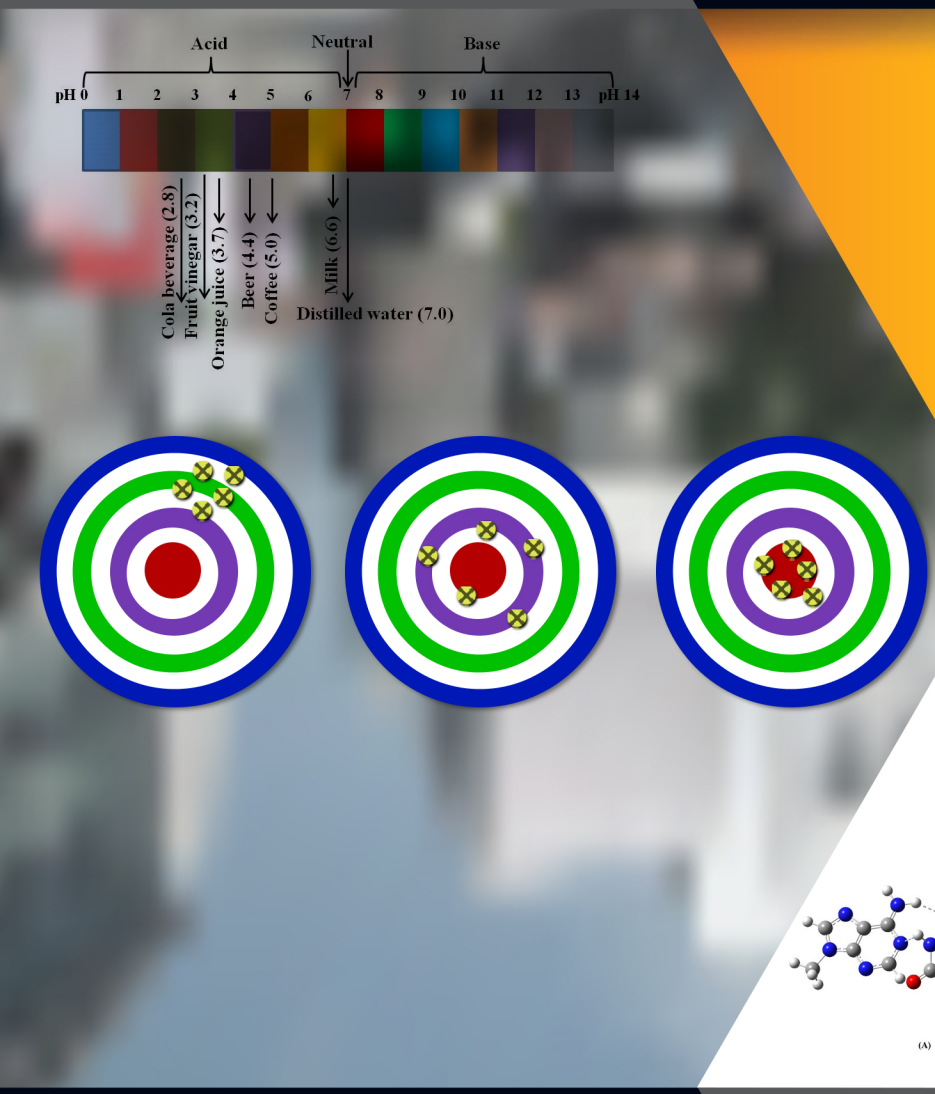
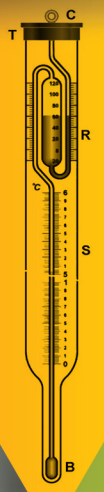
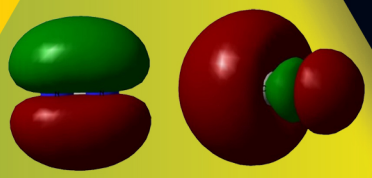
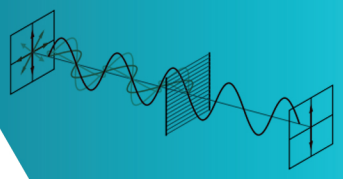
ADVANCED PHYSICAL CHEMISTRY

