PHYSICAL CHEMISTRY LABORATORTY (1)

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Content

Outline

The main purpose of this laboratory course is to implement the experimental approaches to reach and understand the theoretical concepts presented in Physical Chemistry lectures.

During the course, you will be introduced to the basic apparatus and will learn fundamental experimental techniques used in physical chemistry. And you will be able to use the scientific method to solve the scientific problems.

Even if the key factor is to perform the experiments itself, the analysis of the result as well as the reporting system still play the crucial part of any experimental course. So Just as important to the performance of an experiment is the analysis and reporting of the results. The experiment might just as well not be undertaken if the results are not properly interpreted and reported. The report should demonstrate the ability to organize thoughts and understand the concepts involved. It is not unusual to spend more time on the analysis of the data and the writing of the report than on the actual performance of the experiment. To best utilize the time allotted for an experiment, it is necessary for you to come to the lab prepared (***Read the experiment in advance***) and to spend the laboratory period in full concentration on your work.

All work in the laboratory will be done in pairs except under the special permission or direction of the instructor. During the first laboratory period, the instructor will assign your partner. Each pair will be given a group number to facilitate assignment of experiments. Each partner of a given pair is expected to carry their own weight as far as the experimental work is concerned. Although the experiments are performed in pairs, the lab reports are to be done individually **Any two reports that are identical in the theory and/or discussion parts are not acceptable and will be returned to the individuals for rewriting**. Each pair will work on only one experiment at a time. The only exception being that preparation of solutions for a following experiment can be carried out while working on a current experiment.

Experiments schedule

The lab period will be divided into two periods and the experiments will be divided into two sets:

I.   *First set*
   1) *Introduction and group assignment*

   2) *Measurement of the relation between C_P and C_V using CLEMENT and DESORMES method.*

   3) *Viscosity as a function of temperature.*

   4) *Heat of solution from solubility*

   5) *Adsorption from solution*

   6) *Calorimetric measurements of ΔH (at constant pressure) and ΔU (at constant volume). Enthalpy of acid –base reaction. enthalpy of formation*

   7) *Partial molar volume of sodium chloride*

II.   Second set

1) *Freezing point depression of electrolytes.*

2) *Binary Solid liquid-phase Diagram*

3) *The hydrogen bond*

4) *Three component system.*

5) *Chemical equilibrium in solution: Distribution coefficient of I_2 between water and chloroform.(Two Weeks)*
    i. *Determination of the distribution coefficient of I_2 between water and cyclohexane.*
    ii. *Determination of the equilibrium constant for I^-/I_3^-*

III.   Time schedules

First Set		Second set	
Weak 1	*Introduction and group assignment*	*Weak 9*	*Freezing point depression of electrolytes.*
Weak 2	*Measurement of the relation between CP and CV using CLEMENT AND DESORMES method.*	*Weak 10*	*The hydrogen bond*
Weak 3	*Viscosity as a function of temperature.*	*Weak 11*	*Binary Solid liquid-phase Diagram*
Weak 4	*Heat of solution from solubility*	*Weak 12*	*Three component system.*
Weak 5	*Calorimetric measurements of ΔH (at constant pressure) and ΔU (at constant volume).Enthalpy of acid –base reaction.*	*Weak 13*	*Chemical equilibrium in solution: Distribution coefficient of I_2 between water and chloroform*
Weak 6	*Partial molar volume of sodium chloride*	*Weak 14*	
Weak 7	*Adsorption from solution*	*Week 15*	*Final exam*
Weak 8	*Midterm exam*		

Introductory notes

Significant Figures

Look to figure below and report the number:
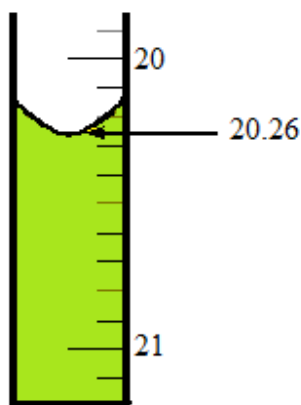
Report 20.26 but it could be 20.25 or 20.27

(2, 0, and 2 are certain; the 6 is uncertain. All 4 digits are significant).

Generally: Number of significant figures = number of digits required to express the number in scientific notation.

Determinining the number of significant figures in an answer depends upon the operations. Always do the calculation using all available significant figures; then round to the correct number of significant figures.

Rule for significant figures
1. **Addition and Subtraction**
   Results must contain the smallest numbers of significant figures after decimal point.
   Example: $3.4 + 0.020 + 7.31 = 10.730$ **report as 10.7.**

2. **Multiplication and Division.**
   Result must contain the smallest number of significant number in original numbers.
   $$(24 \times 4.02)/100.0 = 0.9648 = \textbf{report as 0.96}$$
   24 has only 2 significant figures so the answer can have only 2 significant figures

3. **Logarithms and anti-logs**
   # of digits after the decimal = # of significant figures in original number
   $$\log(4.000 \times 10^{-5}) = -4.3979$$
   $$10^{12.5} = 3 \times 10^{12}$$

ERROR ANALYSIS

Every measurement has a degree of uncertainty associated with it. The determination of the degree of uncertainty can be difficult and requires additional effort on the part of the measure. Nevertheless, evaluation of the uncertainty cannot be neglected because a measurement of totally unknown reliability is worthless.

TYPES OF ERROR

1. Systematic errors have assignable causes and definite values. They are often unidirectional (cause results to be either too large or too small). Types of these errors include:
   a. Instrumental uncertainties (Calibration procedures can usually eliminate these.)
   b. Method uncertainties (non ideal behaviour of substances, slowness of reactions, instability of species, etc.)
   c. Personal uncertainties (personal judgments, bias, and mistakes).
2. Random errors or random fluctuations in results occur when replicate experimental data are collected. The specific causes are unknown because they have many sources, none large enough to be identified or detected.

ACCURACY

Individual results in a set of measurement are seldom identical, making it necessary to select a central "best" value. The **mean or average** of a set of measurements is often used for this purpose.

Accuracy is the closeness of the mean of replicate measurements to the true value. Accuracy is usually described in terms of absolute error, the difference between the experimentally determined value and the accepted (sometimes theoretical or true) value:

$$E = X_{EXPERIMENT} - X_{TRUR} \qquad (1)$$

PRECISION/REPRODUCIBILITY

Precision is a measurement of the reproducibility of results. It is evaluated by performing replicate experiments under the same conditions. *It is defined as an agreement between the numerical values between two or more measurements*. Precision can be measured in several ways:

1. Range or spread is the numerical difference between the highest and lowest result:

$$Range = (X_{HIGH\ VALUE} - X_{LOW\ VALUE}) \qquad (2)$$

2. Deviation from the mean is a common method for describing precision and is simply the numerical difference between an experimental value, xi and the average of the set:

$$\left| X_i - \overline{X} \right| \qquad (3)$$

3. The standard deviation is a significant measure of precision. For a very large set of data, the standard deviation is given by equation 4:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \mu)}{N}} \qquad (4)$$

Where $(x_i - \mu)^2$ are the individual deviations from the mean and N represents the number of individual measurements.

A decrease in the number of individual measurements in a set of data decreases the reproducibility and creates a negative bias, or a tendency for the calculated standard deviation to be small as the number of measurements becomes smaller. Substituting the degrees of freedom (N-1) for N in equation 4 can largely eliminate this bias. Thus, the standard deviation for a small number of measurements is given by equation 5:

$$s = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \overline{x}\right)}{N-1}} \qquad (5)$$

Regression Analyses

When an experimentally measured quantity (y) plotted against (x) approximates a straight line, data seldom fall exactly on that line. Regression analyses refers to the statistical methods used for the generation of such a line and for estimation of the uncertainties associated with its use. The line generated by a least squares evaluation is the one that minimizes the squares of the individual displacements.

$$Y = a + bx$$

Where b is the slope of the line. The standard deviation of the slope is given by equation 6:

$$s_m = \sqrt{\frac{N\left(\sum d_i^2\right)}{(N-2)\left[\sum x_i^2 - \left(\sum x_i\right)^2\right]}} \qquad (6)$$

Here, xi and yi are individual pairs of values for x and y that are used to define points along the least squares line and $d_i = y_i - mx_i - b$. The quantity N represents the number of pairs of data used in preparation of the line (or calibration curve).

Relative Standard Deviation

The use of the relative standard deviation (RSD) can be a more informative way of reporting precision and can be expressed as a percentage or in parts per thousand as shown in equations 7 and 8 (respectively):

RSD (%) = (SD x 100%)/Mean   (7)

RSD(ppt) = (SD x 1000)/Mean = RSD (ppt)   (8)

Examples:

What is the mean of 20.26%, 20.98%, and 19.84%?   Answer (20.36%)

What is the standard deviation of 20.26%, 20.98%, and 19.84%?

Answer: 20.36% ± 0.57%

Propagation of Error

The way that errors propagate, depends upon the formula used to calculate the value. A couple of examples follow. Errors can be determined by measuring several times and taking the standard deviation, estimating the error in a single measurement, or using the error obtained from a curve fit.

Example 1:

The value of *W* is determined by measuring *x*, *y*, and *z*. The relationship between the variables is:

$$W = X + 2Y - 3Z$$

The measured values and the standard deviations of the measurements are:

X= 15.0 ± 0.3
Y= 12.1 ± 0.5
 Z = 10.0 ± 0.5

What is the error in *W*?

Answer:

Errors in *X*, *Y*, *Z*, and *W* will be expressed as *dx*, *dy*, *dz*, and *dw*, respectively.

$$(dW)^2 = \left(\frac{\partial W}{\partial X}\right)^2 (dX)^2 + \left(\frac{\partial W}{\partial Y}\right)^2 (dY)^2 + \left(\frac{\partial W}{\partial Z}\right)^2 (dZ)^2$$

$$\left(\frac{\partial W}{\partial X}\right) = 1 \quad \left(\frac{\partial W}{\partial Y}\right) = 2 \quad \left(\frac{\partial W}{\partial Z}\right) = -3 \ so$$

$$(dW)^2 = (1)^2 (0.3)^2 + (2)^2 (0.5)^2 + (-3)^2 (0.5)^2 = 1.828$$

$$W = X + 2Y - 3Z = 15 + 2(12.1) + 3(10.0) = 9.2$$

$$w = 9.2 \pm 1.8$$

Example:

The molecular weight of an ideal gas may be calculated from the **ideal gas law PV = (W/M)RT** where: P = pressure (atm), V = volume (liters), W = weight (grams), T = temperature (^{o}K), R = 0.08206 l.atm/mole^{o}K

In an experiment with CH4 a student obtains the following values and estimates the indicated errors: P = 735 ± 1 mm, V = 210 ± 2 ml, W = 137 ± 2 mg and T = 25 ± 1 ^{o}C

Calculate M, **the maximum propagated error in M**, and **the most probable propagated error in M from the uncertainties**, assuming CH4 follows the ideal gas law exactly.

$$M = \frac{WRT}{PV} = \frac{(0.0137g)(0.082061 \, atm.mol^{-1}K) \, 298K}{\left(\frac{735}{760} \, atm\right) 0.021L} = 16.47 \, g/mol$$

NOTE: significant figures Require M to be rounded off to 16.5 g/mole

MAXIMUM PROPAGATED ERROR: M = f(W,R,T,P,V) as M = (WRT/PV)

$$dM = \left|\left(\frac{\partial M}{\partial W}\right)\right|dW + \left|\left(\frac{\partial M}{\partial R}\right)\right|dR + \left|\left(\frac{\partial M}{\partial T}\right)\right|dT + \left|\left(\frac{\partial M}{\partial P}\right)\right|dP + \left|\left(\frac{\partial M}{\partial V}\right)\right|dV$$

$$dM = \left|\frac{RT}{PV}\right|dW + \left|\frac{WT}{PV}\right|dR + \left|\frac{WR}{PV}\right|dT + \left|\frac{WRT}{P^2V}\right|dP + \left|\frac{WRT}{PV^2}\right|dV$$

$$dM = \left|\frac{M}{W}\right|dW + \left|\frac{M}{R}\right|dR + \left|\frac{M}{T}\right|dT + \left|-\frac{M}{P}\right|dP + \left|-\frac{M}{V}\right|dV$$

$$dM = M\left[\frac{dW}{W} + \frac{dR}{R} + \frac{dT}{T} + \frac{dP}{P} + \frac{dV}{V}\right]$$

$$dM = 16.5 g/mol\left[\frac{2}{137} + \frac{0}{R} + \frac{1}{298} + \frac{1}{735} + \frac{2}{210}\right] = 0.480 \, or \, 0.5$$

$$so\, M = 16.5 \pm 0.5 \; g/mol$$

At this point, one should answer the Question:

What is the largest error source?

dW/W = 0.0146; dR/R = 0; dT/T = 0.0035; dP/P = 0.00136; dV/V = 0.00955

LARGEST ERROR IS IN WEIGHING.

MOST PROBABLE PROPAGATED ERROR. M = WRT /PV

$$dM = \left[\left(\frac{\partial M}{\partial W}\right)^2 dW^2 + \left(\frac{\partial M}{\partial R}\right)^2 dR^2 + \left(\frac{\partial M}{\partial T}\right)^2 dT^2 + \left(\frac{\partial M}{\partial P}\right)^2 dP^2 + \left(\frac{\partial M}{\partial V}\right)^2 dV^2\right]^{1/2}$$

$$dM = \left[\left(\frac{RT}{PV}\right)^2 dW^2 + \left(\frac{WT}{PV}\right)^2 dR^2 + \left(\frac{WR}{PV}\right)^2 dT^2 + \left(\frac{WRT}{P^2V}\right)^2 dP^2 + \left(\frac{WRT}{PV^2}\right)^2 dV^2\right]^{1/2}$$

$$dM = \left[\left(\frac{M}{W}\right)^2 dW^2 + \left(\frac{M}{R}\right)^2 dR^2 + \left(\frac{M}{T}\right)^2 dT^2 + \left(\frac{M}{P}\right)^2 dP^2 + \left(\frac{M}{V}\right)^2 dV^2\right]^{1/2}$$

$$dM = M\left[\left(\frac{dW}{W}\right)^2 + \left(\frac{dR}{R}\right)^2 + \left(\frac{dT}{T}\right)^2 + \left(\frac{dP}{P}\right)^2 + \left(\frac{dV}{V}\right)^2\right]^{1/2}$$

$$dM = 16.5 g/mol\left[\left(\frac{2}{137}\right)^2 + \left(\frac{0}{0.08206}\right)^2 + \left(\frac{1}{298}\right)^2 + \left(\frac{1}{735}\right)^2 + \left(\frac{2}{210}\right)^2\right]^{1/2}$$

$$dM = 0.294 \quad Or = 0.3$$
$$M = 16.5 \pm 0.3 g/mol$$

QUESTION:

Which is the correct method to use when propagating errors?

ANSWER:

Generally, when the quantity to be determined is a function of three or more experimental variables, the maximum propagated error over estimates the uncertainty (Why?) and the most probable propagated error is a more realistic measure of the uncertainty.

In our example, the molecular weight M is a function of 4 experimental variables (W, T, P, V) and hence the maximum propagated error of $dM = \pm 0.5$ is an over estimate. Hence, the molecular weight should be reported as $M = 16.5 \pm 0.3$ grams/mole.

Many times the quantity of interest is determined from the slope of a linear plot of the data. In this case, the uncertainty in the quantity is best estimated assuming the line is defined by two points, and by propagating using the Most Probable Propagated method. The following example illustrates this method.

