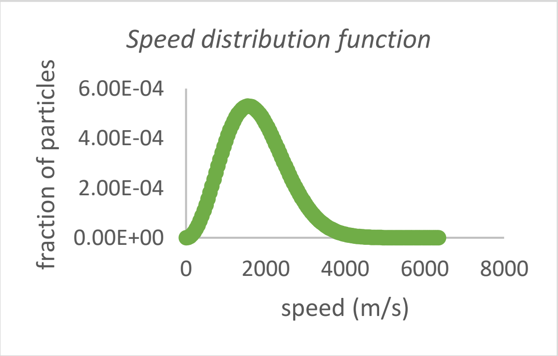
11. Repeat steps 9 and 10 to calculate the distribution (column *f(v)2*) for MW, and Temp2.

Calculation:

Normalize total area under the curve:

1. In a new column, calculate the total area under the curve. Trapezoidal rule can be employed.

2. Normalize the data points, so total area under the curve is unity.



3. Plot the probability distribution function of speed for two different temperatures in one graph.

Procedure to Create the Energy Distribution Function:

Consider translational energy of the particles as follows

$$\boldsymbol{E = \frac{1}{2}Mv^2} \qquad 3.\ 5$$

The energy distribution function can be derived as equation 3. 6.

$$\boldsymbol{f(E) = 2\pi \left(\frac{1}{\pi RT}\right)^{3/2} \sqrt{E}e^{-E/RT}} \qquad 3.\ 6$$

It will be simpler to create a spreadsheet for calculating the energy distribution when you split the function in a similar way like speed distribution.

Coef = $\boldsymbol{2\pi \left(\frac{1}{\pi RT}\right)^{3/2}}$

Sq_root = $\boldsymbol{\sqrt{E}}$

and

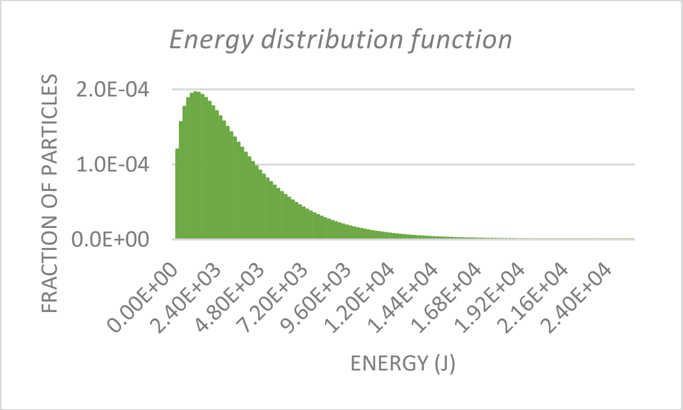
exp = $\boldsymbol{e^{-E/RT}}$

Generate a spreadsheet for energy distribution using equation 3. 6.

1. Use the value of energy increment as 200 J. Create 300 data points.

2. All other parameters as Temp1, Temp2, MW can be used the same as speed distribution calculation.

3. Plot a normalized energy distribution function for two different temperatures in one plot. To check if the area is normalized, sum of all the *f(E)dE* terms should be equal to unity.



The energy distribution function rises sharply at low energies and decays fast at larger energies. The energy distribution plot can be used to determine fraction of molecules having energy equal or higher than a given threshold energy. This threshold energy could be the minimum energy a molecule must have to undergo a specific reaction. By plotting energy distribution at different temperatures, effect of temperature on the reaction could de predicted.

Discussion:

1. With increase in temperature does the speed distribution curve gets narrower or broader?

2. How does molecular weight affect the speed distribution function?

3. Find the most probable velocity (v_{mp}) for oxygen at T=298.15 K from your plot. Compare it with the theoretical value, $v_{mp} = \sqrt{\frac{2RT}{M}}$

4. From the energy distribution plot, calculate the fraction of molecules having energy higher than or equal to 20 kJ at 298.15K? If the temperature is raised to 1192.6 K, how does it affect the fraction? [Hint: fraction of molecules = area under the curve in the range starting from 20 kJ to largest energy value considered]

YOU WILL SUBMIT PRINTOUT OF ALL THE PLOTS YOU HAVE CREATED (speed and energy distribution curves) AND ANSWER THE QUESTIONS IN DISCUSSION.

Pre-Lab Quiz:
"Maxwell Boltzmann Velocity Distribution Statistics"

Assumptions:

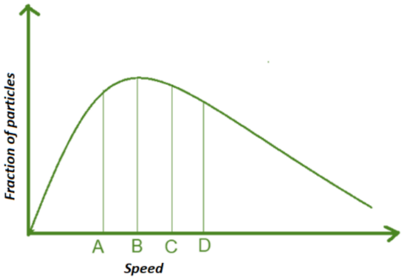
1. For what type of particles Maxwell-Boltzmann velocity distribution is applicable?
a) Distinguishable particles
b) Identical particles
c) Integral spin particles (bosons)
d) Spin half particles (fermions)

2. For which of the following species Maxwell-Boltzmann velocity distribution is **not** applicable?

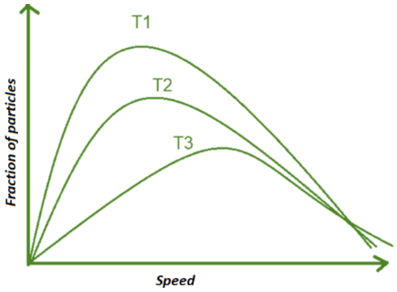
a) Particles of pure elements (atoms or molecules)
b) Energy packets (photons)
c) Particles of pure compounds (molecules)
d) Lattice positions of chemical species

Graphical analysis:

3. Identify the most probable speed, $\boldsymbol{v_{mp}}$ from the figure.



4. Arrange the temperatures (T_1, T_2, T_3) in ascending order.



Calculations:

5. Calculate the **average kinetic energy** of **1mole** of oxygen (O_2) at **25°C**?

6. Calculate the **rms** speed ($\boldsymbol{v_{rms}}$) of methane (CH_4) at **30°C**?

7. Calculate the **most probable velocity (*v_{mp}*)** of nitrogen (N_2) at **300 K**?

Conceptual:

8. Mass of a sample gas A is **4 times** that of sample gas B. What is the ratio of their mean velocities?

9. At which speed is the <u>fractions of molecules</u> maximum?

10. What is the ratio of <u>rms, most probable, and mean velocities</u>?

11. What is **average kinetic energy** associated with each degree of freedom?

12. Are the following statements, correct or incorrect?

As the temperature is raised, number of molecules moving with lower speed increases. _________________

The **average kinetic energy** of gas particles is dependent on temperature only. _______________

Experiment 4:

Solution Calorimetry- Application of Thermochemistry

Objective: In this experiment Dewar Flask Calorimeter will be used to determine the change in enthalpy (ΔH) in thermochemical reactions, e.g., 1. ΔH of neutralization reactions of a strong acid, HCl (*aq*) with strong base, NaOH (*aq*); 2. ΔH of neutralization reactions of a weak acid, HC_2H_3O (*aq*) with strong base, NaOH (*aq*); and 3. ΔH of solvation of NH_4Cl and anhydrous $CaCl_2$ in aqueous medium. ΔH of ionization of acetic acid will be calculated.

Real World Applications:

Solution Calorimetry is widely used in various scientific, clinical, and engineering fields. A few examples are as follows:

1. Clinical research: Quantitative analysis of heat production by biochemical processes, biochemical redox reactions, muscle protein reactions etc.
2. Chemical Engineering: Optimization of known reactions by thermal studies, process safety while scaling up production.

Brief Introduction: Thermochemistry deals with energy transfer in form of heat accompanying any chemical reactions. Reactions in which heat is released or absorbed are known as exothermic or endothermic reactions, respectively. Thermochemical reactions can be categorized under the following groups: (i) Enthalpy of formation (Δ_fH), (ii) Enthalpy of solution, dilution, hydration ($\Delta_{sol}H$), (iii) Enthalpy of neutralization ($\Delta_{neutralization}H$), (iv) Enthalpy of reaction ($\Delta_r H$), (v) Enthalpy of combustion ($\Delta_{com}H$). A thermochemical equation is expressed by writing the chemical formulae and physical states of the reactants and products along with the amount of the heat exchange associated with the reaction.

At constant pressure,

1. Exothermic reaction follows $\Delta H < 0$ and is known as exenthalpic process, and
2. Endothermic reaction follows $\Delta H > 0$ and is known as endenthalpic process.

In thermodynamics, the following state functions are used to characterize substances in equilibrium:

Internal Energy (total thermal motion): $\boldsymbol{U = \int_{T_1}^{T_2} C_V dT}$ 4. 1

Enthalpy (energy content): $\boldsymbol{H = \int_{T_1}^{T_2} C_p dT}$ 4. 2

Entropy: $\boldsymbol{S = \int_{T_1}^{T_2} \frac{C_V}{T} dT}$ or $\boldsymbol{S = \int_{T_1}^{T_2} \frac{C_p}{T} dT}$ 4. 3

Gibbs energy: $\boldsymbol{G = H - TS}$ 4. 4

Helmholtz energy: $\boldsymbol{A = U - TS}$ 4. 5

where C_V and C_p are the constant volume and constant pressure heat capacities of a substance. Calorimetry is a simple yet effective analytical tool to measure amounts of heat transferred by a chemical reaction. The amount of heat change depends on (a) physical state (solid, liquid, or gas) of the reactants, (b) quantity of reactants and (c) the nature of reactants.

Calorimetry is generally bases on the following relation:

$\boldsymbol{q = C \times \Delta T = m \times c \times \Delta T}$ 4. 6

where, q = amount of heat exchange, ΔT = change in temperature, C = calorimeter equivalent, m = mass of sample, and c = specific heat capacity of sample. From calorimetry, heat capacity of different substance can be determined.