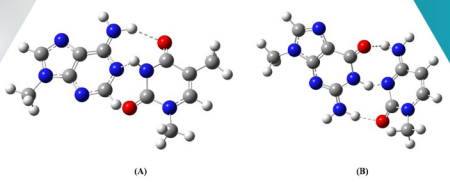
PRACTICAL GUIDE











Charu Arora
Sumantra Bhattacharya

Bentham Books

Advanced Physical Chemistry Practical Guide

Authored by

Charu Arora

Department of Chemistry
Guru Ghasidas University
India

&

Sumantra Bhattacharya

National Institute of Technology Sikkim
India

Advanced Physical Chemistry Practical Guide

Authors: Charu Arora and Sumantra Bhattacharya

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FOREWORD

It is my pleasure to pen down 'foreward' of the book "The Advance Physical Chemistry Practical Guide" by learned authors – Dr. Charu Arora and Dr. Sumantra Bhattacharya. By going through the contents of the book, I can envisage that this book would be highly beneficial to students as well as professionals. I feel honoured and privileged to write preface for the book.

This book is meticulously developed as a laboratory manual devoted to Physical Chemistry and provides a wide spectrum of knowledge of the subject matter. It will help the readers to perform as well as comprehend various experiments pertaining to Physical Chemistry. The book is written in simple language so that students of all levels can easily understand the theoretical and exploratory aspects of every experiment. Beautifully detailed diagrams of experiments will further help the reader easily learn, visualize, and memorize the complicated apparatuses and equipments. During my 30 years of professional career as a physical chemist, I have observed that students always lack confidence in the analysis and presentation of data. Authors have given special emphasis on these issues. Another feature methodically included in this book is pre-lab preparation, which will certainly improve the performance and analytical skills of the students in the laboratory. In view of the recommendations of New Education Policy 2020, the authors have also accentuated the practicability of laboratory knowledge for the benefit of mankind. I am sure this book will help students in demonstrating their skills out of the laboratories and classrooms to villages and towns for the service of society.

I am confident that faculty members, students, and professionals would find this book a very useful reference treasure for their day to day working, be it teaching or research.

Both Dr. Arora and Dr. Bhattacharya deserve special compliments for their painstaking efforts to concentrate the voluminous matter in a well-structured piece of knowledge.

Keep it up! Good Luck…

Alok Mittal, D.Sc.
Department of Chemistry
Maulana Azad National Institute of Technology
(Institute of National Importance)
Bhopal 462 003
India

PREFACE

"*The test of all knowledge is experiment.* Experiment is the *sole judge* of scientific "truth""—R. P. Feynman.

Practical work has had a central and distinct role in chemistry. Experimentation is the essence of learning science. The purpose of doing experiments is to teach the principles of scientific inquiry, to improve understanding of theory through practical experience, to teach specific practical skills, such as measurement and observation, that may be useful in future studies, and to teach generic skills, such as teamwork and problem-solving, to motivate and engage students. It is important to have a clear idea of why we do practice science. It will be helpful to choose which experiments to do and how to integrate them with 'theory'. Physical Chemistry Practical Guide aims to facilitate experimental exercise in the physical chemistry laboratory at the PG level of a student's career. The book will be very helpful for teachers in providing practical knowledge of important aspects of Physical Chemistry experiments. The book covers a wide range of areas from basic to advanced experiments, including calibration of instruments as well as highly accurate software for computational quantum chemical calculations. This book has been divided into four sections: Part I consists of general introduction, calibration of glassware, instruments, and precautions; Part II entails those experiments that have a simple theoretical background and classical methods; Part III comprises of experiments that are associated with more advanced theory, and technique that requires a greater degree of experimental skill and use of instruments. Part IV comprises experiments related to the use of computers and that are investigative in nature. Covering all aspects of classical, advanced, and computational chemistry experiments, this book will be useful for under graduate and post-graduate students to gain confidence in their ability to perform a physical chemistry experiment and to appreciate the value of the experimental approach.