Propagation of Error for Case Where Data are Analyzed Via slope of Line

Example:

$$\ln P = -\frac{\Delta H}{RT} + A$$

and in term of two point

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

We have: P1,P2, T1, T2 and the errors dP1, dP2, dT1, dT2

Use the most probable propagated error as a measure of error in Δ H, as follows:

Δ H = f(P1, P2, T1, T2)

$$d\Delta H = \left[\left(\frac{d\Delta H}{dT_1}\right)^2 dT_1^2 + \left(\frac{d\Delta H}{dT_2}\right)^2 dT_2^2 + \left(\frac{d\Delta H}{dP_1}\right)^2 dP_1^2 + \left(\frac{d\Delta H}{dP_2}\right)^2 dP_2^2\right]^{1/2}$$

$$\Delta H = R\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-1}\left[\ln P_2 - \ln P_1\right]$$

$$\left(\frac{\partial \Delta H}{\partial P_1}\right) = R\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-1}\left[-\frac{1}{P_1}\right]$$

$$\left(\frac{\partial \Delta H}{\partial T_1}\right) = R\left[\ln P_2/P_1\right]\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-2}\left(\frac{1}{T_1^2}\right)$$

$$\left(\frac{\partial \Delta H}{\partial P_2}\right) = R\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-1}\left[\frac{1}{P_2}\right]$$

$$\left(\frac{\partial \Delta H}{\partial T_2}\right) = R\left[\ln \frac{P_2}{P_1}\right]\left[(-1)\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-2}\left(-\frac{1}{T_2^2}\right)\right]$$

Evaluate the partials using the values of P1, P2, T1, and T2, and then substitute these values into the equation for dΔ H. Note that this is only an estimate in error; a more rigorous treatment can be made when a least squares analysis is made.

Safety Precautions

1. Play in the laboratory will not be tolerated.
2. Familiarize yourself with the location of the fire extinguishers.
3. Never perform an unauthorized experiment. Any change of procedure must be instructor approved.
4. Do not <u>eat</u> or <u>smoke</u> in the laboratory.
5. Dispose of all organic solvents by putting them in the waste containers provided.
6. Return all chemicals and solvents to their proper places.
7. Take only that amount of a chemical which you expect to use. Never return unused solutions or chemicals to their bottles. <u>Dispose of them properly</u>!
8. **EYE PROTECTION <u>MUST BE WORN</u> AT ALL TIMES IN THE LABORATORY!** Failure to comply with this rule will result in expulsion from the laboratory.
9. Use a "propipette" (the rubber suction bulb) for all pipetting operations! (Stomach pumping takes valuable laboratory time away from the student.)
10. Under no circumstances is an experiment in progress to be left unattended.
11. In case of accident, notify the instructor immediately.

Failure to comply with the above stated rules and safety precautions is considered POOR LABORATORY TECHNIQUE (PLT) to say the least, and will result in a corresponding reduction in your laboratory grade.

I, as a student in **physical chemistry lab 403242**, have read, understand and will abide by the above stated rules and regulations.

Signed _____

Lab Report Format

I. **<u>TITLE PAGE</u>**

    1. Experiment Number
    2. Experiment Name
    3. Your Name
    4. Partner's Name
    5. Date(s) Experiment was Performed
    6. Date Due
    7. Abstract

II. **<u>INTRODUCTION</u>**

    1. Object of the Experiment (one sentence)
    2. Brief Discussion of the Theory (citing pertinent equations and defining all terms used in the equations)

III. **<u>EXPERIMENT</u>**

A Summary of the method(s) used to obtain the data should be included. It is important to mention any variation from the procedure described in the handout, or operating manuals.

IV. **<u>RESULTS & CALCULATIONS</u>**

    1. Table of Data for Individual Runs, and Calculated Results for
    2. Individual Runs
    3. Graphs
    4. Sample Calculations of Results (for each type of calculation)

V. **<u>ERROR ANALYSIS.</u>**

    1. Systematic and Random Errors; Sources and Estimated Magnitudes
    2. Propagation of Error to Assign Uncertainty to Calculated
    3. Results (Sample Calculation)

VI. **<u>DISCUSSION & CONCLUSIONS</u>**

    1. Results ± Limits of Error and Comparison with Literature Values
    2. Discussion of Reasons for Disagreement
    3. Recommendations for Improving Experiment
    4. Answer Questions at End of Experiment

VII. **<u>RFERENCES & NOTES</u>**

References are to be presented in a <u>formal</u> way. e. g.

References

1. G. N. Lewis and M. Randall, "Thermodynamics," 2d ed., rev. by K. Pitzer and L. Brewer, McGraw-Hill Book Company, New York, 1961.

2. J. M. Sturtevant in A. Weissberger (ed.), "Technique of Organic Chemistry," vol. 1, "Physical Methods of Organic Chemistry," 3d ed., pt. 1, chap. 10, Interscience Publishers, Inc., New York, 1959.

Writing a Lab Report

Notebooks

It will be impossible to write a good lab report without keeping a good laboratory notebook. Data should be in neat tables and include units. The more organized your notebook is the easier it will be to analyze your data and find any errors during calculations. You may want to include drawings of your apparatus since it may more clearly help you understand how things work and why certain steps are taken. Also, if you understand your apparatus clearly, you may discover more possible sources of error.

List observations so that you remember to include them in your report. Don't forget that your lab notebook must be signed and dated following each day you run an experiment by your TA or the lab coordinator.

The Report

Size

The length should be no more than four to five pages double-spaced, 12-point Times Roman or larger with one inch margins. This does not include graphs and tables, but does include their accompanying text. Total length (including tables and graphs) should not exceed ten pages.

Title

Include an appropriate title, your name as well as your partners, your lab section (by day and time) and the date that the lab report is due.

Abstract

Although this part appears first in the report, it should be written last. An abstract is essentially a summary of your experiment in 3-7 sentences. It should include information about the procedure as well as any important theories and formulas used. Results should be listed with errors as well as any major conclusions. You want to highlight the major points of the experiment, so don't include things that aren't essential to determining your results. Good examples can be seen in any major journal.

Introduction

The introduction is essentially a purpose and theory section. You should include a brief experimental/procedural section. What did you do? It does not need to be detailed. Make sure you reference the procedures. Explain the science of the experiment. Develop the theory of the experiment; this includes key concepts, important equations, and assumptions. Why did you do it? What kind of conclusions do you expect to come to? How do you plan to come to them? This should not be taken directly from the lab handouts. The best lab reports are usually written by people who have looked up one or more references cited in the lab handout and have used physical chemistry textbook to develop the background. You need to show that you thoroughly understand the concepts.

Data

Specify the instruments and instrument settings that you used. Be specific. Make and model number are important if they are available for the instrument. List any information about chemicals that you used. Specify manufacturer and purity. If any solutions have been made, record the concentrations. Present a table of data taken during the experiment. Inserting a table into your text is the best way to present your data. Make sure that all entries are clearly labeled and use the correct units and significant figures. Your table must have a title. The word "table" should be capitalized. It there are more that one table, each table should be numbered. For example, "Table 1 – Temperature and Pressure Measurements". If you measured temperature in Celsius while collecting the data, report it as such. Do not automatically convert to Kelvin. This will make any mistakes you make traceable. The entries must be neat and clear. Do not simply reference attached notebook pages. Also list the error in the data from the measurement.

Calculations and Random Error

This section should be typed, but can be neatly hand written. In the calculation section, list the formula with the symbols defined a sample calculation with your data, the corresponding error formula, a sample calculation if applicable, and a table of calculated values for that specific calculation. Include a sentence of description if needed. You must include enough explanation in order for the reader to follow your thought process. Make certain that you use correct units and significant figures. Work carefully. If the final answer doesn't seem correct, check your calculations. It is possible that you made a simple mistake and a TA will know you didn't check your work when they find it. Make sure that you show all equations and error calculations. Graphs should be included in this section. Make certain that your graphs are labeled with an appropriate title. The title "y vs. x" is not appropriate. The title of the graph should convey its importance to the reader. Label each plot with Figure # – then give a description of the figure. Make certain that the axes are labelled with appropriate titles and units, and that the axes have correct significant figures and an appropriate scale.

If you are attaching additional information such as spectra or printouts, make an appendix at the end of your lab report. Title and label your appendix and refer to it in the appropriate section of your report.

Results

You must show your results in one concise table. Report the experimental values as well as their error. Include literature values. (These can always be found!) Be sure to compare the values you obtained to literature values.

Discussion and Systematic Error

Now it's time to analyze your results. This is an important section so make sure that you are addressing relevant issues. What does your answer mean? How does it compare to what you expected? The sign or magnitude of the value will often give some insight into some physical phenomena. If you calculate a value in two different ways make sure you compare the two answers and methods. If you calculate the same quantity for two different molecules make sure you explain differences and similarities. Do you notice any trends in your data? Use your data to draw conclusions. If you have any tables or figures refer to them in this section. What about error? Discuss the systematic error of your experiment and how it affects measurements you've made. Think about the magnitude of the error. An error bar may often seem large, but may in fact be acceptable when you consider the limitations of the theory used. Compare your value to a literature value and give a relative error. Similarity to published values does not mean that you deduced the "correct" answer: it just means that the values are consistent. How well does the theory that you used hold up? Talk about the assumptions made in the theory and their relevance. Suggest changes that could be made to the theory or procedure to improve results.

Answer all questions from the handout. Do not make statements like "This lab was successful" or "These results are reasonable" Statements need to be backed up with proof.

Conclusion

The conclusion should be only one or two sentences long. It is your last chance to report your results and relate them to the purpose of the experiment. Let the reader know the significance of the results.

References

Reference all information you have used. List the lab handout. References should include texts you've used to help write the introduction and discussion, and well as references to literature values. Use standard referencing techniques.

Experiments Procedures

MEASUREMENT OF THE RATIO OF THE MOLAR HEAT CAPACITIES BY THE METHOD OF CLEMENT DESORMES

Purpose:
To measure the ratio of the specific heat capacities of air at constant pressure and volume.

Introduction

The heat capacity for a substance is the amount of heat needed to raise the temperature of the substance by 1 ^{o}C or 1 K. The heat capacities depend on the chemical nature of the substance, on the physical state of the substance, on the temperature, and on whether P or V is held constant during the process: C_P or C_V is obtained (Cp the specific heat capacity at constant pressure and Cv the spesfic heat capacity at constant volume.). For liquids and solids, $C_V \approx C_P$ and the two terms are often used interchangeably. Another important quantity is the amount of heat, Q, Q is the amount of energy is proportional to the change in temperature, mass of material and the specific heat. Equation 1

$$Q = mC\Delta T \qquad\qquad (1)$$

Therefore for solid or liquid:

$$C_p = C_V = \frac{1}{m}\frac{Q}{\Delta T} = \frac{1}{m}\frac{dU}{dT} \qquad\qquad (2)$$

However, for ideal gases, it is well known that

$$C_p = C_V + R \qquad\qquad (3)$$

where

$$C_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_v \qquad and \qquad C_P = \frac{1}{n}\left(\frac{dU}{dT}\right)_p \qquad (4)$$

For a monatomic gas, there is no rotational or vibrational energy and if the temperature is relatively low, only the ground electronic state of the species is populated to any extent. Consequently, only translational energy is involved; and from kinetic theory,

$$C_V = \frac{3}{2}R \qquad and \quad C_P = \frac{5}{2}R \qquad (5)$$

For many simple diatomic molecules, however, the vibrational contribution to the heat capacity is small, and in the neighborhood of room temperature,25RCV=. However, the heat capacities of diatomic molecules increase with increasing temperature as the vibrational modes become active.

From eqn 4 we can see that the changes in internal energy for an ideal gas can be expressed by :

$$\Delta U = nC_v\Delta T \qquad (6)$$

Now suppose that gas is transferred to the systemat constant pressure, Let the temperature increases by ΔT .The heat must be transferred to the gas. Its value is given by

$$Q = n\, Cp\Delta T \qquad (7)$$

Since the volume increase in this process, the work done by the gas is

$$W=PdV. \qquad (8)$$

Applying the first law of thermodynamics we get:

$$\Delta U = Q - W \qquad (9)$$

Or

$$nCv\Delta T = nCp\Delta T - nR\Delta T \qquad (10)$$

From equation 9 a very important relation between the molar heat capacity at constant pressure and constant volume as expressed in equation 3 .

Finally we introduce a new physical quantity, dimensionless called **the Poisson constant (γ)**.
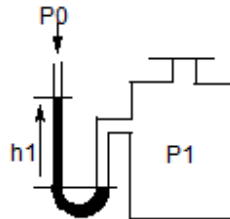
$$\gamma = \frac{C_P}{C_V} \qquad (11)$$

for a monoatomic gas

$$\gamma = \frac{5}{3}$$

The Clement and Desormes method

Consider a mass of gas enclosed in a vessel at a pressure P_1 which is slightly greater than atmospheric pressure P_o (Fig. 1).

Figure 1. Pressure P1 of a gas in avessel measured in terms of difference in heights of manometer columns.

The pressure P1 is measured by the difference in the heights h1 of the two columns of a manometer containing a liquid of density d grams per cubic centimeter so that

$$P_1 = Po + h_1 dg \tag{12}$$

Where both P1 and Po are measured in dynes per square centimeter. The initial temperature of the gas is t°C, i.e., the temperature of the laboratory. Suppose that by momentarily opening a valve the gas is allowed to attain atmospheric pressure Po. The change in pressure takes place so rapidly that there is no transfer of heat to or from external sources and the expansion is said to be purely adiabatic. The compressed gas in the vessel has to do some work in forcing some of the gas out of the vessel during the expansion. Consequently immediately after closing the valve the temperature of the gas remaining in the vessel is below room temperature. If the gas is now allowed to warm up to room temperature, the pressure increases to some value P_2 given by

$$P_2 = P_o + h_2 dg \tag{13}$$

where h_2 is the difference in the heights of the manometer columns.

Let V_1, V_0, and V_2 denote the initial, intermediate and final volumes of unit mass of the gas in the vessel, so that in each case the same mass of gas is considered. If the expansion from the initial state, pressure P1 volume V1, to the intermediate state, pressure Po volume V0, is adiabatic, the pressure and volumes are related by the equation

$$P_1V_1{}^\gamma = P_oV_o{}^\gamma \qquad\qquad (14)$$

where γ is the ratio of the specific heats of the gas at constant pressure and constant volume respectively. Since the gas in the initial and final states is at the same temperature, the relation between the pressures and volumes is given by Boyle's law, or

$$P_1V_1 = P_2V_2 \qquad\qquad (15)$$

Now $V_2 = V_o$ since there is the same mass of gas in the vessel in the intermediate and final states. To find the relationship existing between γ and the various pressures it is necessary to eliminate the various volumes V_0, V_1, V_2 in Eqs. (14) and (15).

From Eq. (15), raising both sides of the equation to the same power γ, it follows that

$$\left(\frac{V_1}{V_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^\gamma \qquad\qquad (16)$$

From Eq. (14) and the fact that $V_2 = V_o$

$$\left(\frac{V_1}{V_2}\right)^\gamma = \frac{P_0}{P_1} \qquad\qquad (17)$$

thus

$$\left(\frac{P_2}{P_1}\right)^\gamma = \frac{P_0}{P_1} \qquad\qquad (18)$$

or

$$\gamma = \frac{\log\left(P_0/P_1\right)}{\log\left(P_2/P_1\right)} \qquad\qquad (19)$$

If the various pressures do not differ greatly from atmospheric, then the expression for γ may be further simplified. Substituting the expressions for P_o and P_2 from Eqs. (12) and (13) in Eq. (18), it follows that:

$$\left[\frac{P_1 - \left(h_1 - h_2\right)dg}{P_1}\right]^\gamma = \frac{P_1 - h_1 dg}{P_1} \qquad\qquad (20)$$

$$\left[1 - \left(h_1 - h_2\right)\frac{dg}{P_1}\right]^\gamma = 1 - h_1\frac{dg}{P_1} \qquad\qquad (21)$$

If $(h_1 - h_2)\dfrac{dg}{P_1}$ is so small compared to unity that its square may be neglected, the left-hand member of Eq. (21) may be replaced by the first two terms in the binomial expansion of this expression. Eq. (21) then becomes:

$$\gamma = \frac{h_1}{h_1 - h_2} \qquad (22)$$

Procedure:

Apparatus: The apparatus consists essentially of a large Pyrex flask the top of which is ground plane, a cover plate of metal also ground plane and provided with a hose nipple, a manometer with light oil or xylol as the indicating liquid, a three-way or T-connecting tube and a small pressure pump with rubber tubing for making the connections (Fig. 2). A small amount of some drying agent such as Dessigel S is needed in the flask to eliminate any water vapor present in the atmosphere. Stopcock grease and a small rod in a clamp with a rubber stopper on one end are required to ensure an airtight seal between the top of the flask and the plate. The pressure pump shown in Fig. 2 may be replaced by the rubber pressure bulb shown in Fig. 2. A large stand and clamps for holding the flask and a pinchcock for preventing any air leak through the pump are required.
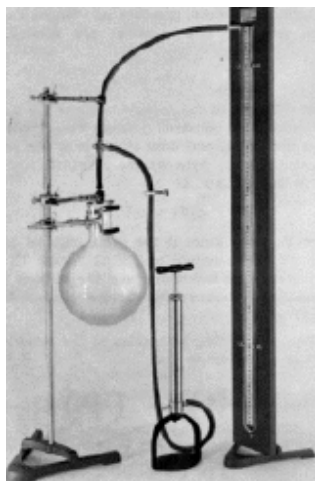
Figure 2. Apparatus for determine the ratio of specific heats of air

1. Place a small amount of drying agent in the flask and mount the apparatus as shown in Fig. 2.
2. Place a liberal supply of stopcock grease over the ground portion of the top of the vessel and slide the plate over the ground part several times so that the grease is evenly distributed.