In aqueous solution strong acids and strong bases, and salts of strong acids and bases are fully dissociated into their ions. The complete thermochemical ionic reaction of neutralization of a strong acid, HCl by a strong base, NaOH can be written as follows:

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$; $\Delta H = -57\ kJ$

Hence the thermochemical net ionic reaction can be written as:

$H^+ (aq) + OH^-(aq) \rightarrow H_2O(l)$; $\Delta H = -57\ kJ$ mol^{-1} 4. 7

ΔH, the enthalpy of neutralization, is independent of the nature of the conjugate base of the acid and the conjugate acid of the base.

Acetic acid, $HC_2H_3O_2$, being a weak acid, is only partially ionized in aqueous solution:

$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$

The degree of ionization (α) can be measured from the pKa value.

$\alpha = \sqrt{K_a}$ (assuming $\alpha \ll 1$)

The neutralization for this acid reacting with strong base, NaOH(aq) occurs in two stages:

$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)\ \Delta H_{ion}$

$H^+ (aq) + OH^-(aq) \rightarrow H_2O(l)$

The total heat released for this reaction can be given by the following equation:
Measured heat (kJ/mol) = $(1-\alpha)\times H_{ion} + 57\ \text{kJ mol}^{-1}$

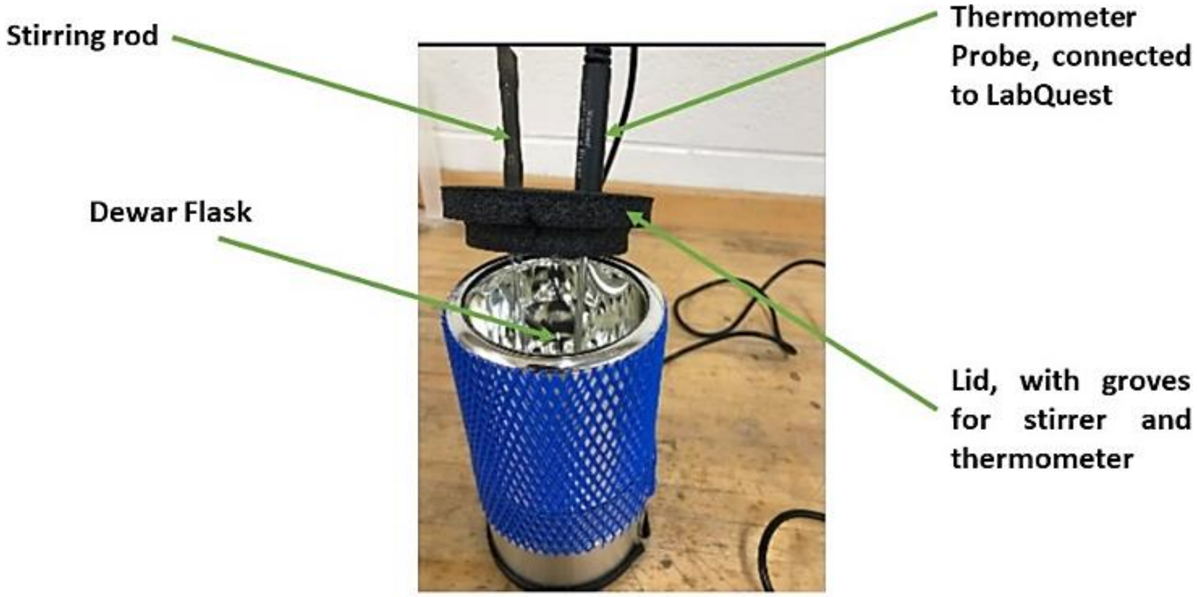


Figure 4. 1 Dewar Flask Calorimeter setup

[H_{ion} = enthalpy of ionization (kJ/mol), α = degree of ionization]

Experimental setup:

Apparatus and chemicals:

Dewar flask calorimeter, glass rod, precision thermometers, digital balance, hot plate, 100 mL glass measuring cylinder, 150 mL beakers, 1 M hydrochloric acid, 1 M sodium hydroxide, 1 M acetic acid, anhydrous calcium chloride, ammonium chloride and DI water.

Experimental Procedure:

There are several parts to this experiment. It can be planned accordingly, so each group of students can perform a part of the experiment. Data can be shared among students.

Part A: Water equivalent determination of the Dewar flask calorimeter

1. Add 50 mL of DI water to the Dewar flask calorimeter and record its temperature estimating it to the nearest 0.1° for 2 min with an interval of 30 seconds.
2. In a beaker take 100 mL DI water and heat it up to a temperature about 30°C above the room temperature.

3. Take 50 mL of the hot water in a measuring cylinder and record its temperature for 2 min with an interval of 30 seconds.
4. Add this hot water instantly to the water in the calorimeter. Stir continuously at a regulated rate.
5. Record the temperature of the water for 5-6 minutes at an interval of 30 seconds with an accuracy to the nearest 0.1^o.
6. Use the data of temperature versus time to prepare a thermogram (see figure 4. 2).

Part B: Determination of $\Delta H_{Neutralization}$ of HCl(*aq*) reacting with NaOH(*aq*)

7. Take 100 ml of 1M NaOH(*aq*) solution in the calorimeter and record the temperature for about 2 minutes at an interval of 30 seconds with an accuracy nearest to 0.1^o.
8. Take 100 mL of 1M HCl(*aq*) solution in a beaker and allow it to stand for about 2 minutes. Record the temperature at an interval of 30 seconds. Record the final temperature of HCl solution.
   NOTE: The temperature of HCl(*aq*) and NaOH(*aq*) should not differ by more than 0.5^oC. Take appropriate measure to make the temperatures identical.
9. Carefully add the 1M HCl(aq) solution to the calorimeter all at once. DO NOT SPLASH.
10. Stir the solution gently at a regulated speed.
11. Record the temperature for next 5 minutes at an interval of 30 seconds.
12. A drop of phenolphthalein can be added to the mixture to check the reaction is completed.
13. Use the data of temperature versus time to prepare a thermogram as shown in figure 4. 3.

Part C: Determination of $\Delta H_{Neutralization}$ of $HC_2H_3O_2$(*aq*) with NaOH(*aq*)

14. Repeat steps 7 – 12 with 1M acetic ($HC_2H_3O_2$) acid solution to study the enthalpy change of neutralization of acetic acid, $HC_2H_3O_2$(aq) reacting with NaOH(aq).
15. Use the data of temperature versus time to prepare a thermogram as shown in figure 4. 3.
16. Additional calculations can be performed to find the enthalpy change of ionization of acetic acid. [See discussion section]

Part D: Determination of $\Delta H_{solvation}$ of NH_4Cl and anhydrous $CaCl_2$

17. Weigh about 20 g of NH_4Cl. Record the weight.
18. Add 150 mL of DI water in the Dewar flask calorimeter. Stir continuously. Record the temperature for 2 min at an interval of 30 seconds, by estimating it to the nearest 0.1^o.
19. Add the salt to the water in Dewar flask instantly without splashing.
20. Stir the solution carefully at a regulated speed and record the temperature for next 5-6 minutes at an interval of 30 seconds, until the temperature becomes constant.
21. Use the data of temperature versus time to prepare a thermogram and measure the heat of solvation of ammonium chloride, NH_4Cl.
22. Weigh about 20 g of anhydrous $CaCl_2$. Record the weight.

23. Follow 18-21 for determining the enthalpy change of solvation of anhydrous calcium chloride, $CaCl_2$.

Calculations: (Show one representative calculation by hand)

Water equivalent of Dewar flask calorimeter:

Calculation of water equivalent (*w*) of the calorimeter: [*w* is the mass of water that will behave the same as the calorimeter]

Volume of room temperature DI water = V_1 mL

Initial temperature of water = t_1 °C

Volume of hot DI water mixed = V_2 mL

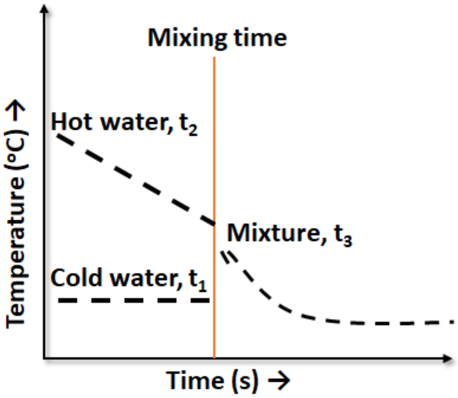


Figure 4. 2 Sample thermogram

Temperature of hot DI water = t_2°C

Temperature of the mixed solution = t_3°C (highest temperature after mixing as shown by the thermogram)

If w is the water equivalent of the calorimeter, then $(w + V_1) \times (t_3 - t_1) = V_2 \times (t_2 - t_3)$ 4. 8

Calculation of ΔH*Neutralization*:

Volume of 1 M HCl(aq) =V_3 mL

Volume of 1 M NaOH(aq) = V_4 mL

Initial temperature of either HCl(aq) or NaOH(aq) = t_4°C

Final temperature after completion of neutralization reaction = t_5 °C (highest temperature after mixing as shown by the thermogram)

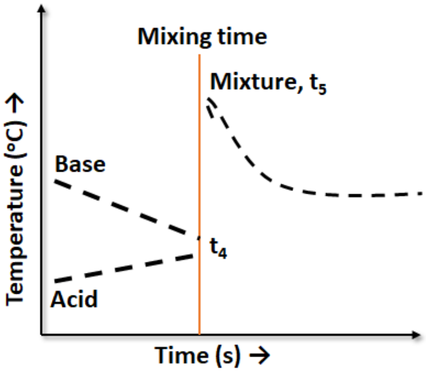


Figure 4. 3 Sample thermogram

Heat released by the neutralization reaction: $q = (w + V_3 + V_4) \times (t_5 - t_4) \times s$ 4. 9

Heat of neutralization for 1 mole of reaction can be calculated from q in equation 4. 8.