We also celebrate this opportunity for expressing bottom-hearted gratitude towards the people who supported us at all stages of our work. The authors acknowledge their parents, spouse, family members, friends, and colleagues for their continuous support and encouragement above all our students. The basis of the book is to overcome difficulties that arise while performing physical chemistry practicals, and this we learned from our experience during our studenthood as well as interacting with the students during practical classes. We would like to acknowledge Mr. Sanju Soni, Ph.D. student of Department of Chemistry, Guru Ghasidas University, Bilaspur, for his dedicated efforts in preparing figures/improving the quality of figures in the book chapters without which this book would not have become a

reality. We are also thankful to Dr. Amlan Das, NIT Sikkim (National Institute of Biomedical Genomics., Kàlyani) for drafting experiment on the denaturation of Bovine Serum Albumin (Protein) and Mr. Happy Mondal from NIT Sikkim for designing experiments on Determination of Hall coefficient of a semiconductor and determination of paramagnetic susceptibility of a given paramagnetic material. We would like to express our gratitude to Bentham Science for publishing the book.

CONSENT FOR PUBLICATION

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Vice Chancellor, Guru Ghasidas University, Bilaspur, and Director, NIT, Sikkim, for providing necessary facilities. The authors acknowledge their parents, spouse, family members, friends, and colleagues for their continuous support.

Charu Arora
Department of Chemistry
Guru Ghasidas University
India

&

Sumantra Bhattacharya
National Institute of Technology Sikkim
India

CHAPTER 1

General Introduction

UNITS AND SIGNIFICANT DIGIT

List of Units Useful for This Book

The concentration of a solution is a measure of the amount of solute which has been dissolved in a given amount of solvent or solution. A concentrated solution has a relatively large amount of dissolved solute. A dilute solution has a relatively small amount of dissolved solute.

Molarity (M) is one of the most common methods to express concentration. Molarity (M) indicates the number of moles of solute per liter of solution (moles/Liter) and is one of the most common units used to measure the concentration of a solution. Molarity can be used to calculate the volume of solvent or the amount of solute.

Molality (m) is another way to represent the concentration of a solution and is defined as the number of moles of solute per kilogram of solvent. The SI unit for molality is mol/kg. For example, a solution with a molality of 3 mol/kg is often described as "3 molal" or "3 m." However, following the SI system of units, mol/kg or a related SI unit is now preferred.

Equivalent weight (also known as gram equivalent) is the mass of one equivalent, which is the mass of a given substance that will combine with or displace a fixed quantity of another substance. The equivalent weight of an element is the mass that combines with or displaces 1.008 grams of hydrogen or 8.0 grams of oxygen or 35.5 grams of chlorine. All these are summarized in Table **1.1.**

Table 1.1. Units of various parameters used in the book.

Parameter	CGS Unit	SI Unit
Concentration	g/cm^3, M	Kg/m^3, mol/kg, M
Molar absorption coefficient	$M^{-1}.cm^{-1}$	$M^{-1}.m^{-1}$
Unit of rate constant (First order reaction)	s^{-1}	s^{-1}
Viscosity	Poise or $Dyncmsec^{-1}$	N-m/sec
Surface tension	$Dyncm^{-1}$	Nm^{-1}
Specific Rotation	$Deg.cm^{-2}g^{-1}$	$Deg.m^{-2}kg^{-1}$

Conductance	Ohm^{-1} or mho siemens	-
Potential difference	Volt	Volt
Universal molar gas constant	1.987 $calmol^{-1}K^{-1}$	8.314 $JK^{-1}mole^{-1}$

Significant Digit

In measurement reporting, a number with a proper decimal place is important. Before representing a value, one experimentalist should know the precision of instruments and apparatus used. To determine how many significant figures are in a number one should follow these rules:

1. Non-zero digits are always significant.

e.g., 123 (3 significant figures)

2. Any zeros between two significant digits are significant.

e.g., 11.102 (5 significant digits)

3. Zeros to the left of the first non-zero digit are not significant.

e.g., 0.05 (1 significant figure)

4. If a number ends in zero to the right of the decimal point, those zeros are significant.

For example, 2.00 (3 significant digits)

5. If a number ends in zeros to the left of the decimal point, those zeros are not essentially significant. *e.g*., If we make a statement that the reading of a burette in some titration process is 12.10 ml. It is good to report more digits after the decimal place, but simultaneously one should keep in mind that any observation can be reported up to the least count of the apparatus. Since generally burette shows one point after the decimal place. Thus, it is not recommended to report beyond the first digit of the decimal place. On the other hand, when an experimentalist is multiplying or dividing two numbers obtained from different apparatus with different least counts, then the experimentalist should report the value having no more significant figures than the least accurate observation.

e.g., If an object has mass of 29.1143 g and a volume of 25.0 cm^3, then its density is given by 29.1143 g/25.0 cm^3 = 1.164572 g/ cm^3 =1.2 g/cm^3

Here please note that if we report only up to the first digit after the decimal, then the final value should be 1.1. Since the digit at the second decimal place is more than 5, so we have used 2 instead of 1. This method is called the round-off method. However, you are required to round off numbers only at the END of calculations; otherwise, errors may be inadvertently carried through.