3. Mount the small rod so that the rubber stopper on its end presses firmly down on the plate.
4. Pump a small amount of air into the flask and cut off the connection to the pump with the pinchcock. The difference in level of the liquid in the manometer arms should be of the order of 15cm.
5. Allow the air in the flask to come to room temperature and be sure that no air is escaping. If air is escaping, regrease the ground top of the flask and again adjust the rod and rubber stopper on top of the plate.
6. After making sure there is no leak, read the manometer arms and determine h_1.
7. The flask is now opened momentarily to the atmosphere by raising the arm and rubber stopper, sliding the metal plate sidewise for about half a second and then sliding it back.
8. The opening to the flask should be as large as possible and the operation performed as quickly and carefully as possible.
9. Replace the rod and rubber stopper so that the plate is pressed against the ground glass top. After a short time the temperature of the gas rises to room temperature and the pressure stops rising.
10. Record the difference in the height h_2 of the two arms of the manometer.

If the pressure of the air begins to fall as shown by the manometer, it means there is a leak in the apparatus and the experiment must be repeated.

Calculation:

From the heights h_1 and h_2 and Eq. (22) calculate the value of γ. If the pressure P_1 has greatly exceeded atmospheric, then it is necessary to use Eq. (19) and the suitable data.

Experiment no	h₁(cm)	h₂(cm)	γ
1			
2			
3			

QUESTIONS:

1. Draw a rough graph typical of the relationship between pressure and volume for the case of a gas compressed (a) isothermally; (b) adiabatically. Which of the two graphs is steeper? Give the reasons for the difference in slopes.
2. If during the course of the experiment the atmospheric pressure should change, would it be legitimate to use Eq. (22) to calculate γ?
3. If the air in the flask contained water vapor, would the value of γ for this damp air be greater or less than the value of γ for dry air?
4. Why is it necessary that the flask be opened only momentarily to the atmosphere?
5. If Cp and Cv are the thermal capacities per gram molecule of a gas at constant pressure and constant volume respectively, what does their difference Cp - Cv represent? Give the derivation and explanation of the equation given for Cp - Cv.

VISCOSITY AS A FUNCTION OF TEMPERATURE

Purpose:

The purpose of this experiment is to measure the viscosity of different liquid and study the effect of temperature on the viscosity, the variation of composition on the viscosity will also be studied using Ostwald viscometer.

Introduction

Definition
Viscosity is the resistance to flow which is a property of fluids, both liquids and gases. When a liquid flows through a tube, layers of liquid slide over each other and intermolecular forces cause resistance to flow.

Theory:
Fluids resist a flow gradient. The resistance produces a frictional force known as a **viscous force**. Specifically the force is proportional to the area of contact, *A*, between the flowing regions and to the velocity gradient, *dv/dx*. The constant of proportionality is called the **coefficient of viscosity**, η, as given in Eq 1.
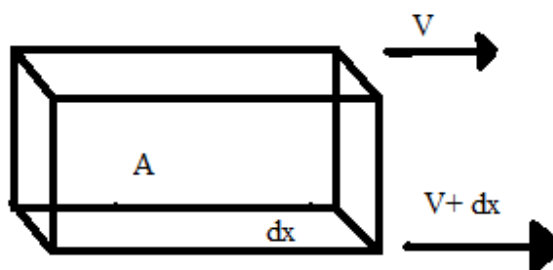
$$F = \eta A \frac{dv}{dx} \qquad (1)$$

Where :
F: the frictional force, **A**: Area of plane, **η:** the **coefficient of viscosity**, **dx**: distance between the two parallel plane and **dv:** velocity of flow.

The unit of viscosity, 1 gm cm^{-1}

Units of Viscosity

The units of viscosity is a **poise** :

$$\eta = \frac{Fdx}{Adv} = \frac{N-m}{m^2.m.s^2} = kg.m^{-1}s^{-1} \text{ or } Ns.m^{-2}$$

Where N is Newton, kg are kilograms, m is meters, s is seconds, and η is viscosity. The unit for viscosity is the Poise. Which is 1 gm cm^{-1} s^{-1}.

The viscosity of water for example at 25 ^{o}C is 0.008937 Poise.

Absolute Viscosity

The absolute viscosity of a liquid through a cylindrical tube of radius r and length l under pressure head P which is proportional to the density is given by equation 2:

$$\eta = \frac{\pi \, Pr^4 t}{8LV} \qquad \text{Pousille equation (2)}$$

Where : V is the volume of liquid, L is the length of the tube, P is the pressure, height t is time and r is the radius of the capillary tube.

For two different liquids, the relative viscosity:

$$\eta_1 = \frac{\pi \, P_1 r^4 t_1}{8LV} \quad and \; \eta_2 = \frac{\pi \, P_2 r^4 t_2}{8LV}$$

so

$$\frac{\eta_1}{\eta_2} = \frac{t_1 P_1}{t_2 P_2}$$

where $P = \rho.g.h$;

ρ is the density, g. is the gravitational forces and his the height

so

$$\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2} \qquad (3)$$

where 1 *is for water*

Temperature effect on viscosity
Temperature affects the viscosity of the most common liquids. As temperature increase, the liquid become thinner and viscosity decrease, contrary behaviour is recorded for gases.

The relation between the viscosity and temperature is expressed in equation 4

$$\eta = A.e^{E/RT} \quad or$$

$$\ln \eta = \ln A + \frac{E}{RT} \qquad (4)$$

Where A is constant and E is the energy required to stop the fluid, Both A and E are characteristics of liquid.

Different Ways to Measuring Viscosity:

There are four different ways of measuring viscosity's of liquids:

1. Using a viscometer (Ostwald or Ubbeholde) to measure the rate of flow through a capillary.
2. Liquids of high viscosities, the measurement of the rate of flow of the liquid through a hole in the bottom of the container.
3. Measuring the rate of fall of a metal sphere through a column of liquid is also used for very viscous liquids.
4. Measuring the resistance experienced by a rotating disc on a torsion measuring device.

Procedure:

Material and apparatus: Viscometer, distilled water. Benzene ,n-propanol, n-buatanol-n-hexan.

Viscosity Measurement

1. Make certain the viscometer is mounted vertically in the constant-temperature bath. The fiducial marks should be visible below the water level.
2. Read the temperature of the bath several times over a few minutes. It should be constant to within ±0.1°C before you begin taking viscosity measurements.
3. Pipette the appropriate amount of solution or water into the viscometer. (Always immediately rinse the pipette thoroughly with water and dry it with acetone and air after use.)
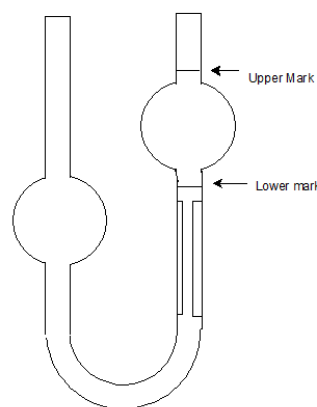
4. Allow the solution to equilibrate in the viscometer. Using a pipette bulb, apply suction to draw the solution into the capillary and up to a point above the upper fiducial mark.
5. Release suction. The solution will begin to flow under the force of gravity.
6. **Measure the time it takes the meniscus to move from the upper fiducial mark to the lower fiducial mark**. Do this at least twice; you do not have to change solutions, just bring the solution above the upper mark and repeat. If the runs differ by more than about 1%, repeat until you have determined the time consistently. This will also give you an estimate of the accuracy of the measurement of the time.
7. Each time you empty the viscometer, it must be washed thoroughly with distilled water, dried with acetone and air. When it is clean, put it back in the temperature bath to equilibrate, and you are ready to measure the next solution.
8. Repeat the above procedure at different temperature, 30,40 and 45 C.
9. When you finish you use of the viscometer, return it to the storage jar IN CLEAN CONDITION.
10. Repeat the above procedure using the same volume of benzene.
11. Repeat the procedure for at least two alcohol.
12. Select a pair of alcohols and make up five mixtures of diffrenet composition covering a wide range (e.g. 10, 30, 50,70 and 90% by volume).determine the viscosity of each mixture.
13. **Tabulate your result.**

Fluid	Time second	Relative density	Temperature

Calculation:

I. Calculate the relative viscosity of different material using equation 3.
II. Using equation 4 to plot the relation between viscosity and temperature.
III. Draw a graph of viscosity versus volume composition.

HEAT OF SOLUTION FROM SOLUBILITY

Purpose:
To determine the heat of solution of benzoic acid from its solubility.

Introduction

One of the simplest cases of equilibrium is that of a saturated solution in contact with excess solute; molecules leave the solid and pass into solution at the same rate at which molecules from the solution are deposited on the solid. Here the solubility (S) in a unit of gram per 100.0 ml solvent will be used

An equilibrium-constant relation may be written for the equilibrium considered :

$$K = \frac{a_2}{a_2^*} \qquad (1)$$

Here a_2 represents the activity of the solute in the saturated solution and a_2^* the activity of the pure solid solute. The conventional choice of standard state for the latter is the pure solute itself at the temperature and pressure involved, making a_2^* identically equal to unity. The activity a_2 is related to the Solubilty (S) of the solute by means of the activity coefficient γ , a function of T, P, and composition which approaches unity as m approaches zero. Then

$$K = [a_2] S = \gamma_s S_s \qquad (2)$$

where the subscript s indicates that the relation applies to the saturated solution. The Z symbol $[a_2]s$ denotes the value of the activity a_2 for the saturated solution.

The change in K with temperature at constant pressure reflects a change in S, and also the change in γs, which is affected by both the variations in temperature and concentration of the solution. The van' t Hoff equation requires that:

$$\left(\frac{\delta \ln K}{\delta T} \right)_P = \frac{\Delta H}{RT^2} \qquad (3)$$

where ΔH° is the standard enthalpy change for the solution process. This quantity should not be confused with any actual experimentally measurable heat of solution; it can be determined indirectly, however.

Taking into account the effects of temperature and concentration on γs there results for constant pressure is expressed by:

$$\left(1+\left(\frac{\delta \ln \gamma}{\delta \ln S}\right)_{T,P,S}\right)\frac{d \ln S}{dT} = \frac{[\Delta H_{DS}]_{s_1,s_2}}{RT^2} \qquad (4)$$

Here $[\Delta H_{DS}]_{s_1,s_2}$ is the ***differential heat of solution at saturation*** at the given temperature and pressure. S is the solubility of benzoic acid at temperature T. S can be calculated by titration with a standard solution of 0.20 M NaOH using phenolphthalein as indicator. For cases in which the activity coefficient γ for the solute changes only slightly with concentration in the immediate neighborhood of saturation, the bracketed term on the left in Eq. (4) becomes unity, and

$$\frac{d \ln S}{dT} = \frac{[\Delta H_{DS}]_s}{RT^2} \qquad (5)$$

In this approximation, then, the differential heat of solution at saturation may be calculated at a given temperature T by multiplying by R the slope at this temperature of the plot of ln S versus 1/T.

If it is assumed in addition that $[\Delta H_{DS}]_S$ is independent of T, an assumption which in general is better for nonelectrolytie solutes than for electrolytic types, then integration of Eq. (5) leads to ;

$$\ln \frac{S_1}{S_2} = \Delta H\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (6)$$

Where S_1 and S_2 are the solubility of benzoic acid at T_1 and T_2, respectively.

The heat of solution with which we are concerned here is the heat absorbed when 1 mole of the solid is dissolved in a solution that is already practically saturated. It differs from the heat of solution at infinite dilution, which is the heat of solution often given in tables, by an amount equivalent to the heat of dilution from saturation to infinite dilution.

Procedure:

Material:

8 Erlenmeyer flasks 250 ml, thermo stated at 25, 35, 45 and 55 C. Sodium hydroxide 0.02 M, benzoic acid, 25 ml pipet ; filter paper (S); rubber tubes

Procedure:

11. Into a dry two Erlenmeyer flasks add about 1 g of benzoic acid, then add to each 100.0 ml of hot water(at 70C)
12. Add one of them an thermostat at temperature of 25 C and another at 35C.
13. Also take additional two Erlenmeyer flasks and add to each 2 g of benzoic acid and to each of them add 100.0 ml of hot water at 70 C
14. Add one of them in a thermostat at T= 45 C and another one at 55C.
15. Leave the four flasks in water bath for about 30 min to reach thermal equilibrium, swirl four of them.
16. Put a piece of cotton in one side of rubber and attach the other side with the 25 ml pipette.
17. Quickly, suck with this pipette from the solutions prepared in 2 and 4, leave the solid material in the bottom of the flask. TO AVOID the recrystalization process, heat the pipette before the sucking process, then pour the solution into other four dry flasks.
18. Titrate these solutions with standard solution of NaOH using phenolphthalein as indicator.
19. Clean up anything you use.

Calculation:

Assume the density of solutions equal to one, calculate the solubility of benzoic acid in 100.0 ml water at each temperature.

Calculate the heat of solution using equation 5 and 6.

Tabulate your results on the following table

Temperature	Volume of benzoic acid (ml)	Volume of NaOH Ml	Solubility g/100.ml
25 C			
35 C			
45 C			
55 C			

ADSORPTION FROM SOLUTION

Purpose:

The adsorption of acetic acid on charcoal is studied using both the Freundlich isotherm and Langmuir isotherm.

Introduction

A distinctive characteristic of a solid material is a distribution of weak surface energy sites. Gas or vapor molecules can become bound to these sites. This generally describes the adsorption phenomenon. The quantity of molecules taken up by the surface depends on several conditions and surface features including temperature, pressure, surface energy distribution, and the surface area of the solid. A plot of the quantity of molecules adsorbed versus pressure at constant temperature is called the adsorption isotherm. Physical adsorption is the result of relatively weak Van der Waal's interaction forces between the solid surface and the adsorbate- a physical attraction. Physical adsorption is easily reversed.

Depending on the gas and solid, the adsorption phenomenon also can result in the sharing of electrons between the adsorbate and the solid surface- a chemical bond. This ischemical adsorption and unlike physiorption, chemisorption is difficult to reverse. A significant quantity of energy usually is required to remove chemically adsorbed molecules. Physical adsorption takes place on all surfaces provided that temperature and pressure conditions are favourable. Chemisorption, however, occurs only between certain adsorbents and adsorptive species and only if the surface is cleaned of previously adsorbed molecules.

Under proper conditions, physical adsorption can result in adsorbed molecules forming multiple layers. Chemisorption, on the other hand, only proceeds as long as the adsorptive can make direct contact with the surface; it is therefore a single-layer process. A characteristic of physical adsorption is that almost all the adsorbed molecules can be removed by evacuation at the same temperature at which adsorption occurred. Heating accelerates desorption because it makes readily available to the adsorbed molecules the energy necessary to escape the adsorption site. A chemically adsorbed molecule is strongly bound to the surface and cannot escape without the influx of a relatively large quantity of energy compared to that necessary to liberate a physically bound molecule. This energy is provided by heat and often very high temperatures are required to clean a surface of chemically adsorbed molecules. Physisorption tends to occur only at

temperatures near or below the boiling point of the adsorptive at the prevailing pressure. This is not the case with chemisorption. Chemisorption usually can take place at temperatures well above the boiling point of the liquified adsorptive.