Calculation of ΔH*Solvation*:

Volume of room temperature DI water taken = V_5 mL

Initial temperature of cold water = t_6 °C

Amount of substance dissolved = M_1 g

Final temperature after mixing the substance = t_7 °C

Heat absorbed/released $q = (w + V_5 + M_1) \times (t_7 - t_6) \times s$ 4. 10

Heat of solvation for 1 mole of the substance can be calculated from q in equation 4. 10.

[Specific heat of water, s = 4182 J kg^{-1} $^{o}C^{-1}$]

Discussion:

1. Compare your experimental $\Delta H_{Neutralization}$ for HCl/NaOH reaction and $HC_2H_3O_2$/NaOH reaction with literature values.

2. What would be the expected value for $\Delta H_{Neutralization}$ for HNO_3/NaOH reaction?

3. Calculate the enthalpy of ionization of acetic acid from your experiment. Use the literature value for pKa = 4.76 of acetic acid.

4. Compare your experimental $\Delta H_{Solvation}$ for anhydrous $CaCl_2$ and NH_4Cl with literature values. Which dissolution process is exenthalpic, and which one is endenthalpic?

Pre-Lab Quiz

1. 50.0 mL of DI water is added to a Dewar flask calorimeter and the temperature recorded is 21.0°C. When 50 mL of hot DI water at a temperature of 60°C is added to it, the equilibrium temperature recorded is 35.0°C.

a. Calculate the water equivalent (*w*) of the calorimeter in units of grams.

b. Calculate the heat capacity of the calorimeter in units of J/°C. [The specific heat of water is 4182 J kg^{-1} $°C^{-1}$]

Use the above calorimeter data, for the following calculations.

2. A quantity of 200 mL of 0.862 M HCl is mixed with 400 mL of 0.431 M NaOH in the calorimeter. The initial temperature is 21.5°C for both the solutions. Calculate the final temperature of the mixed solution. [The enthalpy of neutralization is -57 kJ mol^{-1}]

3. When 20.5 g of ammonium nitrate (NH_4NO_3) is added to 200 mL of water inside the calorimeter, the temperature raised up from 21°C to 25.78 °C.

a. Calculate the enthalpy of hydration in kJ mol^{-1} units.

b. The literature value of enthalpy of hydration of ammonium nitrate is 25.7 kJ mol^{-1}, calculate the absolute and relative error in the experimental value.

Experiment 5:

Polarimetry – Optical rotation of Sucrose and Kinetics of Non-enzymatic Acid Hydrolysis of Sucrose.

Objective: In this experiment, a polarimeter will be used for the following measurements:

1. Determination of specific rotation of sucrose applying Biot's law.
2. Study the solvent effect on the optical rotation of a sucrose.
3. Study chemical kinetics of non-enzymatic acid catalyzed hydrolysis of sucrose.

Real world Applications:

Polarimetry being a highly sensitive and non-destructive method, is widely used in several industrial and scientific fields. A few examples are as follows:

1. Pharmaceutical Industries: Purity determination and characterization of new synthetic compounds, e. g. vitamins, steroids, antibiotics, peptides etc.
2. Food Sciences: Characterization and determination of sugar, starch, lactic acid concentration in food items.
3. Cosmetics and Essential Oil Manufacturing Industry: Quality control of expensive raw materials, monitoring chemical processes.

Brief Introduction: Polarimeter is an apparatus to determine the angle of rotation of plane polarized beam of light by optically active compounds. Optically active compounds must have a chiral center. A chiral molecule does not have an internal plane of symmetry and their mirror images are not superimposable. These are identified as enantiomers. The chiral center in organic molecules, is almost always a sp^3 hybridized tetrahedral C atom, with four different substituents.

When the rotation of plane polarized beam of light is to the right or clockwise, then the compound is called *dextro*-rotatory (*d*-), whereas, when this rotation is to the left or counter-clockwise, then the compound is called *levo*-rotatory (*l*-).

The angle of rotation, *i.e.*, angle through which the plane of the polarized beam of light is rotated, is dependent on the following factors:

a. the nature of the compound
b. length of the sample column through which the light passes
c. sample concentration
d. solvent

e. temperature
f. the wavelength of light
The last factor makes it essential to apply monochromatic light for such measurements.

Polarimetry:

As shown in Figure 5. 1, incident homogeneous light (589 nm) is transmitted through a fixed polarizer that only allows a certain orientation of light to pass into the transparent sample. This plane of the polarized light is rotated at a unique angle by optically active sample. As the analyzer is rotated, the rotated light is maximally transmitted at that unique angle, allowing to determine the optical properties of the sample.

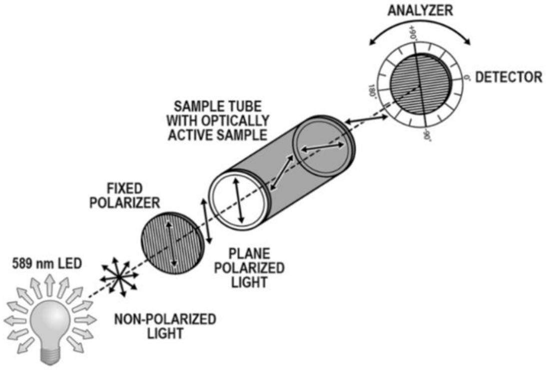


Figure 5. 1 Schematics of Polarimeter adopted from www.vernier.com/

Optical purity of the sample being studied can be calculated by the following relation:

$$\textit{\% Optical purity} = \frac{specific\ rotation\ of\ sample}{specific\ rotation\ of\ pure\ enantiomer} \times \mathbf{100} \qquad 5.\ 1$$

Acid hydrolysis of sucrose solution:

Sucrose is hydrolyzed in presence of an acid producing glucose and fructose as shown in the following reaction:

$$\begin{array}{ccccc} C_{12}H_{22}O_{11} & \xrightarrow{H_3O^+} & C_6H_{12}O_6 & + & C_6H_{12}O_6 \\ \textbf{Sucrose} & & \textbf{Glucose} & & \textbf{Fructose} \\ (d\text{-}) & & (d\text{-}) & & (l\text{-}) \end{array}$$

The aqueous sucrose solution is *d*-rotatory in the beginning of the reaction (time =0). Glucose (*d*-rotatory) and fructose (*l*-rotatory) in equal amounts are produced by hydrolysis of sucrose. The *levo*- rotation of fructose (– 92º), is larger than the *dextro*- rotation of glucose (+ 52.5º). Hence, the mixture produced by hydrolysis becomes *l*-rotatory, and is known as "INVERSION OF SUCROSE".
The reaction progress can be examined by determining the change in the angle of rotation, by means of a polarimeter, with time.

Experimental setup:

Apparatus and chemicals:

Vernier Polarimeter (shown in Figure 5. 2, with Lab Quest2 interfacing, 100 mL round bottom volumetric flasks (7) with stopper, 150 mL Erlenmeyer's flask with stoppers (or sealing can be done with cellophane papers), Sucrose, 100 mL denatured ethanol (95 % or higher), 100 mL pure acetone (95% or higher), 1M HCl, and DI water.

Experimental Procedure:

There are several parts to this experiment. It can be planned accordingly, so each group of students can perform a part of the experiment. Data can be shared among students.

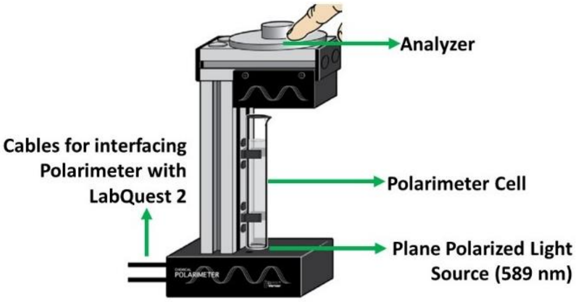


Figure 5. 2 Vernier Polarimeter adopted from www.vernier.com/

Calibration of the polarimeter:

1. The Vernier Polarimeter has two cables (see Figure 5. 2). One is a BTA (CH1 CABLE) connector that should be plugged into CH1 SENSOR PORT of LabQuest2, and one is a BTD connector that should be plugged into DIG1 SENSOR PORT of LabQuest2.
   Both connections are required for data collection.
   After turning on the LabQuest, observe light emitting from the base of the polarimeter.
2. Pour DI water in the polarimeter cell to ~10 cm. Record the height to the nearest 0.1 cm. Put the sample cell in the polarimeter.
3. Begin data collection on LabQuest2. Gently rotate the analyzer (shown in Figure 5. 2) either clockwise or counterclockwise for ~15 s. A cosine-squared waveform as shown in Figure 5. 3 will appear on the screen.
4. There are several ways to estimate these angles of rotation on LabQuest2. However, we will apply the Gaussian fit method. To achieve this, highlight one peak as shown in Figure 5. 3. From the Analyze menu choose Curve fit. Choose Gaussian. The B coefficient from the fitted curve represents the angle at maximum transmission. This will reproducibly give optical rotation measurements within ± 0.3º.
   Record the B coefficient of the blank.