CALIBRATION OF VOLUMETRIC APPARATUS

Since all the volumetric analyses are calculated based on burette reading thus, it is necessary to calibrate the value of all the apparatus, like a pipette, volumetric flask, *etc.*, in terms of burette reading. To illustrate this, let us pick up an example of calibration of the pipette (10 ml). To do so, let us fill up the burette (50 ml) with distilled water up to the mark and then elute the known volume of water and note the reading. Then pipette out water using the pipette to be calibrated. Pour the water into the burette and note the reading and difference. The difference between these two values gives the measurement of the calibration of the pipette. Similarly, other apparatus can also be calibrated.

CALIBRATION OF BALANCE

Calibration weights are specially designed cast iron or stainless-steel weights used to calibrate weighing equipment. For external calibration of a balance, the user must have a set of approved weighing scale calibration weights that should be kept in top condition. The scale calibration weights are put on the balance or scale and their mass or weight is set as the standard.

PREPARATION OF STANDARD SOLUTION

For several titrimetric processes, it is necessary to prepare standard solutions, which are of two types, *viz*. primary standard, and secondary standard. The strength of primary standard solutions is maintained for a long time. While performing an experiment, it is necessary to prepare the primary solution very accurately. To do so, one should weigh the solute very accurately. Pour the solute into a volumetric flask and add solvent up to the mark. Shake the solution very well to make a homogeneous solution. While adding solvent, one should be very careful to avoid the addition of excess water. If mistakenly added, then note down the amount of excess water added and calculate the strength accurately. In this context, it is quite difficult to make an exact solution. So, the coefficient should be calculated accurately. To illustrate this, let us prepare 100 ml 0.1 (M) oxalic acid ($H_2C_2O_4.2H_2O$) solution, *i.e.*, 1.26 g of $H_2C_2O_4.2H_2O$ is required. Someone weighed 1.35 g of $H_2C_2O_4.2H_2O$ and added 101 ml of water instead of 100 ml of water. Thus, the strength of the solution will be 0.108 (M).

CHAPTER 2

Physical Chemistry Practical using Thermo-Chemistry

INTRODUCTORY REMARKS

Thermochemistry deals with heat changes taking place during chemical reactions as well as the heat changes associated with physical transformations. Reactions accompanying evolution or absorption of heat are known as exothermic or endothermic reactions, respectively. The heat of reaction for a chemical process depends upon the following factors:

1) Nature of reacting substances.

2) Physical state of reacting substances (*e.g.*, solid, liquid, and gaseous state are a particular allotropic form).

3) The fraction of reactive species taking part in the reaction.

Heat changes are generally expressed in calories (cal.). It is defined as the amount of heat required to raise the temperature of 1 g of water from 15° C-16° C. Another conventional unit is the joule (J) (Came by the name of James Prescott Joule). 1 cal. = 4.184 J.

A thermochemical result is expressed by writing the chemical formula of reacting substances separated by comma (,) together with the amount of heat change that has accompanied the reaction. A comma is used to separate the chemical formula of reacting species when they are combined directly, while a colon (:) when the reaction takes place, but there is no direct combination. Thus, (N, 3H) indicates that nitrogen and hydrogen react directly to form NH_3, while (NH_3: $3Cl_2$) indicates that ammonia and chlorine react to form HCl and NCl_3.

Thermochemical variables can be classified as follows:

i) Heat of formation

ii) Heat of solution

iii) Heat of dilution

iv) Heat of hydration

v) Heat of neutralization

vi) Heat of reaction

vii) Heat of combustion

The demonstration of measurement of all these is beyond the scope in this book. We will demonstrate only Heat of dilution, Heat of neutralisation and Heat of reaction.