The adsorption of acetic acid on charcoal will be studied using both the Freundlich isotherm and the Langmuir isotherm. *This is an example of physical adsorption*, where dipole and van der Waals forces are the predominant sources of attraction, and the heat of adsorption is typically less than 50 kJ /mol.

The amount of acetic acid (adsorbate) adsorbed per gram of charcoal (adsorbent) will depend on the surface area of the charcoal, the temperature of the solution, and the adsorbate concentration in solution. The adsorption will be followed by titrating the acetic acid not adsorbed by the charcoal, then determining the amount adsorbed by difference. **Isotherms** (plots of moles of adsorbate adsorbed per gram of adsorbent versus solution concentration) will be constructed, then compared with two models:

1. **Langmuir Isotherm:** it assumes a homogenous surface and that the adsorbed layer is only one molecule thick**, and it could be expressed as**

$$\frac{C_e}{q_e} = \frac{C_e}{Q_e} + \frac{1}{Q_0 b} \qquad (1)$$

where C_e is the equilibrium concentration of acetic acid remaining in the solution($mgdm^{-3}$) q_e **is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium (mgg^{-1}) Q_0** and b are Langmuir constant. Langmuir equation can be used to calculate the maximum adsorption Q_0 (mgg^{-1}) and the energy parameters of adsorption b ($dm^3 mg^{-1}$). From a plot of Ce/Qe vs Ce, b and Q_0 can be determined from the slope and intercept.

2. **The Freundlich isotherm:** it assumes heterogenous surface with different types of adsorption sites and has proven to adequately describe adsorption isotherm in many cases.

The The Freundlich isotherm is an empirical equation and shown to be satisfactory for low concentration. The Freundlich isotherm has the following linear form

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \qquad (2)$$

Where Ce is the equilibrium concentration of Acetic acid remaining in solution ($mgdm^{-3}$), q_e is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium(mgg^{-1}), k_F and 1/n are constant that are considered to be relatively indicators of adsorption capacity(or related to the bonding energy) and adsorption intensity, respectively. A value for 1/n below one indicates al Langmuir type isotherm because it becomes more

and more difficult to adsorb additional adsorbate molecules at higher adsorbate concentrations.

A plot of log q_e vs log C_e enables the empirical constants k_F and $1/n$ to be determined from the slope and intercept of the linear regression.

Procedure:
Material:

6 Erlenmeyer flasks 250 ml, 6- volumetric flasks of 100.0 ml, pipettes, rubber ftopper, three funnels, 6-titration flasks of 100 ml, filter paper and burette.

Procedure:

1. To each six of 250 Erlenmeyer flasks add about 1 g weighed accurately to the nearest 0.001 g) of activated charcoal. Label the flask from 1 – 6.
2. Using 100 ml volumetric flask, prepare the following solution by adding the respective quantity of 0.25 M acetic acid stock solution and make up to the mark using de-ionised water, in case of flask 1 fill with acetic acid to the mark.

Flask no.	Acetic acid 0.25 M Ml	De ionised water ml	Total volume
1	100	0.0	100
2	50	50	100
3	25	75	100
4	15	85	100
5	10	90	100
6	5	95	

3. Add these solutions to the six flasks containing the charcoal adsorbent.

4. The flasks should be tightly stopped, then shaken periodically for 30 min, and then allowed to equilibrate for 1 hour in a water bath maintained at constant temperature.

5. While waiting for solution to equilibrate, determine the exact concentration of the stock acetic acid solution by titrating two or three 5.00 ml samples of the stock solution with 0.1 M NaOH using phenolphthalein indicators.

6. After equilibrium has been reached, measure the temperature of solutions. Filter the content of each flask (discard the first 10 ml of filtrates) and titrate samples of the filtrates with 0.1 M NaOH to determine the equilibrium concentration of acetic acid

7. Use the following scheme to titrate the samples:

Filtrate No	Sample volume (ml)	Number of samples	Volume of 0.1M NaOH (ml)
1	5	2	
2	10	2	
3	25	2	
4	50	2	
5	50	2	
6	50	2	

Calculation:

1. Determine the concentration of the original acetic acid solution and the concentration of the acid in equilibrium with the adsorbent.
2. Find out the weight of acid adsorbed (in mg) per gram of adsorbent from the volume of the solutions, their equilibrium concentration and the original acid concentration.
3. Plot the result according equation 1
4. Plot log qe vs log Ce according equation 2
5. Calculate Langmuir and Freundlich parameters.
6. Determine whether a Langmuir or Freundlich parameters isotherm provide a better fit to the data.

CALORIMETRIC METHOD

Purpose:

The object of this experiment is to measure the ΔH and ΔU of acid base reaction using calorimetric method.

Introduction

The first law of thermodynamics (i.e., the conservation of energy) states that internal energy is which is composed of heat (q) and work (w) is conserved, and could expressed mathematically by equation 1

$$\Delta U = q-w \qquad (1)$$

According to the first law of thermodynamic, any chemical or physical changes occurs to the system will be accompanied by transfer of heat (energy); heat may be either evolved (exothermic) or absorbed (endothermic). Heat of the reaction will affect the internal energy (U) or enthalpy of the system (H), depends either the change occurs at constant volume or constant pressure. Changes on enthalpy (ΔH) or internal energy (ΔU) for a chemical reaction could be measured using calorimetric method, in which a calorimeter is used. Calorimeter is apparatus used to measure the quantity and direction of heat flow accompanying a chemical or physical change.

Calorimetric method could be divided into two categories:

1- **Constant-volume calorimeter** or bomb calorimeter is used in measuring the heat of combustion of a particular reaction. Since the change occurs at constant volume, the energy absorbed or released will be related to changes in internal energy (ΔU)

2- **Constant-pressure calorimeter:** For none gaseous reaction an open calorimeter (i.e., under constant pressure) could be used to measure the heat changes, the energy absorbed or released will be related to changes in enthalpy energy (ΔH). Neutralization reaction and solubilisation are an example of the reaction that can be studied using constant volume calorimeter.

Relation between internal energy (ΔU) and enthalpy change (ΔH)

Regardless to the method used to measure heat changes (i.e. constant pressure or constant volume) both quantities could be obtained, since obtain one of them allow us to measure the other one since

$$H = U + PV \qquad\qquad (2)$$

$$dH = dU + d(PV) = dH = dU + PdV + VdP$$

$$under \text{ constant } P$$

$$dH = dU + PdV \text{ .... taking into acount } PV=nRT$$

$$\Delta H = \Delta U + \Delta nRT \qquad\qquad (3)$$

Measurement of enthalpy changes under constant pressure condition:

Calorimeter which is an insulated container does not allow heat to be exchanged with the surroundings, which allow us to measure the heat of the reaction under **adiabatic conditions** (i.e., *An adiabatic process is a thermodynamic process in which there is no heat transfer (q) into or out of the system. q = 0*). So reaction involve exothermic heat transfer will lead raise the temperature of the reaction system, on the other hand, reaction involve endothermic heat transfer will lead to lower temperature of the reaction mixture. The change on the system temperature (ΔT) and the heat capacity allow us to calculate the energy.

Heat capacity (C): is the energy required to change the temperature of material by one degree, the **specific Heat capacity** (p) is the energy required to change one gram of material by one degree.

The energy (q) released or absorbed from the reaction could be calculated as follow:

$$\text{Energy (q)} = p \ m \ \Delta T \qquad\qquad (4)$$

Where: **m** is the mass of the system (in gram), **p** is the specific heat capacity (Joule /g.C) and $\mathbf{\Delta T}$ is the temperature difference (T_2-T_1).

Since the system is composed of Calorimeter (1) and the reaction material (2), the total heat capacity C is summation of heat capacities of the system component: C= C_1 + C_2, thus, the energy (q) is calculated as follow. Equation 5:

$$\text{Energy (q)} = p_1 \ m_1 \ \Delta T + p_2 \ m_2 \ \Delta T \qquad\qquad (5)$$

Notes:

1- The q value will be positive if temperature is increased. Otherwise it will be negative.

2- ΔH is equal to the q value with opposite sign (i.e., since we have adiabatic condition so $\Delta q = 0$)

3- $\Delta H = -q_V$

4- Since ΔH is measured we can calculate ΔU using equation 3
$$\Delta H = \Delta U + \Delta nRT \qquad\qquad (3)$$

5- **Determination of ΔT**, is crucial to measure **q**, ΔT is determined using the following procedure::

    a. Record the temperature of solution as function of time every 20 second before starting the reaction and during the reaction.

    b. Record the temperature of the solution mixture until it reach its maximum and start cooling down

    c. Plot the temperature versus time, figure 1,

    d. The maximum temperature id the intersection point of two lines: (1) The best line drawn through the data points on the cooling portion of the curve and (2) a line drawn perpendicular to the time axis at the mixing time.
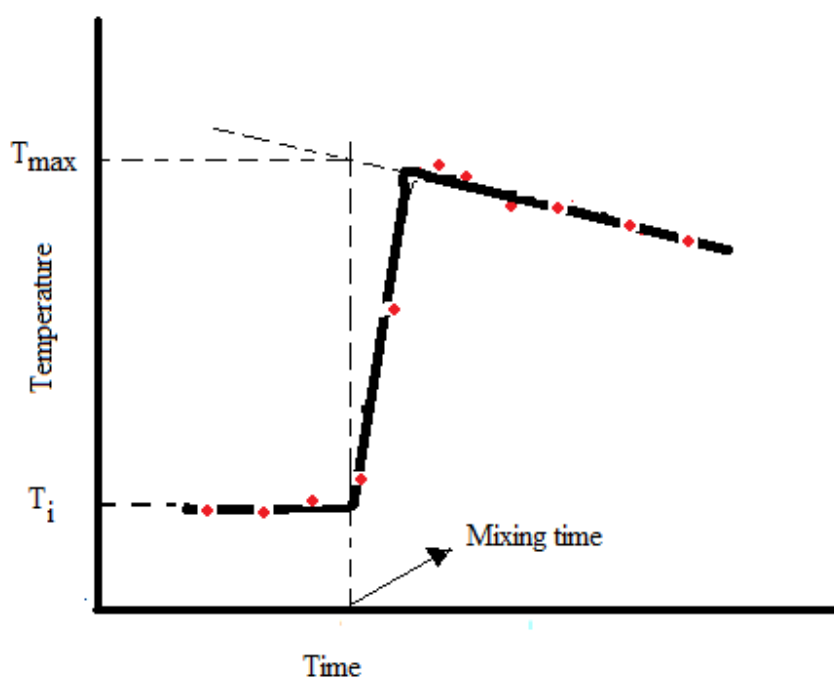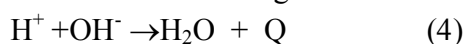

Figure 1. Temperature versus time curve

Method:

In this experiment we will measure ΔH of neutralization of acid base reaction and ΔH of formation for some ammonium salt (NH_4X).

1. Measure the enthalpy of neutralization of an acid-base reaction $\Delta H_{neutralization}$. *Neutralization* is the reaction between strong acid and base

$$H^+ + OH^- \rightarrow H_2O + Q \qquad (4)$$

The enthalpy of neutralization **is defined as:** the enthalpy change when 1 mol of water is formed from complete neutralization of an acid and a base under standard condition. The evolved heat (Q, $-\Delta H_{neutralization}$) is absorbed by the reaction

solution and the calorimeter therefore, temperature of both the solution and calorimeter equation 5

$$Q = -\Delta H_{neutralization} = Q_{solution} + Q_{calorimeter} \quad (5)$$

So it essential to know the heat capacity of the calorimeter in order to measure to $\Delta H_{neutralization}$.

I. Calibration of the calorimeter: To evaluate the calorimeter heat capacity constant (also known as calorimeter capacity constant) in $J/^{o}C$, one adds a known mass of hot water to a known mass of cold water which is in the calorimeter. Heat (Q) is lost by the hot water and is absorbed by the cold water and the calorimeter equation (6). Thus the heat absorbed by the calorimeter calculated by equation (7), *assuming the temperature of the calorimeter is the same as the solution inside it at all times* :

$$Q(\text{Hot water}) = Q(\text{Cold water}) + Q(\text{Calorimeter}) \quad (6)$$
$$Q(\text{calorimeter}) = Q(\text{Hot water}) - Q(\text{Cold water}) \quad (7)$$

The calorimeter constant is given by equation 8
$$\text{Calorimeter constant} = (Q\text{Calorimeter}/\Delta t\text{Cold water}) \quad (8)$$

II. The ΔH of neutralization is found by mixing known quantities (moles) of an acid and a base (both initially at the same temperature) in a calorimeter and measuring Δt of the mixture and the calorimeter.

The heat given off by the neutralization reaction, ΔH could be evaluated using the following equations:

$$-\Delta H = Q_{solution} + Q_{calorimeter} \quad (5)$$
$$Q_{calorimeter} = C_{heat\ capacity\ of\ calorimeter} . \Delta T \quad (9)$$
$$Q_{solution} = p.m.\Delta T = p.V.\rho.\Delta T$$
$$where\ V : solution\ volume\ and\ \rho\ is\ the\ density$$
$$\Delta H = \frac{Q}{n} \quad (10)$$
$$where\ n\ is\ numebr\ of\ mole\ of\ produced\ water$$

2. Measure the enthalpy of formation of ammonium salt (NH_4X).
Standard heat of formation of a compound ΔH_f^0 is the change of enthalpy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (Pressure = 1 bar and temperature at 298.15 K). Since it is not easy to measure, **directly,** the enthalpy of formation of the ammonium salt, we will use Hess law to measure ΔH_f of the ammonium salt using the following equation 15:

$$NH_{3(aq)} + HCl_{aq} \xrightarrow{\text{nutralization}} NH_4Cl_{(aq)} \qquad \Delta H_{nutr} \qquad (11)$$
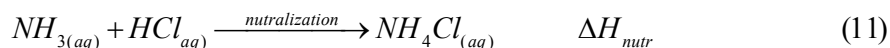
$$\Delta H_{nutr} = \Delta H_{f(NH_4Cl_{(aq)})} - \left(\Delta H_{f(NH_{3(aq)})} + \Delta H_{f(HCl_{(aq)})} \right) \qquad (12)$$

$$NH_4Cl_{(s)} \xrightarrow{\text{solution}} \quad NH_4Cl_{(aq)} \qquad \Delta H_{sol} \qquad (13)$$
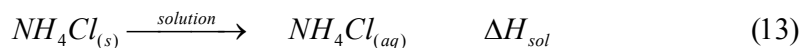
$$\Delta H_{solu} = \Delta H_{f(NH_4Cl_{(aq)})} - \left(\Delta H_{f(NH_4Cl_{(s)})} \right) \qquad (14)$$

from 13 *and* 14 we can calculate the enthalpy of formation of $NH_4Cl_{(s)}$ *as*:

$$\Delta H_{f(NH_4Cl_{(s)})} = \Delta H_{nutr} + \Delta H_{f(NH_{3(aq)})} + \Delta H_{f(HCl_{(aq)})} - \Delta H_{solu} \qquad (15)$$

Procedure:

Material:

Calorimeter, sodium hydroxide, Hydrochloric acid. Amunia, thermo prop or thermometer.