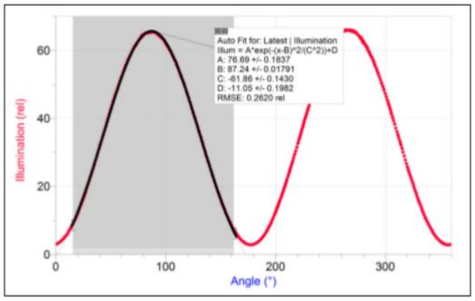


Figure 5. 3 Selection of peak for fit adopted from www.vernier.com/

5. Calculate the optical rotation (α) of sample solution by equation 5. 2.

$$\boldsymbol{\alpha = B_{sample} - B_{blank}} \quad 5.\ 2$$

6. Prepare 100 mL of 20 % aqueous solution of sucrose. This is the stock solution.
7. Prepare 100 mL of 15%, 10%, 5% and 2% aqueous solution of sucrose by serial dilution.
8. Record the room temperature.

Part A: Effect of path length on specific rotation:

9. Pour 15% sucrose solution in the polarimeter cell to ~10 cm. Record the liquid height to the nearest 0.1 cm.
10. Put the sample cell in the polarimeter. Follow step 4 for data collection. Be consistent with the direction of rotation of the analyzer.
11. Repeat step 10 for the following path lengths: 8.0, 6.0, 4.0, and 2.0 cm. Record the actual heights of the sucrose solution in the polarimeter cell to the nearest 0.1 cm, and the angle of maximum transmission.

Part B: Effect of concentration on specific rotation:

12. Pour 2% sucrose solution to the clean dry polarimeter cell to about 10 cm. Record the actual heights of the sucrose solution in the polarimeter cell to the nearest 0.1 cm, and the angle of maximum transmission.
13. Repeat step 12 for 5 %, 10 %, 15 %, and 20 % sucrose solutions.

    MAKE SURE TO CLEAN THE PPOLARIMETER TUBE WITH ADEQUATE AMOUNT OF DI WATER. NEXT WASH IT WITH A LITTLE AMOUNT OF THE SUCROSE SOLUTION OF INTEREST FOR DATA COLLECTION.

Part C: Effect of solvent on specific rotation:

14. Take 10 mL of 10% sucrose solution and dilute it with 10 mL of pure acetone to make a 20 mL solution.
15. Take 10 mL of 10% sucrose solution and dilute it with 10 mL of pure ethanol to make a 20 mL solution.
16. Take 10 mL of 10% sucrose solution and dilute it with 10 mL of DI water.
17. Measure the optical rotation of these solutions. Pour these solutions to a height of 10 cm in the clean polarimeter tube. Repeat steps 14-15.

Part D: Non-enzymatic hydrolysis of sucrose solution in acidic medium:

18. Prepare 100 mL of 10% aqueous sucrose solution. Record the temperature of the solution.
19. Mix 50 mL of 1M aqueous HCl solution to 50 mL of 10% sucrose solution in a 250 mL beaker, stir it for proper mixing. Be prompt but careful.
20. Promptly fill the polarimeter cell to 10 cm height, with the reacting mixture and start recording data. Record the actual height of solution in the sample cell and use step 4 to record the angle of maximum transmission.
21. The first data is for time 0, i.e., rotation value at the beginning of the reaction.
22. Continue taking the readings at 2, 5, 8, 10, 12, 15, 17, 20, 25, 30, 35, 40, 45, and, 50 minutes time interval.
23. Keep reaction mixture without disturbing. The final reading should be taken after 24 hours. This reading will correspond to r_∞, i.e., reading at the completion of the reaction.

Calculations: (Show one representative calculation by hand)

Specific rotation of the sample can be determined by Biot's law:

$$\boldsymbol{\alpha = [\alpha]cl} \qquad 5.\ 3$$

where α = experimental optical rotation in units of degrees,

$[\alpha]$ = specific rotation in units of degrees,

l = height of sample solution in the polarimeter cell in dm,

and

c = concentration of sample solution in g/mL

1. Studying Dependence on Path Length:

Plot height of solution in cm (x-axis) vs. optical rotation in degrees (y-axis). Calculate the angle of rotation for sample height = 10.0 cm, from the best fitted line.
Determine the specific rotation of sucrose using Biot's law.

2. Studying Dependence on Concentration:

Plot concentration of solution (g/mL) (x-axis) vs. optical rotation in degrees (y-axis). From the best-fit line through the data points, find the concentration of the unknown sucrose solution as shown in figure 5. 4.

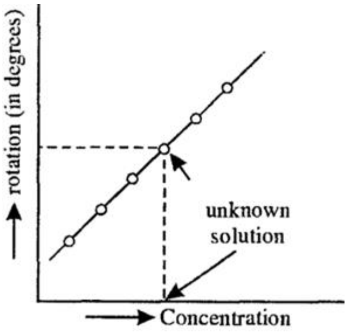


Figure 5. 4 Calibration curve to measure unknown

3. Studying Solvent Effect:

Measure the angle of rotation of sucrose/acetone and sucrose/ethanol solution. Compare the values of specific rotation of sucrose in aqueous solution to acetone/water and ethanol/water solutions, to appreciate the solvent effect.

4. Exploring Non-Enzymatic Acid Hydrolysis of Sucrose:

This reaction is first order, as only the sucrose concentration changes during the reaction (pseudo unimolecular reaction). The change in concentration of water can be neglected as water is present in large excess in the reaction medium. The integrated rate equation for first order reaction is given by eqn. 5. 4,

$$\mathbf{ln}([\boldsymbol{A}]_{\boldsymbol{o}} - \boldsymbol{x}) = \boldsymbol{ln}[\boldsymbol{A}]_{\boldsymbol{o}} - \boldsymbol{kt} \qquad 5.\ 4$$

k = rate constant
$[A]_o$ = initial concentration of sucrose

x = amount of sucrose hydrolyzed at time t
$[A]_o$ -x = amount of unhydrolyzed sucrose at time t

For inversion of sucrose angle of rotation can be related to the concentration of sucrose as follows,

$$\boldsymbol{[A]_o = \alpha_o - \alpha_\infty \; ; \; x = \alpha_o - \alpha_t} \qquad 5.\,5$$

α_o = angle of rotation at time 0, α_∞ = angle of rotation upon completion of reaction,
and α_t = angle of rotation at time t

Discussion:

1. Compare experimental value of the specific rotation of sucrose to the literature value and determine the percent absolute error.

2. Comment on the solvent effect of acetone and ethanol on sucrose solution.

3. Prepare a full-page plot of $\ln([A]_0 - x)$ (mol/L) (*y axis*) versus time (s) (x axis) for hydrolysis of sucrose in acidic medium. Determine the rate constant (*k*) from the plot at the room temperature.

Pre-Lab Quiz:

1. A student collected a set of data from a polarimetry experiment on 0.1M sucrose solution as following: Use this data to answer the questions (a-d) below.

Path length (cm)	***Optical rotation α (^{o})***
2.1	1.0323
4.3	2.2709
6.1	3.2843
8.3	4.5229
10.8	5.9304
12.0	6.606

a. Prepare a full-page plot optical rotation α (^{o}) versus path-length (cm) and fit the data with a straight line.

b. Use the equation of best fitted line to find the optical rotation α (^{o}) at 10 cm path length.

c. What is the calculated specific rotation from this experiment?

d. Literature value of specific rotation of sucrose is 66.5^{o}, calculate the absolute error in the experimental value.

2. From a series of experiments, the specific rotations were calculated as 55.0, 60.6, 53.8, 59, 57.1^{o}. Calculate the relative and absolute error in the data.

Experiment 6:

Thermodynamical Studies of an Electrochemical Cell

Objective: To understand the construction of voltaic and Daniell cells and determine the thermodynamic functions e.g., change in Gibbs Energy, ΔG, enthalpy, ΔH, and entropy, ΔS by measuring the cell potential of the prepared cell at various temperatures.

Real World Applications:

Electrochemical cells have multidisciplinary applications in several scientific and industrial fields. A few examples are as follows:

1. Battery technology: Advancement of ecofriendly battery powered vehicles, lithium-ion battery, fuel cells, etc.
2. Health Science: Monitoring neurotransmitters, drug and bacteria detection in biological samples.

Brief Introduction:

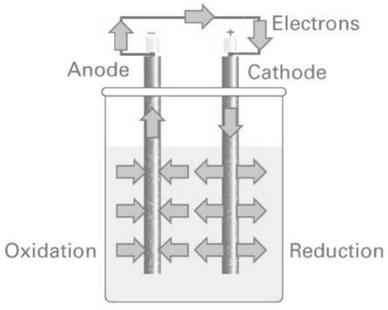


Figure 6. 1 Voltaic cell adopted from Atkin's Physical Chemistry

Voltaic Cell: In voltaic cells, redox reactions are utilized to produce electrical energy. A redox reaction is the simultaneous occurrence of the two half reactions as follows:

a. Oxidation in anode: loss of electrons by a chemical species.
b. Reduction in cathode: gain of electrons by a chemical species.

The oxidation process in anode delivers the electrons required for reduction in cathode to occur. Figure 6. 1 illustrates a typical voltaic cell where both electrodes, cathode and anode are dipped in one electrolyte solution.

Electrochemical cells can be prepared by two electrode compartments as shown in Figure 6. 2. The electrolytes are different for anode and cathode. Here, Zn electrode is dipped in $ZnSO_4$ solution, and Cu electrode is dipped in $CuSO_4$ solution. A fine frit (porosity ~ 10 μm) connects the compartments. The fine frit is to facilitate the flow of ions from both half cells. Polarization of the electrodes can be avoided by this. The two half-cell reactions can be combined to get the overall redox reaction as follows:

		Standard Reduction Pot. (E^o)
Left Hand Electrode: Oxidation (Anode)	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Zn\|Zn^{2+} = -0.76$ V
Right Hand Electrode: Reduction (Cathode)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Cu\|Cu^{2+} = 0.34$ V
Net Reaction:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$E^o_{Cell} = E^o_{Cathode} - E^o_{Anode}$

British Chemist John Frederick Daniell (1790-1845) built the cell for the first time.
The system **$Zn|Zn^{2+}||Cu^{2+}|Cu$** is named the Daniell cell in his honor.