DESCRIPTION OF CALORIMETER

A calorimeter is a device used to measure the heat flow of a chemical reaction or physical change. The process of measuring this heat is called calorimetry. A basic calorimeter consists of a metal container of water above a combustion chamber, in which a thermometer is used to measure the change in water temperature. However, there are many types of more complex calorimeters.

The basic principle is that heat released by the combustion chamber measurably increases the temperature of the water. The temperature change may then be used to calculate the enthalpy change per mole of substance A when substances A and B are reacted.

The equation used is:

$$q = C_v*(T_f - T_i)$$

Where, q, C_v, T_f, and T_i are the amount of heat in joules, calorimeter's heat capacity in joules per Kelvin (J/K), final and initial temperatures of the system.

I. TO FIND WATER EQUIVALENT OF CALORIMETER AND DETERMINATION OF HEAT OF DILUTION OF H_2SO_4

Chemicals and Apparatus

Sulphuric acid, oxalic acid, sodium hydroxide, distilled water, calorimeter.

Theory

Heat capacity or water equivalent of a calorimeter is defined as the number of calories required to heat the calorimeter by unit temperature. If M is the mass of the calorimeter and S is the specific heat then heat capacity is obtained by multiplying M by S. During the heat changes the calorimeter takes up some of the heat evolved, it should be taken into account by determining the water equivalent (w.e.) or heat capacity of the calorimeter.

In the case of glass vessels, the value of w.e. is found for such part of the vessel which is actually in contact with the reacting system. In this case, the method of obtaining w.e. by multiplying the mass and specific heat of the material of the vessel is not significant. During the experiments, equal volumes are used so that the area of the calorimeter in contact with the system remains unaltered as far as possible.

The heat of dilution is a quantity of heat evolved or absorbed when a solution containing 1 g-mol of a substance in an unknown quantity of water or other solvent is diluted by the known quantity of that solvent. Students should keep in mind that the dilution process is not a chemical reaction.

Procedure

1) Calculate the density of water at two different temperatures, sulphuric acid using the method described in Experiment 2, Chapter 4.

2) Take 25 ml of distilled water in the calorimeter and record its temperature. Take some water in a beaker and heat it to a temperature of about 30° C-35° C, higher than the room temperature.

3) Pipette out 24 ml hot water and add it to another beaker and record its temperature after every half minute for five minutes.

4) Add this hot water quickly to the water in the calorimeter.

5) Mix the content properly and record the temperature after every half minute.

6) Plot a graph of temperature *vs.* time and from it find out the temperature of hot water and that of the mixture at the time of mixing.

7) On the graph draw a vertical line for the moment of mixing (when the half volume of water has been transferred) and extrapolate the temperature-time curve

CHAPTER 3

Chemical Kinetics Experiments

INTRODUCTORY REMARKS

As the chemical reaction proceeds the concentration (amount) of reactant decreases while the product is formed. For a particular reaction, the change of concentration of reactant or product with respect to time is known as the rate of the reaction. Thus, in terms of mathematical representation, we can represent the rate of a chemical reaction as: $-\frac{dc}{dt}$. Chemical kinetics is a branch of physical chemistry that deals with the rate of a chemical reaction and its mechanism. The general form of rate of a chemical reaction can be represented in terms of concentration of reactant:

$$-\frac{dc}{dt} \propto (C_{Reactant_1})^{x^1}(C_{Reactant_2})^{x^2}....(C_{Reactant_n})^{x^y}$$
$$\text{where, } x^1+x^2+...+x^y=n \qquad \textbf{(3.1)}$$

Here k and n are the rate constant and order for the reaction. Order of reaction can have non-negative integer values as well as fractional values. Every reaction has unique order. Based on the order of reaction we can classify it as zeroth order, first order, second order, *etc*.

The general expression of the unit of the rate constant of a reaction can be expressed as $(\text{concentration})^{1-n}\times\text{time}^{-1}$. Thus, if the concentration is expressed in terms of mole/lit, then the rate constant can be expressed as $(\text{mole})^{n-1}\times (\text{lit})^{1-n}\times (\text{sec})^{-1}$. The rate of reaction is expressed as concentration/time.

> Always keep in mind that, the reaction rate is very much dependent on time, concentration and temperature. So, measure accurately time interval, concentration and never forget to read and note temperature.