Procedure:

A- Calibration of the calorimeter:

1. Weigh the calorimeter with its entire component, record the weight.
2. Transfer 50 ml of distilled water into your assigned calorimeter.
3. Weigh the calorimeter with the cold water.
4. Calculate the weight of the cold water.
5. Transfer 100 ml of distilled water into 250 ml beaker. Heat this water to $15 - 20^{\circ}C$ above the temperature of the cold water
6. Be sure to note the starting time when measuring temperatures. Starting with the hot water, alternately measure the hot and cold water temperatures for a 4.5 minute period. You will have 5 measurements of each water sample. At the 5.0 minute mark quickly add the hot water to the cold water (in the calorimeter) and record the temperature of the mixture at 30 second intervals for 10 minutes.
7. Weigh the calorimeter with the hot and cold water. Calculate the weight of the hot water.
8. Clean and dry the beaker and calorimeter for the neutralization reaction.
9. Determine the ΔT as previously described.
10. Tabulate your result and show all of your calculations.

B- Acid-Base neutralization reaction:

1. Pipet 50.00 mL of your assigned acid into the clean dry calorimeter. Suspend the thermometer in the acid.
2. Pipet 50.00 mL of your assigned base into a 100 mL beaker. Since both the acid and base have been at room temperature for several hours, we can safely assume that both are at the same temperature.
3. Record the acid (and base) temperature every 30 second 4.5 minutes.
4. At the 5 minute mark quickly add the base to the acid in the calorimeter.
5. Record the solution temperature every 30 second for 10 minutes giving a total of 15 minutes of readings.
6. Record all temperatures to the nearest $0.01^{o}C$.
7. Clean and dry the beaker and calorimeter and repeat the above procedure for a second trial.
8. Plot graphs of temperature vs time for the two neutralization reaction trials. Determine the temperature changes (Δt) as before.

C- Heat of formation of ammonium chloride:

1. Repeat the procedure in part B to measure the enthalpy of neutralization between ammonia (NH_3) and hydrochloric acid (HCl) use equal concentration of both material.
2. Calculate the weight of the produced salt.
3. **Measure the enthalpy of solution of $NH_4Cl(s)$**
4. Weigh the calorimeter with its entire component, record the weight.
5. Transfer 50 ml of distilled water into your assigned calorimeter. Record every 30 second for 4 minutes.
6. **Transfer 2 g of solid $NH_4Cl(s)$ into the calorimeter. Stirrer the solution and quickly record the temperature every 30 second for 10 minutes.**
7. Weigh the calorimeter with its entire component.
8. Clean and dry the beaker and calorimeter and repeat the above procedure for a second trial.
9. Plot graphs of temperature vs time for the two neutralization reaction trials. Determine the temperature changes (Δt) as before.

Calculation:

Tabulate your results using the following tables:

1- Heat capacity of calorimeter.

Time (second)	Hot Water Temp, ^{o}C	Cold Water Temp, ^{o}C	Mixture Temp
0.00			
30			

2- Acid-Base neutralization(HCl and NaOH)

Time (second)	Acid and base Temp, ^{o}C	Salt solution temp Temp, ^{o}C
0.00		
30		

1- Acid-Base neutralization(NH_3 and HCl)

Time (second)	Acid and base Temp, ^{o}C	Salt solution temp Temp, ^{o}C
0.00		
30		

2- Calorimeter Heat capacity Determination

    I.   Mass of hot water (g) _____

    II. Δt of hot water (oC) (absolute value) _____

    III.   Heat lost by hot water (J) _____

    IV.   Mass of cold water (g) _____

    V. Δt of cold water (oC) _____

    VI.   Heat gained by cold water (J) _____

    VII. Heat gained by calorimeter (J)) _____

    VIII. Calorimeter Constant (J/oC) _____

3- Acid base Neutralization:

    Assigned Acid and Base: _____ _____

    Balanced Equation for Complete Neutralization

    Density of Salt Solution (g/mL) _____

    Specific Heat of Salt Solution (J/g-oC) _____

    I.   Volume of Salt Solution (mL) _____

    II.   Mass of Salt Solution (g) _____

    III. Δt of Salt Solution (oC) (from graph) _____

    IV.   Heat Gained by Salt Solution (J) _____

    V.   Heat Gained by Calorimeter (J) _____

    VI.   Total heat Evolved by Reaction (J) _____

4- Heat of formation

    A- Assigned Acid and Base

        Assigned Acid and Base: _____ _____

        Balanced Equation for Complete Neutralization

        Density of Salt Solution (g/mL) _____

        Specific Heat of Salt Solution (J/g-oC) _____

  I.   Volume of Salt Solution (mL) _____

  II.   Mass of Salt Solution (g) _____

  III. Δt of Salt Solution (oC) (from graph) _____

  IV.   Heat Gained by Salt Solution (J) _____

  V.   Heat Gained by Calorimeter (J) _____

  VI.   Total heat Evolved by Reaction (J) _____

B Heat of solution:

5- Calculate the heat of solution.

6- Using standard enthalpy of formation of NH_3 and HCl to **Calculate the heat of formation.**

7- Calculate the error of your results.

PARTIAL MOLAR VOLUME

Purpose:
To determine the partial molar volumes of sodium chloride solution.

Introduction

1. **Definitions:**

    I.   **Intensive** property is a physical property of a system that does not depend on the system size or the amount of material in the system. (Examples include: include: Temperature, chemical potential, density, specific gravity, viscosity, velocity, specific energy, specific heat capacity, melting point and boiling point).

    II.   **Extensive** property of a system does depend on the system size or the amount of material in the system. (Examples: mass, length, volume, entropy, enthalpy, Gibbs energy).

    III.   **Partial molar volume**: is the change in volume per mole of A added to a large volume of the mixture: $V_J = (\partial V/\partial n_j)_{p,T,n}'$. The total volume of a mixture is $V = n_A V_A + n_B V_B$ ***In general, the partial molar volume*** of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture.

    IV.   **Apparent Molar Volume (ϕ)**, is closely related to the partial molar volume of the solute.

2. **What is Practical definition of Partial molar volume:**

    Imagine a huge volume of pure water at 25°C. When a further 1 mol H_2O is added, the volume increases by 18 cm^3 and we can report that 18 cm^3 mol^{-1} is the **molar volume of pure water**. However, when we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm^3. **WHY??.** The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules, and the packing of the molecules results in the H_2O molecules increasing the volume by only 14 cm^3. The quantity 14 cm^3 mol^{-1} is the ***partial molar volume*** of water in pure ethanol.

3. Background:

The partial molar Gibbs Free energy, which is called the chemical potential, is central to the study of solutions thermodynamics. Take an example of a two-component solution with n1 moles of component 1 and n2 moles of component 2. The change in Gibbs Free Energy with concentration at constant temperature and pressure is given by equation 1:

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n1} dn_2 \qquad (1)$$

The partial molar Gibbs Free Energy with respect to changes in the number of moles of component 1 is called chemical potential and is given by equation 2

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \mu_1 \qquad (2)$$

The partial molal Gibbs Free Energy with respect to changes in the number of moles of component 2 is given by equation 3, substituting these definitions into equations 1 gives:

$$\left(\frac{\partial G}{\partial n_2}\right)_{n1} = \mu_2 \qquad (2)$$
$$dG = \mu_1 dn_1 + \mu_2 dn_2 \qquad (3)$$

Which determines the change in Gibbs Free Energy for changes in concentration.

Of all the extensive thermodynamic properties, the volume is the easiest to visualize; this also holds true for the partial molar volumes, which are defined as

$$\left(\frac{\partial V}{\partial n_1}\right)_{n2} = \overline{V_1} \qquad and \qquad \left(\frac{\partial V}{\partial n_2}\right)_{n1} = \overline{V_2} \qquad (5)$$

Again, **the partial molar volume** of component 1 is defined by the increase in the volume of an infinite amount of solution when 1 mol of component i is added.

The total change in volume for changes in the concentration of the solution is:

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{n2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{n1} dn_2 \qquad (6)$$

and this leed to

$$dV = \overline{V}_1 dn_1 + \overline{V}_2 dn_2 \qquad (7)$$

since $\overline{V}_1$ *and* $\overline{V}_2$ *are* constant, the integrated form of equation 7 is

$$V = n_1 \overline{V}_1 + n_2 \overline{V}_2 \qquad (8)$$

Equation 8 is an interesting and surprisingly simple result. Let look to the **_meaning of equation 8:_**

1. For ideal solution: its volume is just the sum of the volumes of the pure solute and pure solvent:

$$V = n_1 \overline{V}_{0,1} + n_2 \overline{V}_{0,2} \qquad (9)$$

Where $\overline{V}_{0.1}$ *and* $\overline{V}_{0,2}$ are the molar volume of pure component 1 and 2, respectively..

for example: Benzene and toluene form an ideal solution. The volume of 1 mole pure benzene is 88.9 ml; the volume of 1 mole pure toluene is 106.4 ml. Equation 8 states that 88.9 ml benzene mixed with 106.4 ml toluene results in 88.9 ml + 106.4 ml, or 195.3 ml of solution. This mean that the volumes add up, since the volumes of substances in solution are extensive properties.

2. For none ideal solution the volume is not added up; water and ethanol do not form an ideal solution. The volume of 1 mole pure ethanol is 58.0 ml and the volume of 1 mole pure water is 18.0 ml. However, 1 mole water mixed with 1 mole ethanol does not result in 58.0 ml + 18.0 ml, or 76.0 ml, but rather 74.3! According to **Equation 7**, it is the partial molar volumes that are additive or extensive properties. When the mole fraction is 0.5, the partial molar volume of ethanol is 57.4 ml and the partial molar volume of water is 16.9 ml. With **Equation 8**, we can now calculate the volume of the solution:
[1 mole x 57.4 ml/mol + 1 mole x 16.9 ml/mol = 74.3 ml]
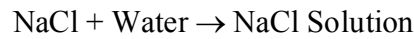(10)
which is exactly what is observed.

Method:

Partial molar volume will be calculated through the measurement of the density of sodium chloride solutions, so we need to relate the partial molar volume to the molality m and the density (d) of the solution.

For the system composed from Nacl and water we have :

$$NaCl + Water \rightarrow NaCl\ Solution$$

Since density is an intensive quantity we can choose any amount of solution as a starting point. If we choose an amount of solution containing 1kg of solvent then the number of moles of solute in that same solution is m. Then by using equation 8

$$V = n_1 \overline{V}_1 + n_2 \overline{V}_2 \qquad (8)$$

$1 \rightarrow Solvent$

$2 \rightarrow Solute$

For solution containing 1Kg (i.e., 55.51 mol) of water and m mol of solute is:

$$V = 55.51 \overline{V}_1 + m \overline{V}_2 \qquad (11)$$

substitute $\overline{V}_1$ *by* $\overline{V}_0$ molar volume of pure water and $\overline{V}_2$ by the apparent molar volume of the solute ϕ

$$V = 55.51 \overline{V}_0 + m\phi \qquad (12)$$

$$\phi = \frac{1}{m} \left(V - 55.51 \overline{V}_0 \right) \qquad (13)$$

and

Density of solution (d)

$$d = \frac{mass}{Volume(V)}$$

the solution containing 1Kg (i.e., 55.51 mol) of water and m mol of solute (Molar mass of solute=M_2) from the density,

$$V = \frac{mass\ of\ solution}{d} = \frac{water\ mass + solute\ mass}{d} = \frac{1000g_{water} + mM_2}{d} \qquad (14)$$

and

$$55.51 \overline{V}_0 = 1000g / d_0 \qquad (15)$$

where d_0 is the density of pure water (g/cm^3)

so equation 13 *become* :

$$\phi = \frac{1}{d}\left[M_2 - \frac{1000g}{m}.\frac{d-d_0}{d_0}\right] \tag{16}$$

or simplly

$$\phi = \frac{1}{d}\left[M_2 - \frac{1000g}{m}.\frac{w-w_0}{w_0-w_e}\right] \tag{17}$$

where:

W_e is the weight of empty pycnometer.

W_0 is the weight of pycnometer filled with water.

W is the weight of pycnometer filled with solution.

For solution contains electrolyte (i.e., NaCl), it is known that the apparent molar volume ϕ varies linearly with $\sqrt{m}$, $(\phi \, \alpha \sqrt{m})$, according to Debye-Huckel theory .So $\overline{V}_1 \; and \; \overline{V}_2$ could be express as described by equations 18 and 19:

$$\overline{V}_1 = \overline{V}_1^0 - \frac{m}{55.51}\left[\frac{\sqrt{m}}{2}\frac{d\phi}{d\sqrt{m}}\right] \tag{18}$$

$$\overline{V}_2 = \phi^0 + \frac{3\sqrt{m}}{2}\frac{d\phi}{d\sqrt{m}} \tag{19}$$

Where ϕ^0 is the apparent molar volume extrapolated to zero concentration.

from equation (19) *we get* 19′

$$\overline{V}_2 - \phi = \frac{1}{2}\sqrt{m}\frac{d\phi}{d\sqrt{m}} \tag{19′}$$

the above equation means that $\overline{V}_2 - \phi^0$ = zero if $\sqrt{m} = 0$ or $d\phi/d\sqrt{m} = 0$

$$\phi = \phi^0 + \frac{d\phi}{d\sqrt{m}}\sqrt{m} \tag{20}$$

Procedure:
Material:

Sodium chloride, pycnometer. Four decimal balance.

Procedure:

1. Prepare a solution of 4 M NaCl.
2. Prepare 4 diluted solutions from the 4 M NaCl, with concentration equal to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{16}$ from the orginal concentration.
3. Weigh an empty, dry and clean pynometer using four decimal analytical balance. **Record the weight as W_e.**
4. Fill the pycnometer with distilled water, place it in water bath at 25 C for 5 min.
5. Remove the pycnometer and **weigh** it with distilled water. **Record the weight as W_0.**
6. Empty the pycnometer, dry it with acetone.
7. Weigh the pynometer again to if you get the same weight as step 1.
8. Fill the pycnometer ith NaCl solution, **START** with the diluted one, place it in the water bath, and Weigh it, Record the weight as W.
9. Clean up anything you use.

Calculation:
1. Determine the volume of the pycnometer (cm^3) using the following equation (21)
$$V = \frac{W_0 - W_e}{d_0} \qquad (21)$$
d_0 for water at $25C = 0.997044 g/cm^3$
2. Use the volume obtained in step 1 to calculate the densities of four NaCl solutions. equation 22
$$d = \frac{W - W_e}{V} \qquad (22)$$
3. Determine the molality (mol/Kg) of each solution using equation 23
$$m = 1/\left[\left(d/Molarity\,of\,the\,solution\right) - \left(M_2/1000\right)\right] \qquad (23)$$
where M_2 is the molar mass of solute (NaCl)
Molarity (mol/L)

4. Calculate ϕ (ml/L) for each solution using equation 17
$$\phi = \frac{1}{d}\left[M_2 - \frac{1000g}{m} \cdot \frac{w - w_0}{w_0 - w_e}\right] \qquad (17)$$

5. Plot the relation between ϕ and $\sqrt{m}$ according to equation 20. Calculate the slope $d\phi/d\sqrt{m}$ and intercept ϕ^0.

6. Calculate $\overline{V_1}$ and $\overline{V_2}$ using equations 18 and 19.

7. Plot the relation between $\overline{V_1}$ agains $\sqrt{m}$ and $\overline{V_2}$ against $\sqrt{m}$.

8. Tabulate your results on the following table

9. **Answer the following questions**:
   a. Is the total volume greater or less than the sum of the volume of the pure components?.
   b. Are the partial molal volumes of the solute and solvent greater or less than the pure molar volumes?

FREEZING POINT DEPRESSION OF ELECTROLYTES

Purpose:

The object of this experiment is to study the effect of electrolyte and non-Electrolyte solutes on the freezing point depression of water.

Introduction

Colligative properties are properties of solutions that depend on the concentrations of the samples and (*approximation*) do not depend on the chemical nature of the samples. A colligative property is measured through the measurement of the difference between a property of a solvent in a solution and the same property of the pure solvent.

Colligative properties include: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. We are grateful for the freezing point depression of aqueous solutions of ethylene glycol or propylene glycol in the winter and continually grateful to osmotic pressure for transport of water across membranes. Colligative properties have been used to determine the molecular weights of non-volatile non-electrolytes.