The cell potential is given by Nernst equation (6. 1), where Q, the reaction quotient given by $\frac{[Zn^{2+}]}{[Cu^{2+}]}$, depends on the composition of the cell.

$$\boldsymbol{E_{cell} = E^o_{cell} - \frac{RT}{\nu F} lnQ} \quad 6.\ 1$$

The cell potential can be measured by applying a voltmeter. In electrochemical cell, the maximum additional work ($w_{\text{add, max}}$) is identified by the electrical work (w_e)

$$\boldsymbol{w_e = \Delta_r G = -\nu F E_{Cell}} \quad 6.\ 2$$

$\nu =$ the number of moles of electrons transported
F = Faraday's constant = 96485 C mol^{-1}

Gibbs energy of the cell can be expressed in terms of change in enthalpy and entropy of the cell as:

$$\boldsymbol{\Delta_r G = \Delta_r H - T\Delta_r S} \quad 6.\ 3$$

Over a small temperature range $\Delta_r H$ and $\Delta_r S$ are almost constant for a cell, but $\Delta_r G$ is strongly dependent on temperature.
Hence,

$$\boldsymbol{\frac{d}{dT}(\Delta_r G) = -\nu F \frac{d}{dT}(E_{cell}) = -\Delta_r S} \quad 6.\ 4$$

This provides a relation of entropy change of the cell with cell potential.

$$\boldsymbol{\Delta_r S = \nu F \frac{d}{dT}(E_{cell})} \quad 6.\ 5$$

Equation 6. 3 can be rearranged as

$$\boldsymbol{-\nu F E_{Cell} = \Delta_r H - \nu T F \frac{d}{dT}(E_{cell})} \quad 6.\ 6$$

which gives a linear relation between cell potential and temperature as follows:

$$\boldsymbol{E_{Cell} = T\frac{d}{dT}(E_{cell}) - \frac{\Delta_r H}{\nu F}} \qquad 6.7$$

The change in entropy, $\boldsymbol{\Delta_r S}$ of the system, can be calculated from the slope, $\boldsymbol{\frac{d}{dT}(E_{cell})}$ and change in enthalpy of the cell can be calculated from the intercept $\boldsymbol{-\frac{\Delta_r H}{\nu F}}$.

Experimental setup:

Apparatus and chemicals:

Electrochemical H-cell, Voltage probe with alligator clips, LabQuest2, temperature probe, 1000 mL beaker, hotplate, stand and clamps, Zn and Cu electrodes, 0.01 M $ZnSO_4$(aq) solution, 0.1 M $CuSO_4$(aq) solution, and DI water.

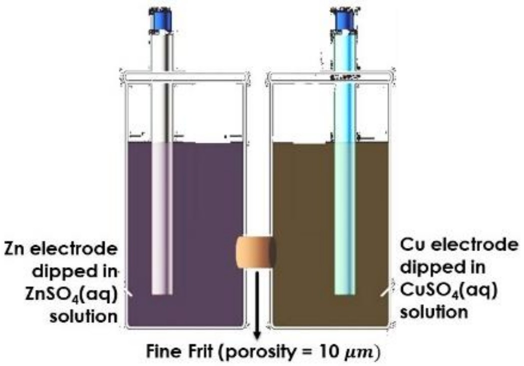


Figure 6. 2 Electrochemical Cell with two electrode-compartments connected via a fine frit

Experimental Procedure:

Calibration of the Voltage sensor:

1. Zero the voltage probe before any measurement by connecting the two alligator clips together and zeroing the reading on interfaced LabQuest2. Set it aside.

While one group of students is preparing the cell, another group should set the water bath, so data can be recorded promptly after preparing the cell.

Preparing the cell:

2. Obtain the Zn and Cu electrodes. They must be properly cleaned by scrubbing with steel wool or sandpaper until they are shiny. Dip the Cu in dilute HNO_3 in separate beakers, and Zn electrode in dilute H_2SO_4 if necessary. Wash them with adequate amount of DI water, dry them, and set aside.
3. Take 30 mL of 0.1 M $CuSO_4$ solution and 30 mL of 0.01 M $ZnSO_4$ solution and pour in the two compartments of the clean and dry electrochemical H-Cell simultaneously.

4. Insert the Cu electrode into $CuSO_4$ solution and Zn electrode in $ZnSO_4$ solution. Do not spill any liquid.

5. Connect the electrodes with the alligator clips of the voltage probe interfaced with LabQuest2 to record cell potential.

Preparing the water bath:

6. In 1000 mL beaker fill about 500 mL of DI water and keep it on a hot plate to prepare the water bath. Insert a thermometer probe inside a test tube filled with ~30 mL of DI water and keep it inside the water bath. The temperature probe must be interfaced with LabQuest2 to record temperature.

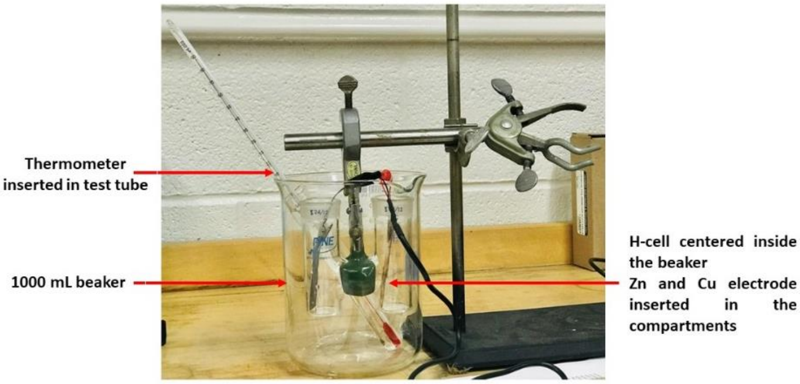


Figure 6. 3 Experimental setup

7. Use the stand and clamp to hold the cell and lower it inside the center of the bath by adjusting the height of the clamp. Make sure the wires and electrodes are not in contact with any other metals and the hot plate should not be in contact with any wires.

Data Collection:

8. Record the initial temperature and voltage reading. Wait for ~2 minutes. Watch the temperature of the cell and the voltage readings. The change should be slow at the beginning, but it should become rapid as the bath warms up.

9. Record temperature and voltage at an interval of 2^{o}C, starting from ambient up to 65^{o}C.

10. Once the temperature has reached ~ 65^{o}C, stop heating the water bath. Raise the cell carefully out of the water bath without disrupting the connections and wires.

11. Take the test tube with the temperature probe out of the water bath and keep it in a test tube holder.

12. As the H-Cell starts to cool down, record temperature and cell potential at the same temperature positions as step 9.

13. Discard the electrolytes in a waste collection beaker, clean and dry the electrochemical H-cell.

14. Repeat steps 2-13 to record a second set of data.

Calculations: (Show one representative calculation by hand)

1. Create a data sheet on excel. Find the average cell potential ($\overline{E_{cell}}$) and the standard deviation for each temperature (T in Kelvin units).
2. Prepare a full -page plot of average cell potential $\overline{E_{cell}}$ ($y\ axis$) versus T ($x\ axis$). Show the uncertainties of each data point.

3. From best fitted line, calculate the slope and intercept and the cell potential at 298K.

Discussion:

Use equations 6. 5, 6. 6 and 6. 7 to answer the following.

1. Calculate $\Delta_r S$ of the cell.
2. Calculate $\Delta_r H$ of the cell.
3. Calculate $\Delta_r G$ of the cell.
4. Comment on the spontaneity of the reaction.

Pre-Lab Quiz:

Species	$\Delta_f H^o$ *(kJ mol^{-1})*	S^o *(J mol^{-1} K^{-1})*
Zn(s)	0	41.6
Zn^{2+} (aq)	-152.4	-106.5
Cu(s)	0	33.3
Cu^{2+} (aq)	64.39	-99.6

1. Use the thermodynamic data (298 K) from the table to calculate the following:

a. $\Delta_r G^o$

b. $E_{Cell}{}^o$

c. Estimate the maximum work available at 298 K from a Daniell cell at standard condition.

2. Calculate the cell potential at 298 K for the following cells. What is the maximum work available from each of the cells?

Cell	E_{Cell}	$w_{elec,\,max}$
Zn|Zn^{2+}(0.1M)||Cu^{2+}(0.01M)|Cu		
Zn|Zn^{2+}(0.1M)||Cu^{2+}(0.001M)|Cu		
Zn|Zn^{2+}(0.1M)||Cu^{2+}(0.003M)|Cu		
Zn|Zn^{2+}(0.1M)||Cu^{2+}(0.3M)|Cu		
Zn|Zn^{2+}(0.1M)||Cu^{2+}(0.1M)|Cu		

Experiment 7:

Enzyme catalyzed kinetics of sucrose hydrolysis

Objective: Study the enzyme kinetics of inversion of sucrose solution and compare it with non-enzymatic acid-catalyzed hydrolysis of sucrose [Experiment 5 - Part-D].

Real World Applications:

Enzyme kinetics is extensively used in various fields like, biotechnology, biochemistry, and pharmaceutical sciences. A few examples are as follows:

1. Studies of enzyme activity in biochemical metabolic processes.
2. Large scale biosynthesis.
3. Drug metabolism: study of drug transportation pathways, and kinetics of drug metabolizing enzymes.