Zero Order Reaction

In the case of a zero-order reaction, the rate is entirely independent of the concentration of reactants. For example, for any reaction A→B If the rate is independent of the concentration of A, then we can say that the reaction is obeying zero order in terms of reactant.

Zero-order reactions are often referred to as pseudo-zero-order reactions because the zero-order kinetics cannot continue when the reactant gets completely consumed.
Mathematically we can express the rate of a reaction as:

$$-\frac{dc}{dt}=k \qquad \textbf{(3.2)}$$

Example:

Decomposition of nitrous oxide at ~575° C. Hot Platinum wire plays a catalytic role. If a platinum wire is not applied, it follows second-order kinetics.

$$2N_2O \rightarrow 2N_2+O_2$$

First Order Reaction

In the case of a first-order reaction, the rate is dependent on the concentration of reactants. For example, for any reaction A→B if the rate is dependent on the concentration of A, then we can say that the reaction is obeying the first order in terms of reactant.

Example:

There are huge numbers of reactions, which follow first-order kinetics. Among them, dissociation of ethyl bromide:

$$CH_3CH_2Br \rightarrow C_2H_4 + HBr$$

Mathematically, we can express the rate of a first-order reaction (A→ Product), following first-order kinetics as:

$$-\frac{dc}{dt}=kc_A$$

$$-\frac{dc}{c_A} = kdt \qquad \textbf{(3.3)}$$

Upon integration, Equation (3.3) becomes:

$$-\int \frac{dc_A}{c_A} = k\int dt$$

On integration,

$$\ln c_{A_0} - \ln c_{A_t} = kt$$

$$\ln(\frac{c_{A_0}}{c_{A_t}})=kt \quad \textbf{(3.4)}$$

Where c_0, c_t is the concentrations of the reactant at time 0 and time t, respectively. Thus, the unit of rate constant for a first-order reaction is time^{-1}. Graphically, the rate constant of the first-order reaction can be measured by plotting time *versus* the logarithm of concentration. A straight line is obtained for the first-order reaction, where c_0 is the intercept of the concentration axis and the slope is equal to the rate constant.

Second-Order Reaction

In the case of a second-order reaction, the rate is dependent on the product of two concentrations of reactants. For example, for any reaction A + B → product.

Example: Example of second-order reactions is base-catalysed hydrolysis of ester, esterification of acids, *e.g.*

$$CH_3COOC_2H_5+^-OH \rightarrow CH_3COO^-+C_2H_5OH$$
$$CH_3COOH+CH_3OH \rightarrow CH_3COOCH_3+H_2O$$

The formation of hydrogen iodide also follows second order kinetics:

$$H_2 + I_2 \rightarrow 2HI$$

General mathematical expression for the rate of second-order (A + B → product) reaction is: $-\frac{dc}{dt}=kc_Ac_B$, where c_A and c_B are the concentration of A and B, respectively. Two cases can arise here:

1) When the concentrations of A and B are different.

2) When the concentration of A and B are the same.

For the first case the rate constant can be expressed as:

$$k=\frac{1}{t(a_0-b_0)}\ln\left(\frac{b_0a_t}{a_0b_t}\right)$$

$$\text{or, } kt=\frac{1}{(a_0-b_0)}\ln\left(\frac{b_0a_t}{a_0b_t}\right) \quad \textbf{(3.5)}$$

CHAPTER 4

Properties of Liquid

I. TO MEASURE THE DENSITY OF A LIQUID USING A PYKNOMETER

Chemicals and Apparatus Required

Pyknometer, given liquid, distilled water.

Theory

The density of a given liquid (d_t) at a certain temperature is given by the following formula:

$$d_t = \frac{W'D}{W} - \frac{0.012}{W(W'-W)} \quad \textbf{(4.1)}$$

W', W and D are the weight of a given volume of the liquid, the same of water and density of water at temperature t° C, respectively. A small fraction is subtracted due to the correction of buoyancy of the air, which can be neglected for ordinary laboratory work.

Procedure

1) Clean the pyknometer properly with chromic acid, wash with water thoroughly and take weight after drying. Let this weight be W_1 g.