The equation for the freezing point depression of a solution of a non-electrolyte as a function of molality is described by equation 1:

$$\Delta T_F = K_F\, m \tag{1}$$

The constant K_F, the freezing point depression constant, is a property of the solvent only, as given by equation 2:

$$K_F = \frac{Mw_{solvent} R \left(T_F^0\right)^2}{1000\Delta H_F} \tag{2}$$

Where R is the gas constant in J/K*mol, T_F^o is the freezing point of the solvent (K), ΔH_F is the heat of fusion of the solvent in J/mol, and the factor of 1000 is needed to convert from g to kg of water for molality.

It was noted that the freezing point depressions (i.e., in fact also noted for other colligative properties, particularly osmotic pressure) of aqueous solutions of salts were

larger than the freezing point depressions (i.e., polyhydroxy-compounds (non-electrolytes) at the same molality).   The data were analyzed as the freezing point depression for the salt solution divided by the freezing point depression for a non-electrolyte solution at the same molality to give the van't Hoff **i** factor:

$$i = \frac{\Delta T_F}{K_F m} \qquad (3)$$

The van't Hoff **i** factor is a measure of the deviations of behaviour of an electrolyte solution from an ideal solution of a non-electrolyte. It is important to note the following

1. Van't Hoff **i** values <u>increased </u>with <u>decreasing concentration </u>of the salt (increasing dilution), and appeared to approach integral values in very dilute solutions.
2. Same values for **i** were obtained from freezing point depressions and from osmotic pressure experiments.
3. Theory and experiment indicate that both ionic concentrations and ionic charges affect **i** (or deviations from ideal behavior).

In this experiment we want to test the hypothesis state that: at higher the molality of a solution the greater would be its effect on the freezing point depression of water. Moreover, an electrolyte (salt) would have a higher effect than a non-electrolyte (sugar).

Method:

In this experiment we will measure the freezing point depression of solution of electrolyte and none electrolyt, but first we need to determine the freezing point of distilled water. The relation between vant hoff factor will also be established.

Procedure:
Material:

Sodium Chloride, Sugar, Calcium Carbonate. thermo prop or thermometer.

Procedure:

1. measure the freezing point of pure distilled water
   a. Place a test tube that is ½ full with the water in an ice bath.
   b. Place the thermometer (or thermo prop) in the solution.
   c. When the 1st ice crystals appear on the inside wall of the test tube, record the temperature, this should be the freezing point of the liquid.
   d. Repeat the process. You should get the same value; however, if the results differ significantly, try again. If the difference is small, calculate and use the average value.

2. Prepare different solutions of sodium chloride with different molalties (0.5, 1.0, 1.5, 2 m) for example by adding 5.8 grams of NaCl salt to 100 mL of distilled water. This makes a 1 molal solution.
3. Prepare different solutions of Calcium carbonate ($CaCO_3$) with different molalties (0.5, 1.0, 1.5, 2 m) for example by adding 10.0 grams of $CaCO_3$ salt to 100 mL of distilled water. This makes a 1 molal solution.
4. Prepare different solutions of sugar with different molalties (0.5, 1.0, 1.5, 2 m) for example by adding 34 grams of sugar to 100 mL of distilled water. This is a 1 molal solution
5. Measure the freezing point of solutions prepared in step 2 and step 3, following the procedure described from (a → d) in step 1.
6. Tabulate your results.

Calculation:

1. Tabulate your results using the following tables:

    a. Freezing point of distilled water.

Experiment:.	1	2	3
Freezing point ^{o}C			

    b. Freezing point of NaCl solution.

Concentration (m)	Freezing point Temp, ^{o}C		
	First run	Second run	Third run
0.5			
1.0			
1.5			
2.0			

    c. Freezing point of $CaCO_3$ solution.

Concentration (m)	Freezing point Temp, ^{o}C		
	First run	Second run	Third run
0.5			
1.0			
1.5			
2.0			

d. Freezing point of Sugar solution.

Concentration (m)	Freezing point Temp, $^{\circ}$C		
	First run	Second run	Third run
0.5			
1.0			
1.5			
2.0			

3- Calculate the freezing point depression use the absolute difference:

$$\Delta T_F = |T_{solution} - T_{solvent}|$$

4- Plot your results as ΔT_F vs. molality.

5- Plot your results as ΔT_F vs. Molarity.

6- Fit the data to a curve with the intercept fixed at 0. And calculate the slope of your plot.

7- Use the value of molal freezing point depression constant(**K_F = 1.860 C/molal**) to calculate the value of i for the three experiments, comment on your results.

8- Calculate the error of your results.

Questions .

1- what is the trend you observed from the two plot (3 and 4).

4. By comparison between the results obtained for experiment with NaCl and $CaCO_3$ solutions, is there any effect of the type of the ionic charges on the value of **i.**

2- Comment on the hypothesis state that (the higher the molality of a solution the greater would be its effect on the freezing point depression of water regardless to the type of solute)

3- Use equation 2 to calculate the theoretical value of **K_F** molal freezing point depression factor. And compare it to the literature value: for water, **K_F = 1.860 C/molal.**

# HYDROGEN BOND STRENGTH BETWEEN ORGANIC ACID MOLECULES

Purpose:

The purpose of this experiment is to measure the strength of the hydrogen bond formed between dimer of organic acid.

Introduction

Intermolecular forces are forces that act between stable molecules or between functional groups of macromolecules. Intermolecular forces can be divided into the following categories:

1. Electrostatic interactions, which include: ion-ion interaction, Ion-diplole interaction, Dipole-dipole interaction, Ion-induced dipole and Dipole-induced dipole.

2. Induced dipole-induced dipole, also called dispersion force or London forces.

3. H-Bonding: is the attractive force between one electronegative atom and a hydrogen covalently bonded to another electronegative atom. It results from a dipole-dipole force with a hydrogen atom bonded to nitrogen, oxygen or fluorine. The energy of a hydrogen bond (typically 5 to 30 kJ/mole) is comparable to that of weak covalent bonds (155 kJ/mol), and a typical covalent bond is only 20 times stronger than an intermolecular hydrogen bond. The hydrogen bond is somewhere between a covalent bond and an electrostatic intermolecular attraction. This type of bond occurs in both inorganic molecules such as water and organic molecules such as DNA. Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C). This is because of the strong hydrogen bond, as opposed to other group 16 hydrides. Intramolecular hydrogen bonding is partly responsible for the secondary, tertiary, and quaternary structures of proteins and nucleic acids.

It is known that Acetic or benzoic acid exist in aqueous solution as a monomer and they form dimer in organic solvent due to the hydrogen bond formation, figure 1
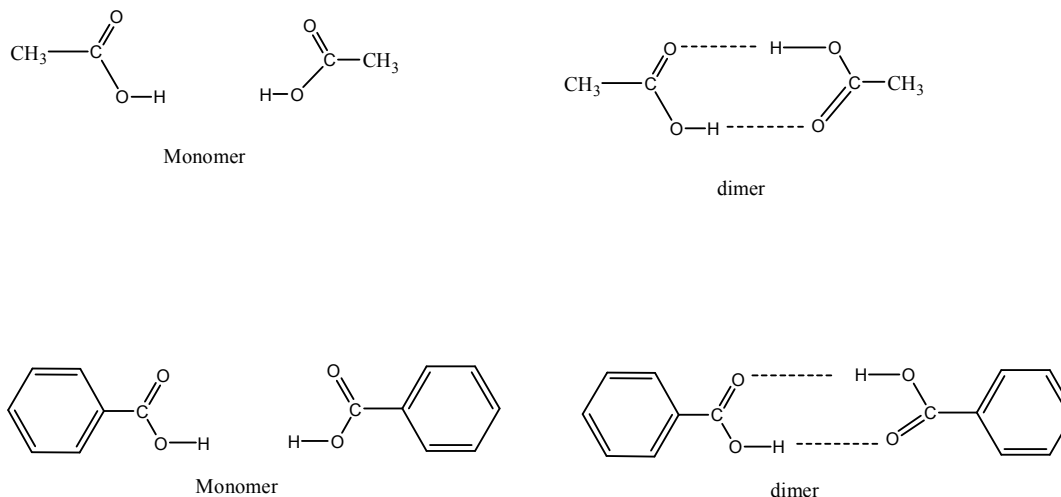
Figure 1: The monomer and dimer of acetic and benzoic acid

When an organic acid exist in immiscible solvents (i.e., organic and aqueous solvent) it will distribute between the two layers in which aqueous solvent layer contain **ONLY** a monomoric form and the organic layer contain both monomer and dimer form of the acid.

Let
1. C_W is the acid concentration on the aqueous layer (exist as a monomer) .
2. C_{01} the concentration of monomoric acidic form exist in Organic layer
3. C_{02} the concentration of dimeric form of the acid exist in Organic layer
   Thus the distribution coefficient (D) of the monomer between the two layers is given by equation 1

$$D = \frac{C_{o1}}{C_W} \qquad (1)$$

and the equilibrum constant, K, for the dimer formation

$$2RCOOH \rightleftharpoons RCOOH.....RCOOH$$

$$K = \frac{C_{o2}}{(C_{o1})^2} \qquad (2)$$

Let C_O represent the total amount of the acid in organic layer, suppose there is NO association between the two molecules:

$$C_o = C_{o1} + 2C_{o2} \qquad (3)$$

NOW from equation 1 and 2 we have

$$C_{01} = DC_w \qquad (4)$$

$$C_{02} = K(C_{o1})^2 \qquad (5)$$

From all of the above we have

$$\frac{C_o}{C_W} = D + \frac{2K(C_{o1})^2}{C_W}$$

$$\frac{C_o}{C_W} = D + 2KD^2C_W \qquad (6)$$

so plot of $\frac{C_o}{C_W}$ against C_w results in a staright line with intercept equal to D and slope equa to $2KD^2$

Measuring of the equilibrium constant at different temperature allow us to calculate the dissociation energy of the dimer (i.e., the energy require to breakdown the hydrogen bond between the dimer, which is equal to energy required to form the hydrogen bond with opposite sign) .

The dissociation energy could be calculated using Van Hoff equation:

$$\ln K = \text{Constant} - \frac{\Delta H}{RT} \qquad (7)$$

so plot of ln K against $1/T$ will allow us to calculate ΔH

and if two temperature are used:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (7a)$$

Procedure:

Material and apparatus: Acetic acid (1M), benzoic acid. Sodium hydroxide (0.01M and 0.5 M)

Procedure

1. Prepare the following solution:

Number	Organic solvent (ml)	Solution of organic acid (1M) ml	Water (ml)
1	25	10	40
2	25	20	30
3	25	30	20
4	25	40	10
5	25	50	0.0

2. Suspend the solution in a water bath set at approximately 25 °C.

3.   Record room temperature as measured by your thermometer.

4. Separate the two layers using separatory funnel.

5. Use sodium hydroxide to titrate each solution using phenolphthalein as indicator . Record volume of NaOH used for both portions.

6. Repeat the above procedure for solution maintained at DIFFRENT temperature: 30 °C, 35 °C and 45 °C.

7. **Tabulate your result.**

8. Clean up any remaining waste, and clean out your test tubes.

Calculation:

1. Use volume of NaOH to calculate the concentration of acid in organic and aqueous layers.

2. Use equation 6 to calculate the equilibrium constant at each temperature.

3. Use equation 7 or 7a to calculate ΔH.

4. Estimate the source of error

Question:

Why we use different concentration of NaOH to titrate the organic acid in both solvent layers.

BINARY SOLID-LIQUID PHASE DIAGRAM

Purpose:

The purpose of this experiment is to:

1. Investigate the equilibrium between solid and liquid phases in a two component system.
2. Construct the phase diagram by measuring the cooling curves of the mixture at different composition.
3. Determine the eutectic temperature and melting points and heat of fusion for Naphthalene and diphenylamine.
4. Measure the freezing behaviour of differing mole ratios of naphthalene and diphenylamine, and extract a phase diagram and the heats of fusion.

Introduction

Theory:

Colligative properties are the properties that depend on the number of solute species present but not on their chemical identity. The vapor pressure reduction that is observed upon adding solute to a pure liquid is one example colligative properties. Freezing point depression is another example.

A pure liquid that is cooled will exhibit a steady decline in temperature until the freezing point is reached. At this temperature, the chemical potential (usually Gibbs Free Energy, or ΔG) of the solid and liquid are equal, and the two phases are in equilibrium. If energy continues to leave the system, liquid molecules will freeze out of solution. If energy if put into the system, solid molecules will melt back into liquid form. In the event that cooling continues, the observed temperature of the system will not change until all of the liquid molecules have been converted into solid phase. Only after this conversion is complete will the temperature of the system again begin to decline. This "**plateau**" in the temperature vs. time plot is called a thermal arrest, and is one of the tell-tale signs of a phase change. When a solute is added to a pure liquid, the presence of the solute molecules interferes with the cohesive forces of the liquid. As we have seen, this produces a reduction in the vapor pressure of the liquid. This is the same thing as saying that that the liquid-vapor equilibrium line is shifted to lower pressures on a classical Pressure vs. Temperature phase diagram. This produces one unintuitive consequence: the temperature at which the solid and liquid phase lines intersect (the melting point, or freezing point) is shifted to lower temperatures.
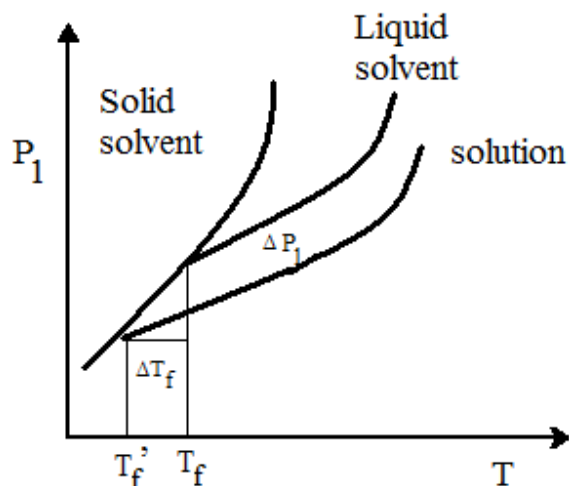
Figure 1: The depression of freezing point as a consequence of reduced vapor pressure

When the solution temperature reaches this depressed freezing point, however, something interesting occurs. The solid that forms is that of the pure solvent, as the solute molecules are rarely soluble in the solid phase of the solvent. **If the added solute is itself a liquid**, this produces a new system wherein solid solvent crystallizes out and leaves behind pure solute. As this happens, the solution must necessarily become more concentrated in solute, which leads to further depression of the freezing point of solvent. Thus, the temperature of the system does not "arrest" at a fixed freezing point. Rather, there is a temperature range over which this process occurs. Furthermore, the crystallization of a solid is a process which gives off heat. Thus, the rate of cooling of the system is slowed as the solid continues to freeze out of the liquid. This produces a change in the slope of the cooling curve beginning at the point where solid begins to form. The point where the slope changes is called a "**break**" in the cooling curve. Eventually, the system will cool to the point where the remaining component of the system also freezes. At this point, both liquids freeze at the same time and the cooling curve does not exhibit the "break" behavior. The temperature at which this second freezing event occurs is the same for any mole ratio of the two liquids! It is the minimum temperature to which the freezing point of either liquid can be depressed. It is possible to produce a solution of two liquids in a mole ratio such that their freezing points are depressed to the same temperature, and they freeze simultaneously to produce pure solids. This solution composition is called the **eutectic composition** (from the Greek, "easily melted"), and the temperature at which it freezes is the **eutectic temperature**.
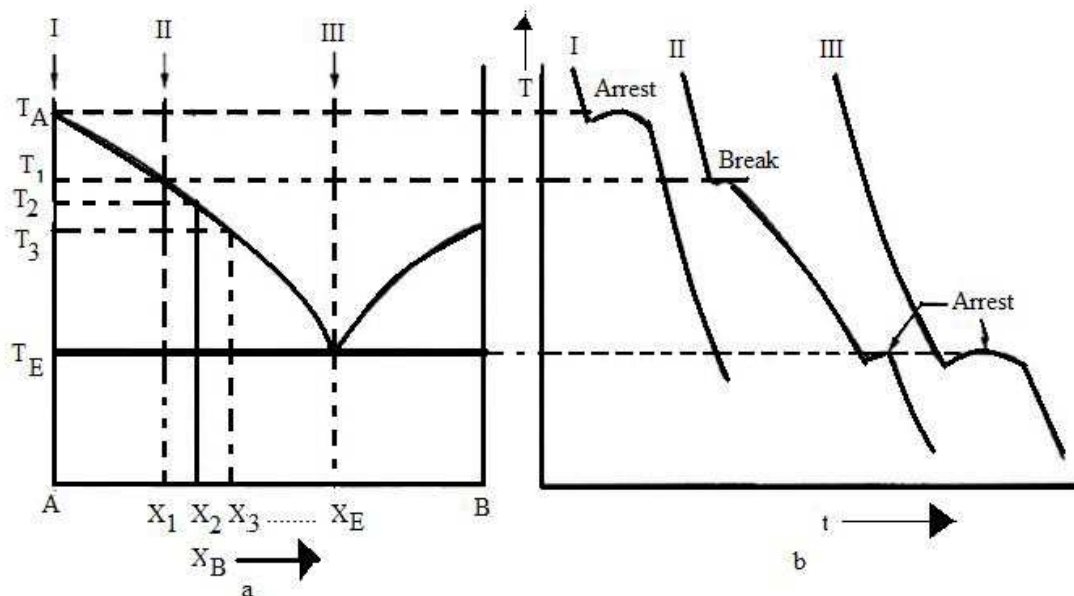
Figure 2.a. Phase diagram showing the freezing points of two mutually soluble liquids, A and B, as a function of increasing mole fraction of B.