Brief Introduction:

Enzyme: Enzymes are a special type of proteins, which act as catalyst in biochemical reactions**.** Enzyme molecule contains one or more active sites, comprising a few amino acid residues, where reaction with substrate takes place. Enzyme catalysis leads to very high increase in reaction rate. The present experiment is aimed to study Invertase (β-fructofuranidase) catalyzed hydrolysis of sucrose. The rate of enzyme catalyzed reaction will be compared with non-enzymatic acid-catalyzed hydrolysis of sucrose.

Michaelis – Menten mechanism:

Invertase (I) forms a labile complex (SI) upon binding with sucrose (S) and is in equilibrium with the enzyme. This is a fast process, and a steady state is achieved rapidly. This complex is the intermediate in this reaction. The complex, in the product forming step releases the enzyme, and forms one molecule of glucose (G) and 1 molecule of fructose (F). Hydrolysis of sucrose is illustrated in the figure 7. 1. Sucrose, glucose and fructose are chiral molecules, and rotate the plane of polarized light when passed through a transparent liquid sample of an aqueous solution

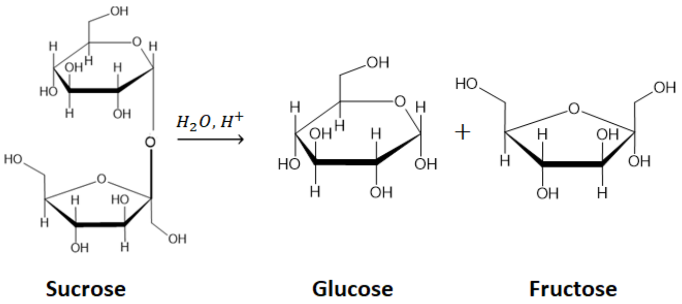


Figure 7. 1 Hydrolysis of sucrose

containing these compounds. Sucrose and glucose are *dextro*-rotatory compounds, whereas fructose is *levo*-rotatory compound. Hence the reaction of hydrolysis of sucrose results in a shift from *dextro*-rotation to *levo*-rotation with time and is popularly known as “INVERSION OF SUCROSE”.

The mechanism is given by equation 7. 1 and 7. 2.

$$\boldsymbol{I + S \rightleftharpoons SI\ (k_1\ and\ k_{-1}\ are\ forward\ and\ reverse\ rate\ constants)} \qquad 7.\ 1$$

$$\boldsymbol{SI \overset{k_2}{\rightarrow} I + G + F\ (slow\ process)} \qquad 7.\ 2$$

The rate of reaction is proportional to the concentration of enzyme-sucrose complex.

The concentration of enzyme at time zero, can be given by

$$\boldsymbol{[I]_0 = [I] + [SI]} \qquad 7.\ 3$$

where [I] and [SI] are the concentrations of free enzyme and enzyme-substrate complex at time t.

The dissociation constant, K_S is the ratio of reverse rate constant (k_{-1}) to forward rete constant(k_1) in the first step of reaction mechanism, given by 7. 4.

$$\boldsymbol{K_S = \frac{k_{-1}}{k_1}} \qquad 7.\ 4$$

The rate of the reaction is given by equation 7. 5

$$\boldsymbol{v = \frac{k_2[I]_0}{1+K_M/[S]}} \qquad 7.\ 5$$

K_M is known as Michaelis -Menten constant. It is the substrate concentration at half the maximum rate $\frac{V_{max}}{2}$, is given by equation 7. 6.

$$\boldsymbol{K_M = \frac{k_{-1}+k_2}{k_1}} \qquad 7.\ 6$$

A plot of reaction rate (v) versus sucrose concentration [S] is illustrated in figure 7. 2.

When sucrose concentration is low, $[S] << K_M$, the reaction is first order with respect to [S],

$$\boldsymbol{v = (\frac{k_2}{k_M}[I]_0)[S]}$$

When sucrose concentration is high, $[S] >> K_M$, then rate is zero order with respect to [S] and reaches the asymptotic limit V_{max}.

$$\boldsymbol{v = k_2[I]_0 = V_{max}}$$

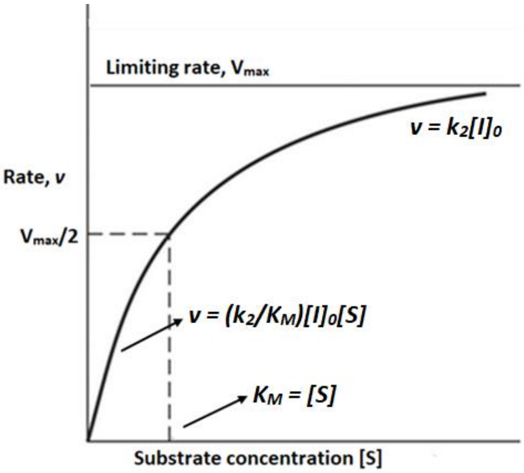


Figure 7. 2 Reaction rate versus sucrose concentration

For enzymes where the number of active sites per molecules is known, the turnover number (TON) is equal to k_2 (s^{-1}). TON is the number of substrate molecules converted to product per unit time.

In general, a quantity specific activity is measured for enzymes.

Specific activity = amount of enzyme that produces 1 μmol of product per unit time.

Enzyme reactivity depends on pH and temperature and presence of inhibitors. Inhibitors are chemical compounds or ionic species that decreases the rate of enzyme-catalyzed reaction.

Invertase reaches its maximum activity at an optimum pH of 4.5-4.8. Invertase remains active over a temperature range varying ~20^{o}C to 60^{o}C.

Experimental Setup:

Apparatus and Chemicals:

Vernier Polarimeter with Lab Quest2 interfacing, 250 mL Erlenmeyer's flask with stoppers (or sealing can be done with cellophane papers), 250 mL beakers (2), sodium acetate, glacial acetic acid, sucrose, and DI water.

Experimental Procedure:

Preparation of Enzyme solution:

1. All apparatus utilized to prepare this solution needs to be sterilized.

2. Boil 200 mL of DI water on a hot plate and then cool it down inside an ice bath.

3. Weigh ~8 mg of powdered invertase (from baker's yeast) [MW ~ 100,000 g mol^{-1}] and mix with 25 mL of sterilized water.

4. The enzyme solution must be kept tightly covered and chilled.

Preparation of acetate buffer:

5. Dissolve 0.410 g of sodium-acetate in 100 mL of DI water. Then add 0.265 mL of glacial acetic acid to the solution to prepare a buffer of pH ~ 4.7. Record the pH by measuring with a pH-meter.

Kinetics study:

6. Record the room temperature.

7. Add 10 mL of the sucrose solution, with 10 mL of enzyme solution, and 10 mL of acetate buffer in a reaction vessel. Shake it well.

8. Promptly pour the reaction mixture into a clean dry polarimeter cell to ~10 cm height. Record the liquid height to the nearest 0.1 cm.

9. Begin recording data as described in step 4 of experiment 5.

10. The first data is for time 0, i.e., rotation value at the beginning of the reaction.

11. Continue taking the readings at 2, 5, 8, 10, 12, 15, 17, 20, 25, 30, 35, 40, 45, and, 50 minutes time interval.

12. Keep reaction mixture without disturbing. The final reading should be taken after 24 hours. This reading will correspond to r_∞, i.e., reading at the completion of the reaction.

Calculations: (Show one representative calculation by hand)

Test for the order of the reaction.

1. Plot x versus time t(s). If it is straight line, then it is a 0th order reaction with respect to sucrose concentration.

2. Plot $ln\left(\frac{[A]_o}{[A]_o - x}\right)$ versus time (s). If it is a straight line, then the reaction is 1st order reaction with respect to sucrose concentration.

Discussion:

1. Compare the non-enzymatic acid-catalyzed hydrolysis of sucrose with enzyme catalyzed reaction. Comment on the order of reaction for both cases.

2. Calculate the specific activity of invertase. [Specific activity = number of micromoles of sucrose hydrolyzed per minute per gram of enzyme present.]

Pre-lab Quiz:

1. An enzyme catalyzed reaction has the following rate constants.

Rate Constants	***Value***
k_1	$8.0 \times 10^{6}\ M^{-1}\ s^{-1}$
k_{-1}	$6.8 \times 10^{4}\ s^{-1}$
k_2	$4.0 \times 10^{3}\ M^{-1}\ s^{-1}$

a. Does the enzyme-substrate binding follow the equilibrium or the steady state approximation?

b. What will be a better estimate of k_2 when the enzyme-substrate binding follows the equilibrium?

2. The initial rates of an enzyme catalyzed reaction at various substrate concentrations are as follows:

[S] (M)	***v_o (M s^{-1})***
2.50×10^{-5}	0.633333
4.00×10^{-5}	0.89
6.00×10^{-5}	1.143333
8.00×10^{-5}	1.333333
1.60×10^{-4}	1.78
2.00×10^{-4}	1.9
2.80×10^{-4}	1.95
4.00×10^{-4}	1.96

a. Make a plot of rate, v_0 vs. substrate concentration, [S].
b. Does the reaction follow Michaelis-Menten kinetics?

c. Calculate the value of V_{max} of the reaction.

d. Calculate the K_M value of the reaction.

e. What is the total number of products formed during the first 3.4 minutes of at [S] = 6.50×10^{-5}M?

f. Calculate the initial rates at [S] = 5.00×10^{-5} M and 3.00×10^{-5} M.

Experiment 8:

Bomb Calorimetry- Application of Thermochemistry

Objective: To understand the function of a bomb calorimeter and determine the specific enthalpy of naphthalene by performing combustion reaction.

Real world Applications:

The concept of adiabatic Bomb Calorimetry is widely used in various scientific and technical fields. A few examples are as follows:

1. Food Sciences: Energy content of food is determined by calorimetry
2. Biological Sciences: Metabolic combustion energetics of living systems is determined by calorimetry
3. Physical and Chemical Sciences: Heat content of fuels, and other systems are determined by calorimetry

Brief Introduction:

Hess's Law: The standard heat of formation ($\Delta_f H^o$) of chemical compounds are one of the most useful sets of thermodynamic data. $\Delta_f H^o$ can be calculated by applying Hess's law.

Hess's law is acceptable as enthalpy is a state function. According to the law, when reactants are transformed to products, the change in enthalpy of the chemical reaction is independent of the series of steps taken to achieve the final products, starting from the reactants.

The enthalpy of formation of a common hydrocarbon, naphthalene, $C_{10}H_8$, can be determined by measuring the enthalpy of combustion ($\Delta_{com}H^o$).

The combustion reaction of $C_{10}H_8$ is as follows:

$$\mathbf{C_{10}H_8(\mathit{s}) + 12O_2(\mathit{g}) \rightarrow 10CO_2(\mathit{g}) + 4H_2O(\mathit{l}) \qquad (\Delta_{\mathit{com}}H^o)} \qquad 8.1$$

According to Hess's law, the following can be written:

$$\mathbf{\Delta_{\mathit{com}}H^o = 4\times\Delta_{\mathit{f}}H^o\ (H_2O, \mathit{l}) + 10\times\Delta_{\mathit{f}}H^o\ (CO_2, g) - \Delta_{\mathit{f}}H^o\ (C_{10}H_8, \mathit{s})} \qquad 8.2$$

Knowing the molar enthalpy of common compounds like $H_2O(l)$ and $CO_2(g)$ and experimentally measuring the $\Delta_{com}H^o$, the $\Delta_f H^o$ of unknown compounds can be obtained.

Bomb Calorimetry: Combustion reaction is carried out at constant volume, under adiabatic condition inside a bomb calorimeter. The reaction is usually carried out in presence of excess of oxygen inside a closed combustion vessel, commonly known as the "Bomb". This measure is taken to ensure complete combustion.

Determination of the internal energy (ΔU) change of a reaction can be done by bomb calorimetry.

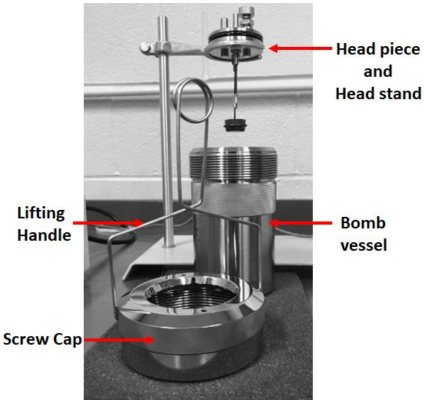


Figure 8. 1 Parts of the 'Bomb'

The change in enthalpy of a reaction is related to change in internal energy by the following equation:

$$\Delta \mathbf{H} = \Delta \mathbf{U} + \mathbf{p}\Delta \mathbf{V} \qquad 8.\ 3$$

$$\mathbf{p}\Delta \mathbf{V} = \Delta \mathbf{n}_{\mathbf{gas}}\ \mathbf{RT} \qquad 8.\ 4$$

In the combustion of 1 mole of naphthalene, where there are 10 moles of product gas and 12 moles of reactant gas, $\Delta \mathbf{n}_{\mathbf{gas}} = \mathbf{-2}$.

Calorimetry is generally bases on the following relation:

$$\boldsymbol{q}_{total} = \boldsymbol{C}\times\Delta\boldsymbol{T} + \boldsymbol{q}_{rxn} = 0 \qquad 8.\ 5$$

where, $\mathbf{q}_{total}$ = amount of heat exchange, ΔT = change in temperature (T_{final} -$T_{initial}$), C = calorimeter equivalent, $\mathbf{q}_{rxn}$ = heat released or absorbed by the reaction.

From 8. 5, heat of the reaction can be obtained as

$$\mathbf{q}_{\mathbf{rxn}} = -\,\boldsymbol{C}\times\Delta\boldsymbol{T} \qquad 8.\ 6$$

Applying, $\Delta \boldsymbol{U}_{\boldsymbol{molar}} = \frac{\boldsymbol{q}_{\boldsymbol{rxn}}}{\boldsymbol{n}}; n = \text{number of moles of naphthalene}$ 8. 7

molar enthalpy change can be obtained from 8.3.

Experimental Setup:

Apparatus and Chemicals:

The apparatus used are Parr 1341 plain jacket bomb calorimeter, along with an ignition unit, temperature recorder, and a pellet press, nichrome wire, 2L beaker, benzoic acid (BA) pellet, naphthalene (or moth balls ~99.5% naphthalene content), and DI water.

Cross sectional view of the calorimeter is illustrated in figure 8. 2. It consists of a well-insulated outer jacket and lid, a chrome-plated oval bucket, a thick-walled stainless-steel oxygen combustion vessel, stirrer, and thermistor.

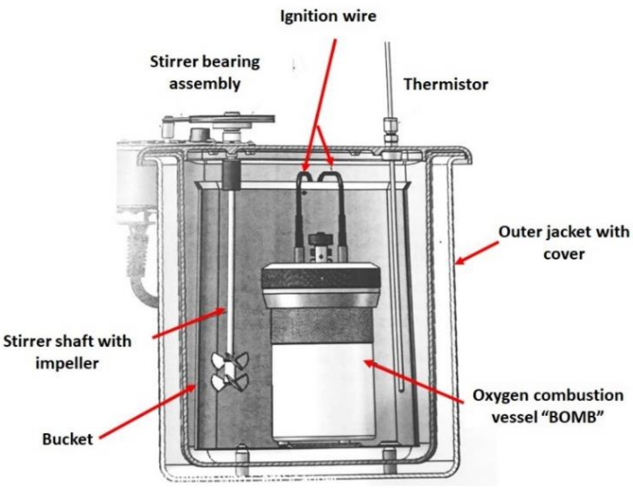


Figure 8. 2 Complete Bomb Calorimeter setup

Experimental procedure:

Calibration of the calorimeter to obtain the calorimeter equivalent

1. Check the following connections:

a. One of the lead wires from the calorimeter jacket is connected to the ignition unit terminal labeled "10cm".

b. The second lead wire from the calorimeter jacket is connected to the ignition unit terminal labeled "COMMON".

c. The thermistor is connected to the temperature recorder.

d. The power cords of the ignition unit and calorimeter are connected to appropriately grounded main electrical outlet.

2. Measure 2 kg of DI water in a 2L beaker and fill the oval bucket. Place the oval bucket properly inside the calorimeter.

3. Record the water temperature and the room temperature.

4. Get a benzoic acid pellet and weigh it. Record the weight of the sample.

5. Open the screw cap of the bomb, put the head piece on the head support. Check the O-ring, for any visible damages. A few drops of water can be added to moisten the O-ring for a smooth fit into the bomb.

6. Cut a piece of nichrome wire of ~10 cm length and record the length. Fix the wire between the two electrodes as shown in figure 8. 3.

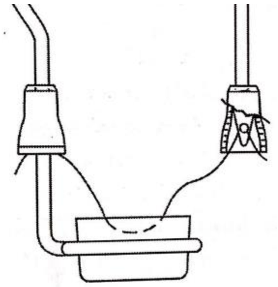


Figure 8. 3 Nichrome wire fastened between the electrodes

7. Place the BA pellet in the capsule and bend the nichrome wire so it touches the top of the sample pellet.

8. Take about 2-3 mL of water from the bucket and add it inside the bomb. Place the head piece back on the bomb and close the screw cap (make it finger tight). **BE CAREFUL**- SAMPLE MUST NOT GET DISPLACED.

9. Now attach the slip connector of the filling hose from the oxygen tank to the gas inlet fitting of the bomb. Start a regular flow of oxygen while keeping the valve open on the bomb. First purge the air out of the bomb, and then fill it with oxygen gas, by closing the valve. Keep the pressure within 20-25 atm.

10. Push the lever of the relief valve downward to release the remaining pressure in the filling hose.

11. Attach the lifting handle to the two holes in the side of the screw cap and submerge the bomb completely into the water inside the bucket. Make sure the feet of the bomb are spanning the circular boss at the bottom of the bucket. Attach the ignition lead wires to the bomb sockets. Carefully detach the lifting handle and shake off any drops of water back into the bucket.

CAUTION: If there is a continuous flow of bubbles check with the instructor.

12. Close the lid of the jacket and set the stirring assembly by slipping the drive belt onto the pulleys.

13. Start the stirrer and digital thermometer.

14. Record temperature at an interval of 30 seconds. The inner bath's temperature is virtually stable when it is rising less than 0.001 °C per minute. This should occur within 2 - 3 minutes.

15. **Firing the bomb:** Press the "ignite" button and hold it for 2- 3 seconds. The indicator light will glow momentarily. **CAUTION:** Do not have your head, hands, or any body parts over the calorimeter when firing the bomb.

16. Continue to record the temperature at an interval of 15 seconds for first 3 minutes and then at an interval of 30 seconds for about 2-3 minutes, until the temperature is leveled off.

17. Turn off the stirrer and digital thermometer.

18. Disassemble the calorimeter, take the bomb out and release the pressure by slightly opening the valve. Open the screw cap. Check for complete combustion. Take out any leftover pieces of the nichrome wire from the head piece electrodes. Record the length of the left-over wires.