Figure 2b. Cooling curves of three different solutions taken from the phase diagram at left.

As can be seen in the phase diagram in Figure 2, it is awkward to refer to one of the two liquid components of such systems "solvent" and the other "solute". Rather, it is easier to simply refer to one as component A and the other as component B. It can be shown that the solid-liquid phase line on the left of this diagram, or the "liquidus" curve for component A is given by equation 1 which can expand to obtain equation 2:

$$T = T_A + \frac{RT_A^2}{\Delta H_{fus,A}} \ln\left(1 - \chi_B\right) \qquad (1)$$

$$T = T_A - \frac{RT_A^2}{\Delta H_{fus,A}} \left[\chi_B + \frac{\chi_B^2}{2} + ... \right] \qquad (2)$$

for very small values of χ_B becomes:

$$T = T_A + \frac{RT_A^2}{\Delta H_{fus,A}} \chi_B \qquad (3)$$

and for liquidus curve starting with pure B:

$$T = T_B + \frac{RT_B^2}{\Delta H_{fus,B}} \ln\left(\chi_B\right) \qquad (3)$$

$$T = T_B - \frac{RT_B^2}{\Delta H_{fus,B}} \left[1 - \chi_B\right] \qquad (4)$$

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Where : TA is the normal freezing point of component A, R is the ideal gas constant, and $\Delta H_{fus,A}$ is the heat of fusion of pure A.

The experiment today will serve to produce a phase diagram as seen in Figure 2, and from that phase diagram you will be asked to obtain the heat of fusion for two organic compounds.

Figure 3. represent a general phase diagram for a two-component system in which the solids are partially miscible as a function of mole fraction of A (X_A) and temperature. Point C represents the eutectic point. $T_{f,A}$ represents the freezing point of pure A, while $T_{f,B}$ represents the freezing point of pure B. α(s) represents a solid state composed predominantly of A, with B present as an impurity; β(s) represents a solid state composed predominantly of B, with A present as an impurity.
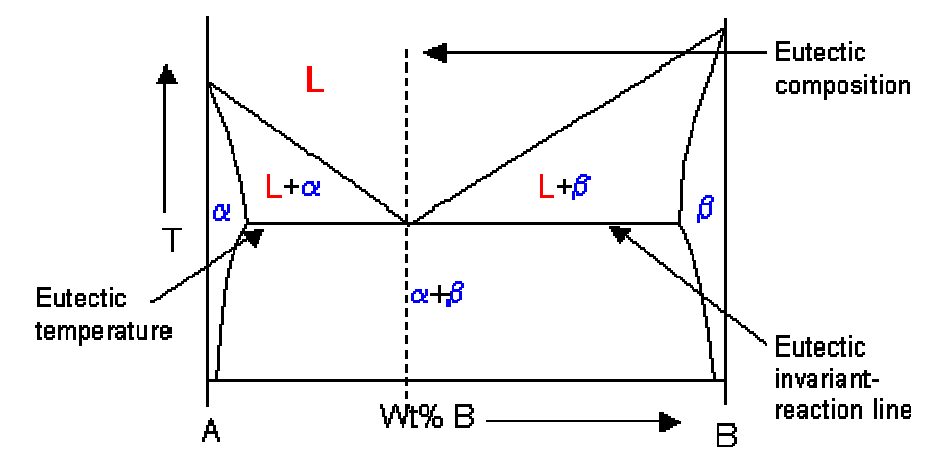
Figure 3. phase diagram for two component system

Procedure:

Material and apparatus: naphthalene (C10H8) and diphenylamine (C6H5)2NH..

Procedure

1. Acquire approximately 5 grams of each of the pure substances. Place each into a separate test tube and stopper the tubes with a cork. Suspend the tubes in a water bath set at approximately 90 °C.
2. Record room temperature as measured by your thermometer.
3. Wearing insulating gloves remove one of the test tubes from the water and clamp it securely above the benchtop. **Working quickly**, remove the cork stopper and replace it with a rubber stopper. Insert your thermometer and record the temperature versus time.
4. Observe the temperature as a function of time over 25 minutes. Note that initially the temperature decrease will be quite rapid! Gently stir your solution constantly using the thermometer,
5. Record any observed phase changes in your notes. Continue taking temperature measurements until the solid has completely formed and the system cools to about 30 °C or lower. Re-melt the solid and pour the liquid into the waste container.
6. Make up the first mixture in as specified in Table 1 in a small test tube. Make sure to record exactly how much of each compound you add to the tube.

First run		Second run	
% Wt. N	**Add to tube**	**% Wt. N**	**Add to tube**
100	**5.0 g N**	**0.00**	**5.g D**
90.9	**0.5 g D**	**9.0**	**0.5 g N**
67.9	**1.0 g D**	**23.0**	**1.0 g N**
62.5	**1.5 g D**	**37.5**	**1.5 g N**
47.6	**2.5 g D**	**52.4**	**2.5 g N**
38.5	**2.5 D**	**61.5**	**2.5 N**
N stands for naphthalene and D stands for diphenylamine			

7. **Tabulate your result.**
8. Clean up any remaining waste, and clean out your test tubes.

Calculation:

1. Convert the mass fractions of ALL of the mixtures into mole fractions of naphthalene.
2. Plot your own sets of data (2 pure compounds and mixtures) as Temperature versus Time. Identify any "breaks" or "arrests" in each plot in your analysis.
3. Plot the break and arrest temperatures for ALL mixtures as a function of mole fraction of naphthalene,
4. Plot the naphthalene portion of the data as a function of the natural log of X. Fit the liquidus curve using a linear fit to obtain an expression similar to (4). From this fit, determine the heat of fusion of naphthalene. Compare with the literature value.
5. Plot the diphenylamine portion of the data as a function of the natural log of $(1 - X)$. Fit the liquidus curve using a linear fit to obtain an expression similar to (1). From this fit, determine the heat of fusion of diphenylamine. Compare with the literature value.
6. Calculate the melting points of both naphthalene and diphenylamine from the phase diagram.
7. Find the eutectic mixture and eutectic temperature from the intersection of the trendlines for the liquidus curves. Estimate the error.
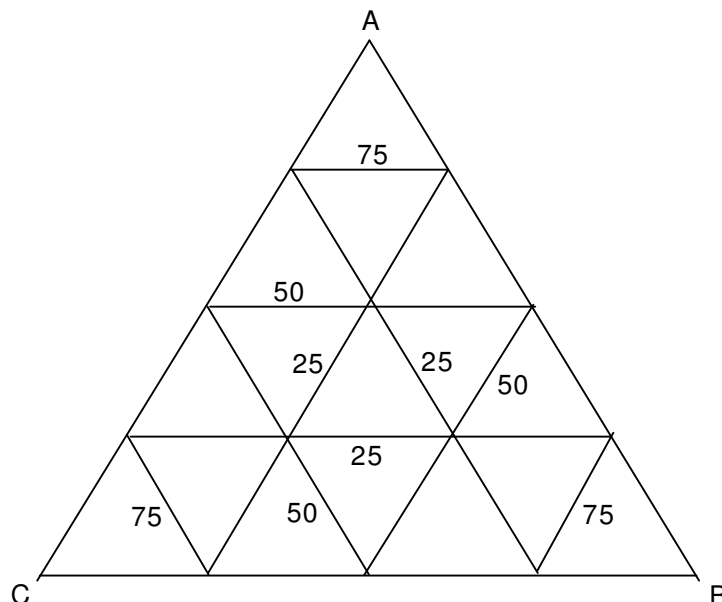
THREE COMPONENT SYSTEM

Purpose:
To determine the solubility of water, acetic acid and chloroform in each other and to determine the tie line and plait point using phase diagram at 25 C.

Introduction

According to the Gibb's phase rule for a ternary, three component, system where only 1 phase is present:

$$F = C - P + 2 = 3 - P + 2 = 3 - 1 + 2 = 4$$

four variables would have to plotted against each other to fully describe the system. Since plots of four variables are difficult to construct and visualize, the usual procedure is to hold one or more of these variables constant and plot the remaining variables against each other. For a ternary system the temperature and pressure are commonly held constant and the composition variables are plotted against each other on triangular graph paper:

The pure components are located at the corners of the triangle. The set of lines parallel to a triangle edge opposite one of the corners, gives the total percentages in the system of the component located at that corner. Where in the above diagram would you locate the overall composition of a system composed of 6 grams of A, 3 grams of B, and 3 grams of C?

When a pure component is added to the system, the overall composition of the system moves along the line connecting the original system composition and the corner of the triangle where the pure component is located. For example when B is added to a system that originally contained only A and C and was 35% in A, the overall composition of the system will lie along the line shown below:
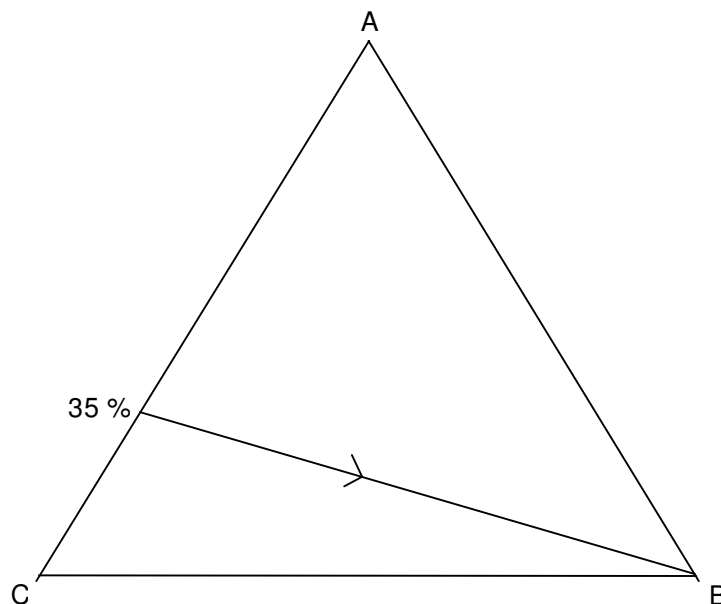

In the case where the three pure components are liquids at the temperature and pressure at which the diagram is constructed, there may be system compositions where two immiscible liquid phases form. If we start with a system composition where only one phase is present and add a component that will move the overall system composition into the region where two phases are stable, the point at which the phase boundary is crossed and a second phase begins to form can be recognized by a cloudiness or turbid appearance in the system when it is shaken:
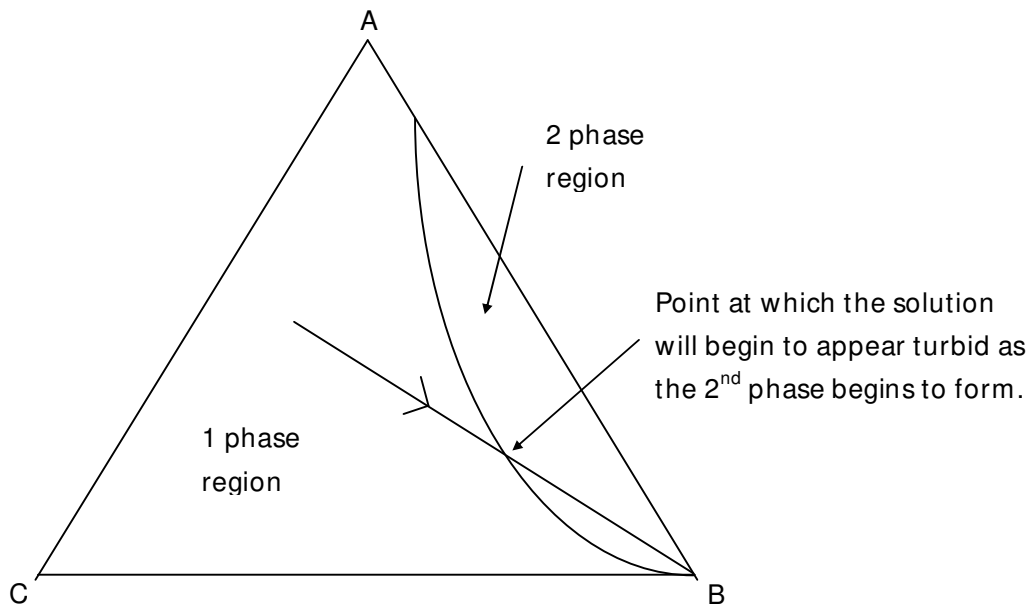
The cloudiness results from scattering of light by the large number of very small droplets of the second phase that are produced when the system is shaken.

If components A, B, and C are mixed to give an overall system composition that falls in the 2 phase region, the system will separate into two phases — a phase rich in B and a phase rich in A. The compositions of the phases that form will be given by the intersections of a tie-line with the phase boundary. The tie-line must also contain the point describing the overall system composition:
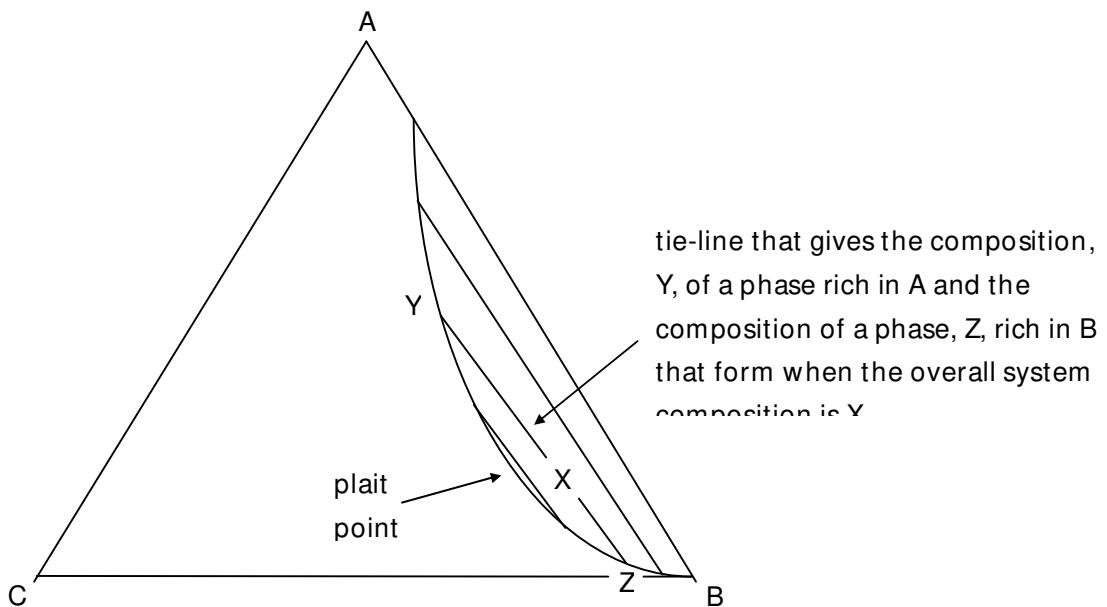
The location of the tie lines cannot be determined a priori and must be determined experimentally. The tie lines do, however, converge on a point on the phase boundary called the plait point.