19. Clean and dry the bomb, head piece, and the capsule.

20. Repeat 2-19 to get two set of data for calibration of the calorimeter with benzoic acid pellet.

Enthalpy of formation of naphthalene

21. Weigh out ~ 0.7 g of naphthalene powder (or finely crushed moth ball).

22. With a thin spatula put the power into the pellet press capsule and make a pellet. Record the weight of the pellet.

23. Use a clean dry bomb, head piece and capsule.

24. Repeat 2-19 with the naphthalene pellet.

Calculations: (Show one representative calculation by hand)

1. In this experiment, the calorimeter will be calibrated by measuring the heat released by the combustion of benzoic acid (BA), which has the specific energy ΔU^{o}_{molar}= -26,434 ± 3 J g^{-1}

From the weight of benzoic acid burned, calculate
$\Delta U(BA) = m_{BA} \times \Delta U^{o}_{molar}(BA)$

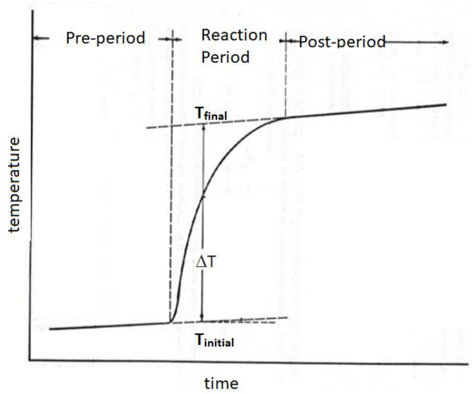


Figure 8. 4 Thermogram of an exothermic combustion reaction

2. Determine the length of wire burned and the heat released, q_{wire}, in burning the wire. [Use 2.3 cal/cm]

The total energy change for the combustion of the BA sample is
$\Delta U_{total} = -C\ (T_{final} - T_{initial}) = \Delta U(BA) + q_{wire}$

3. Make thermograms by plotting of temperature versus time, as shown in figure 8. 4 for all three runs.

4. Calculate the calorimeter equivalent C. Calculate the error in C.

5. Calculate the molar energy change, $\Delta U^{o}_{molar}(Nap)$ for the combustion of naphthalene. Calculate the error.

Discussion

1. Write the balanced equation for combustion of 1 mole of BA.
2. From the weight of benzoic acid burned, determine the $\Delta_{com}H^{o}$ (BA), the molar enthalpy change on combustion of the benzoic acid. Use equation 8. 3.

3. Determine the molar enthalpy change of combustion of naphthalene $\Delta_{com}H^{o}$ (*Nap*).

4. Calculate the specific enthalpy of combustion of naphthalene in kJ g^{-1} units. [Specific enthalpy = Enthalpy of combustion divided by molar mass].

5. Determine the molar enthalpy change of formation of naphthalene $\Delta_f H^o$ (*Nap*, *s*). Use equation 8. 2.

6. Find the literature value of $\Delta_f H^o$ (*Nap*, *s*). Compare your experimentally determined value to the literature value.

Pre-Lab Quiz:

1. The enthalpy of combustion ($\Delta_{com}H^o$) of benzoic acid ($HC_7H_5O_2$) is commonly used as a standard to calibrate bomb-calorimeter. The value of $\Delta_{com}H^o$ is -3226.7 kJ mol^{-1}.

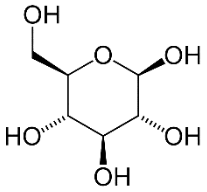
a. When 0.986 g of benzoic acid was combusted in presence of excess oxygen inside a bomb-calorimeter, the temperature raised from 21.8 ^{o}C to 25.7 ^{o}C. Calculate the calorimeter equivalent.

b. In a separate experiment 1.030 g of naphthalene ($C_{10}H_8$) was completely combusted in presence of excess oxygen. If the total heat released is 41.56 kJ, calculate the following quantities:

Molar energy of combustion $\Delta_{com}U^o$

Molar enthalpy of combustion $\Delta_{com}H^o$

c. When 0.465 g of glucose ($C_6H_{12}O_6$) was combusted in presence excess oxygen, temperature raised from 21.2^{o}C to 23^{o}C. Calculate the specific enthalpy of combustion of glucose in kJ g^{-1} units.



Molecular structure of glucose

Write a balanced equation of complete combustion of glucose.

Using the following data table to calculate the molar enthalpy of combustion $\Delta_{com}H^o$

Bond	***Bond Energies (kJ/mol)***
$C-C$	347
$C-O$	358
$C-H$	413
$O-H$	467
$C=O$	799

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12. R. M. Izatt, E. H. Reed, J. J. Christensen, *Applications of Solution Calorimetry to a Wide Range of Chemical and Physical problems*, Thermochimica Acta, **64**, 355-372 (1983).

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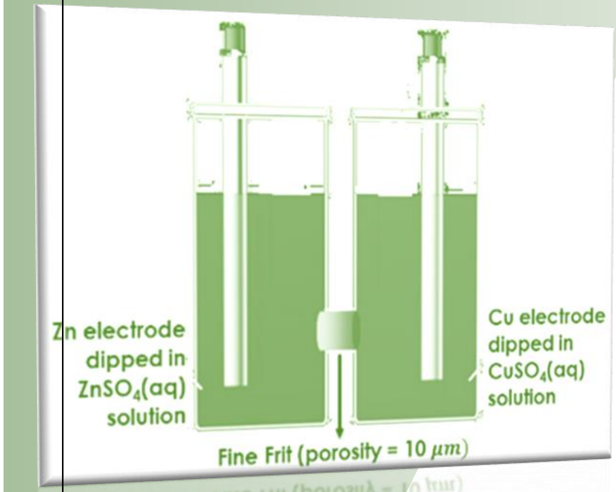
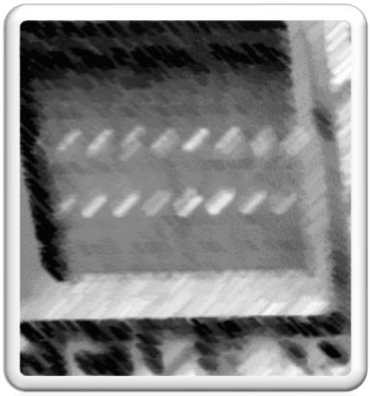
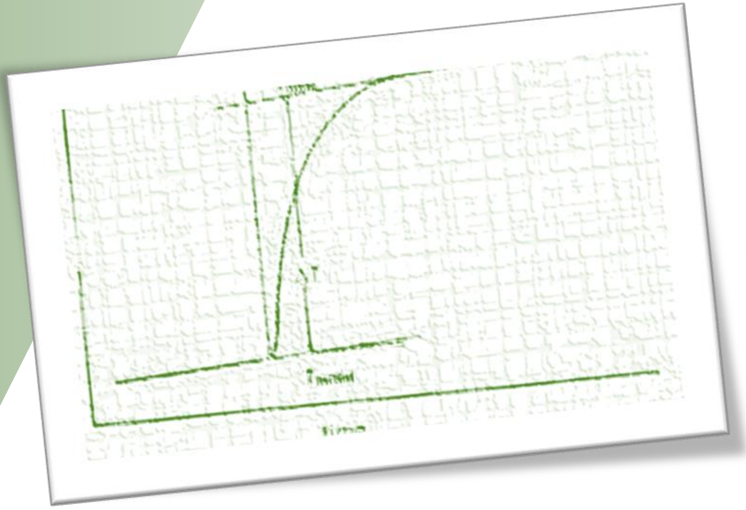
Instruction manual of instruments:

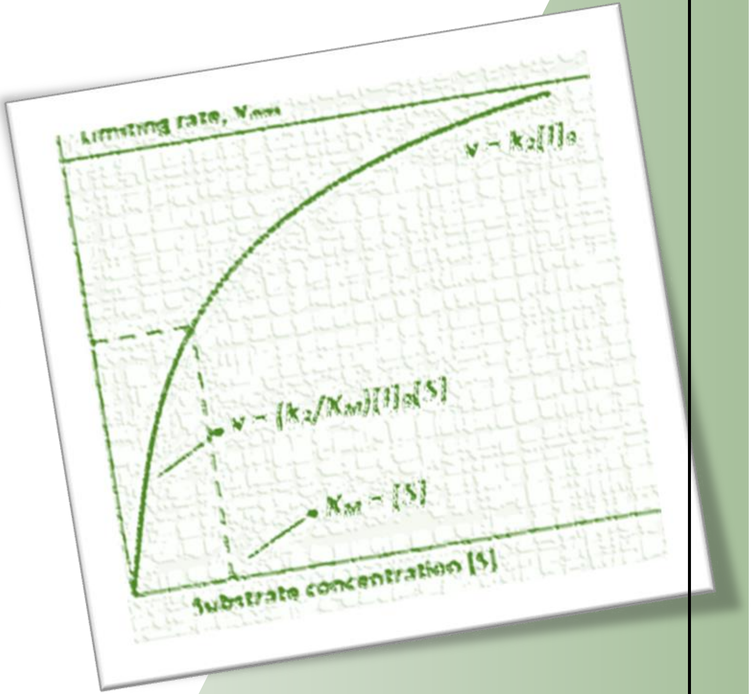
16. *Oxygen bomb calorimetry and combustion methods*, Tech. Manual 130 Parr Instrument Co., Moline, IL

17. LabQuest 2 user manual, https://www.vernier.com/product/labquest-2/


Zn electrode dipped in $ZnSO_4(aq)$ solution
Cu electrode dipped in $CuSO_4(aq)$ solution
Fine Frit (porosity = 10 μm)






Limiting rate, V_{max}
$v = k_2[I]_0$
$v = (k_2/K_M)[I]_0[S]$
$K_M = [S]$
Substrate concentration [S]