Procedure:

Material and apparatus: 18 ~125 mL Erlenmeyer flasks, 2 burets and buret clamps, 1 L plastic bottle and cap, 4 of 100 mL separatory funnels, 2 of 5 mL pipettes and pipet bulbs, 50 mL volumetric flask and stopper, Labels, Scotch tape, Oven capable of operating at ~105 °C, Top loading single pan balance with +/- 0.01 g precision and water bath thermostated to 25.0 °C.

Chemicals : 500 mL of glacial acetic acid, 1 L of chloroform, 60.00 g of solid NaOH pellets, 20.0 g of reagent grade potassium hydrogen phthalate (this should be dried for several hours at ~ 105 °C before use) and 1 dropper bottle of phenolphthalein

<u>First part</u>:

In the first lab period, you will prepare solutions of acetic acid in water, solutions of acetic acid in chloroform, and solutions of acetic acid, chloroform, and water. You will also standardize ~ 1.0 M NaOH with KHP.

To prepare solutions of acetic acid dissolved in water:

In ~125 mL erlenmeyer flasks prepare four solutions of acetic acid in water that are approximately 10%, 25%, 40%, and 60% by weight acetic acid. The total mass of each solution should be ~20 g. The solutions can be prepared on a top loading balance with +/- 0.01 g precision. The solutions should be labeled with a water proof label, tightly stoppered, shaken, and suspended in a 25.0 °C thermostated bath. For each solution record the following data:

solution no	Weight of HAC(g)	Weight of H_2O
1	5	15
2	8	12
3	12	8
4	15	5
5	18	2

To prepare solutions of acetic acid dissolved in chloroform:

In an ~125 mL erlenmeyer flasks prepare four solutions of acetic acid in chloroform that are approximately 10%, 25%, 40%, and 60% by weight acetic acid. The total mass of each solution should be ~20 g. The solutions can be prepared on a top loading balance with +/- 0.01 g precision. The solutions should be labeled with a water proof label, tightly stoppered, shaken, and suspended in a 25.0 °C thermostated bath. For each solution record the following data:

solution no	Weight of HAC(g)	Weight of H_2O
6	3	17
7	5	15
8	8	12
9	12	8
10	15	5

In this lab period, you will titrate acid water solutions with chloroform to a turbid endpoint, titrate the acetic acid chloroform solution with water to a turbid endpoint. record the volume of water or chloroform added to each solutions (solution 1 to 10)

Titration of the acetic acid water solution with chloroform:

While solutions still in the water bath, titrate each solution of the acetic acid-water solution with chloroform, shake the Erlenmeyer flask each time you add chloroform, record volume of the chloroform added upon the first appearance of cloudiness or turbidity.

Titration of the acetic acid chloroform solution with water:

While solutions still in the water bath titrate each solution of the acetic acid-chloroform solution with water, shake the Erlenmeyer flask each time you add water, record volume of the water added upon the first appearance of cloudiness or turbidity.

Second Part (to determine the tie line)

Determination of the equilibrium composition of the phase in two-phase region.

To prepare solutions of chloroform, acetic acid, and water:

In an ~125 mL erlenmeyer flasks prepare four solutions that are approximately 45% by weight chloroform and approximately 10%, 20%, 30%, and 40% by weight acetic acid in water. The total mass of each solution should be ~50 g. The solutions can be prepared on a top loading balance with +/- 0.01 g precision. The solutions should be labeled with a water proof label, tightly stoppered, shaken, and suspended in a 25.0 °C thermostated bath. For each solution record the following data:

| Solution No.	% HAC	%CHCl$_3$	%H$_2$O
11	10	45	45
12	20	45	35
13	30	45	25
14	40	45	15

Transfer the acetic acid - chloroform - water mixtures that you prepared to separatory funnels in the thermostated water bath and allow the phases to separate. Pipet a 5.00 mL aliquot of the upper phase into a tarred ~ 125 mL Erlenmeyer flask and record the mass of this aliquot and the flask to +/- 0.01 g. Now titrate this aliquot with the standardized NaOH to a phenolphthalein endpoint. Note - for phases that contain little acetic acid, you may have to dilute the standard NaOH solution to obtain a satisfactory precision. Repeat this procedure for a 5.00 mL aliquot of the lower phase. Record the following data:

Solution No	Phase	Volume of NaOH (ml)	Mass of phase (g)
11	Upper		
	Lower		
12	Upper		
	Lower		
13	Upper		
	Lower		
14	Upper		
	Lower		

Calculation:

Note: No error analysis is required for this laboratory report.

1. Calculate the weight percent composition of the initial acetic acid water solutions 1 - 5 and plot these compositions on triangular graph paper. Place pure acetic acid at the apex of the triangular graph paper.
2. Calculate the mass of chloroform required to just induce phase separation in the acetic acid water solutions 1 - 5.
3. Calculate the weight percent composition of the initial acetic acid chloroform solutions 6 - 10 and plot these compositions on triangular graph paper.
4. Calculate the mass of water required to just induce phase separation in the acetic acid chloroform solutions 6 -10.
5. Calculate the weight percent compositions of the boundary separating the 1-phase and 2-phase regions and plot these compositions on triangular graph paper.
6. For each of the acetic acid - chloroform - water solutions 11 – 14
7. Plot the overall weight percent composition of these solutions on triangular graph paper.
8. Calculate the moles of acetic acid in both the upper and lower phases.
9. Calculate the weight percent acetic acid in each phase.
10. On triangular graph paper plot the intersections of the tie lines for these solutions with the boundary separating the 1-phase and 2-phase regions. To plot these tie line intersections you will have to decide whether the upper or lower phase is the chloroform rich phase.
11. Completely label the ternary phase diagram with the number of phases present in each region, the identity of the pure components present at the corners of the diagram, the plait point, the units on the axes, and the temperature and pressure for which the diagram is applicable.
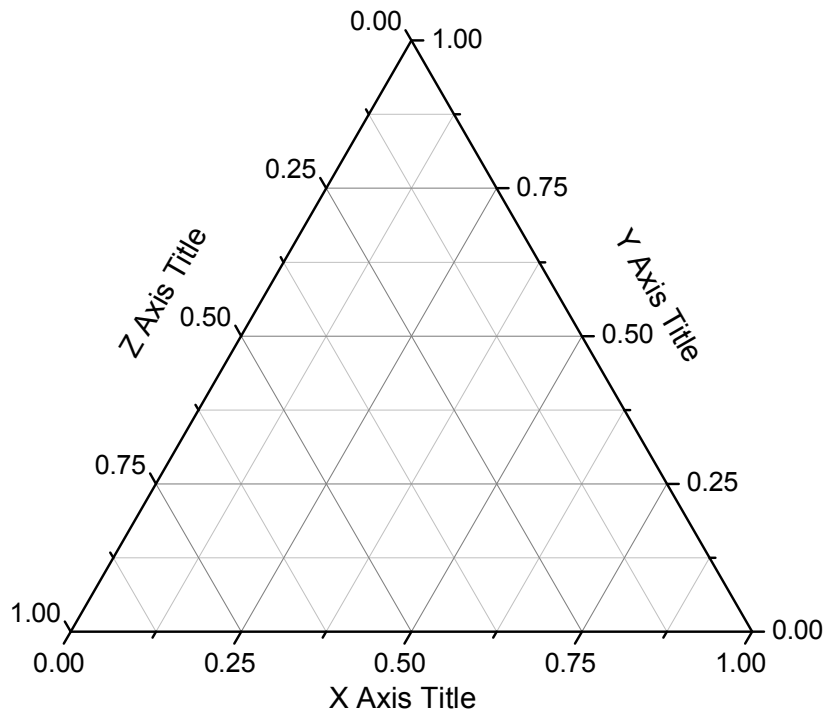
CHEMICAL EQUILIBRIUM IN SOLUTION: DISTRIBUTION COEFFICIENT OF I$_2$ BETWEEN WATER AND CHLOROFORM

Purpose:

To determine the distribution coefficient (Kd) of iodine between the immiscible solvents water and cyclohexane (C$_6$H$_{12}$). The distribution coefficient will be derived from data obtained by performing a chemical analysis for iodine in the water layer. Then the distribution coefficient will be used to determine the equilibrium constant for I^-/I_3^-.

Hint. This experiment will be done in two week periods.

Introduction

When a solute (the iodine in this case) is mixed with two immiscible liquids in contact with each other (i.e., the water and cyclohexane), the solute dissolves in each solvent to some extent, and so distributes itself between the layers. When equilibrium has been reached, the ratio, Nernst distribution law, equation 1:

$$K_d = \frac{molar\ concentration\ of\ solute\ in\ solvent\ 1}{molar\ concentration\ of\ solute\ in\ solvent\ 2} \qquad (1)$$

The ratio is constant, independent of the two individual concentrations but dependent upon the temperature and the nature of the specific solute and solvents involved.

Kd is an equilibrium constant called the **distribution coefficient**. For the iodine-water-cyclohexane system:

$$K_d = \frac{[I_2]_{cyclohexane}}{[I_2]_{water}} \qquad (2)$$

where Kd is now specifically the distribution coefficient (or molar concentration ratio) of iodine between water and cyclohexane. This type of procedure is used during the

common industrial separation technique known as "extraction." During extraction, compounds are separated by taking advantage of their different solubilities in each of a pair of immiscible solvents. Drugs and compounds of plutonium are examples of substances separated and purified using extraction techniques.

In this experiment, the molar distribution coefficient at room temperature will be determined by chemical analysis of the iodine in a water solution before and after shaking it with cyclohexane. The analysis will be done by titrating these aqueous solutions with sodium thiosulfate solution using starch indicator. Since the solubility of Iodine in cyclohexane is larger than water, more concentrated solution of sodium thiosulfate is used to titrate the organic layer.

The equation for the reaction between iodine and the sodium thiosulfate is

$$I_2 \ + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 \ + 2NaI \qquad\qquad (3)$$
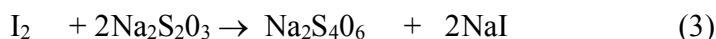
Blue + Colourless $\rightarrow$ Colourless + colourless in presence of **starch**

In the presence of starch (a small amount of which is added to the solution just before the end of the titration. All the reactants and products are colorless except I_2, which forms a deep blue complex. The titration is continued until the end-point indicated by the disappearance of the blue color. **Solid potassium iodide** (KI) is added during the titration to prevent loss of iodine vapor from the open flask. Iodide ion from the KI combines with iodine to form the nonvolatile triiodide ion.

$$I_2 \ + \ I^- \ \leftrightarrow \ I_3^- \qquad\qquad (4)$$
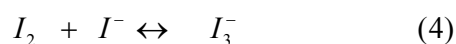
Once the distribution constant (Kd) is known, it could be used to determine the concentration of iodine (I_2) in an aqueous phase containing I_3^- by means of a titration of I_2 in cyclohexane layer that has equilibrated with this phase. The use of distribution constant in this way depend upon the assumption that its value is unaffected by the presence of ions in the aqueous phase.

In this experiment, once the distribution constant (Kd) is determined, it will be use to determine the equilibrium constant of iodine, triiodied equilibrium in aqueous solution, equation (5)

$$I_2 \ + \ I^- \ \leftrightarrow \ I_3^-$$

$$K_C = \frac{\left[I_3^- \right]_{eq}}{\left[I_2 \right]_{eq}\left[I^- \right]_{eq}} \qquad\qquad (5)$$
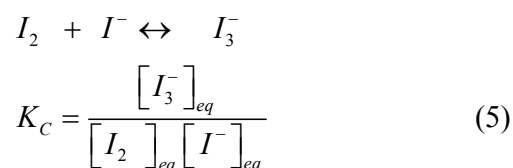
In order to calculate the equilibrium constant (Kc) we need to determine the equilibrium concentration of $[I_2]$, $[I^-]$ and $[I_3^-]$ and of course use the obtained Kd value.

For $[I_2]$

remmber that $K_d = \dfrac{[I_2]_{cyclohexane}}{[I_2]_{water}}$ *so* $[I_2]_{water} = \dfrac{[I_2]_{cyclohexane}}{K_d}$

K_d is known from the first part and the concentration of $[I_2]_{cyclohexane}$ could be estimated by titration against $S_2O_3^{-2}$

$$[I_2]_{cyclohexane} = \frac{1}{2} MV(S_2O_3^{-2})$$

For $[I_3^-]$

$[I_2]_{total}$ is the total concentration of I_2 in aqueous layer

$[I_2]_{total} = [I_2]_{free} + [I_3^-]$

so

$$[I_3^-] = [I_2]_{total} - [I_2]_{equilb}$$

and finally For $[I^-]$

$[I^-]_0$ is the initial concentration of I^- in aqueous layer

$[I^-]_0 = [I^-]_{free} + [I^-] \Rightarrow$ produce from reaction wtih I_3^- according to equation 4 and it equal to $[I_3^-]_{eq}$

so

$$[I^-]_{eq} = [I^-]_0 - [I_3^-]_{eq}$$

Procedure:
Material:

50 mL buret, two test tubes (25 x 200 mm), two No. 4 rubber stoppers, Pasteur pipette, ring stand, burette clamp, 120 mL aqueous iodine solution, 75 mL $Na_2S_2O_3$ solution, 13 mL C_6H_{12}, starch solution, potassium iodide.

Experimental Procedure:

First period: *determination of the distribution coefficient of I_2 between water and cyclohexane.*

1. Prepare the following mixtures using 250 mL Erlenmeyer flask with stopper:

Experiment .No	Volume of saturated iodine solution in cyclohexane (ml)	Volume of cyclohexane added (ml)	Volume of water ml
1	30	0	100
2	25	5	100
3	15	15	100
4	10	20	100

2. Stopper the flasks, shake them for 5 minutes and then place them in a thermostated water bath at 25 C for 30 minutes. Shake the content from time to time.
3. Pippeteout 5 ml of the cyclohexane layer (upper layer) into an Erlenmeyer flask containing 25.0 mL of distilled water . Add a few crystals of KI, and titrate with sodium thiosulfate solution (0.05M) using starch as indicator, use i ml of starch near to the end of titration.
4. Pipette out 20 ml of aqueous layer (lower layer) into 250 mL Erlenmeyer flask, add a few crystals of KI, and titrate as before with sodium thiosulfate solution (0.002M). The starch may be added at the beginning of the titration.

Second period: *determination of the equilibrium constant of* I^-/I_3^- .

1. Prepare the following mixtures using 250 mL Erlenmeyer flask with stopper:

Experiment .No	Volume of saturated iodine solution in cyclohexane (ml)	KI solution 100 ml volume added
1	30	0.25 M
2	30	0.20M
3	30	0.1 M
4	30	0.05M

2. Stopper the flasks, shake them for 10 minutes and then place them in a thermostated water bath at 25 C for 30 minutes. Shake the content from time to time.
3. Pipette out 10 ml of the cyclohexane layer (upper layer) into an Erlenmeyer flask containing 25.0 mL of distilled water . Add a few crystals of KI, and titrate with sodium thiosulfate solution (0.05M) using starch as indicator, use i ml of starch near to the end of titration.
4. Pipette out 25 ml of aqueous layer (lower layer) into 250 mL Erlenmeyer flask, add a few crystals of KI, and titrate as before with sodium thiosulfate solution (0.02M). The starch may be added at the beginning of the titration.

Calculation:

7. Determine the concentration of the iodine in aqueous and organic solvent
8. Calculate the distribution coefficient(Kd)
9. Calculate the equilibrume concentration of $\left[I_2 \right], \left[I^- \right]$ *and* $\left[I_3^- \right]$
10. Calculate the equilibrium constant Kc