2) Fill the pyknometer with water, using a hypodermic syringe or an aspirator. Else, attach a rubber tube at the end of part A of the pyknometer. Place the other end, B, in water and suck gently. In case a volatile or poisonous liquid is used in place of water, interpose a vapour trap between the liquid and mouth. (A drying tube filled with activated carbon is a convenient and effective trap). If any air bubble is trapped, tilt the pyknometer, so that the bubble is at the entrance to the outlet tube. Then suck more liquid into the pycnometer.

3) Ensure that the water stands at A. To remove excess water, tilt the pyknometer until a drop forms at the B end and the water level comes to A. Then wipe the drop away with a filter paper. This adjustment of the water level can be most conveniently done by slightly tilting the pyknometer toward B and withdrawing the

excess water by touching the B-end with a piece of filter paper. Add water if necessary. Dry the outer wall of the pyknometer and take the weight. Let that weight be W_2 g.

4) Replace water with the liquid under investigation. Repeat the above procedure and weigh the pyknometer with the given liquid. Let the weight be W_3 g.

Observation and Results

Temperature = …...° C

W_1= Mass of pyknometer

W_2= Mass of pyknometer + water

W_3= Mass of pyknometer + liquid

Therefore, $(W_2 – W_1) = W$= Mass of water at t° C

$(W_3 – W_1) = W'$= Mass of liquid at t° C

The density of water at t° C = D

Thus, the Density of liquid $(d_t) = (W'/W) *D$.

II. TO MEASURE THE DENSITY OF A LIQUID USING A DENSITY BOTTLE

Chemicals and Apparatus Required

Density bottle, given liquid, distilled water.

Theory

Same as Experiment I.

Procedure

1) Clean the density bottle properly with chromic acid, wash with water thoroughly and take weight after drying. Let this weight be W_1 g.
2) Fill the density bottle with water using a burette and note the volume. Dry the outer wall of the density bottle and take the weight. Let that weight be W_2 g.

3) Replace water with the liquid under investigation. Repeat the above procedure and weigh the density bottle with the given liquid. Let the weight be W_3 g.

Observation and Results

Same as of previous experiment (Experiment I).

SURFACE TENSION OF LIQUID

General Introduction

In liquid, the molecules have an intermolecular force of attraction. The liquid molecules can be classified into two parts. One is bulk and another is the surface of the liquid. The bulk molecules experience only attraction between liquid molecules, so the force is uniform throughout, whereas the surface molecules experience attraction forces from liquid molecules as well as vapor molecules. Since the number of vapor molecules is much less than the liquid counterpart, the attraction is unbalanced. As a result, the surface molecules of liquid behave like a stretched membrane, with a tendency to contract to a minimum area. Such property of a liquid is known as the surface tension of the liquid, which is a measure of inward pulls resulting from the unbalanced force on the surface molecules.

Definition

The force acting along the surface of a liquid at a right angle to an imaginary line of unit length drawn on the surface at a definite temperature is called the surface tension of the liquid. Generally, Surface tension is denoted by γ.

SI unit: $N\text{-}m^{-1}$, **CGS unit:** $dyne\text{-}cm^{-1}$.

Surface Energy

To increase the surface area more molecules will have to be brought to the surface. This requires some work to be done. Thus, surface energy is defined as the work done in increasing the surface area by unity, which is an alternative definition of surface tension. Thus, surface tension and surface energy have the same unit.

The surface tension of a liquid decreases with the increase in temperature. The relationship can be explained using the Ramsay-Shields-Eötvös equation. The concentration of a liquid has an effect on surface tension. The change is purely individual and depends on the nature of the solute.

CHAPTER 5

Phase Diagram

GENERAL DISCUSSION

The phase rule is used for the quantitative treatment of systems in equilibrium. It helps to predict the conditions that must be specified for a system to exhibit equilibrium. One should know terms like phase, components, and degree of freedom before going through the phase rule.

A phase (P) is defined as any homogeneous and physically distinct part of a system that is bounded by a surface and is mechanically separable from other parts of the system.

The number of components (C) of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in terms of the chemical equation.

Let us take an example of ice, water, and vapour in equilibrium:

$$\text{ice} \leftrightharpoons \text{liquid water} \leftrightharpoons \text{vapour}$$

Here, at equilibrium three phases can coexist, but the number of components is 1 (As only water is considered). In 1876 A.D., J. W. Gibbs proposed a rule to make a correlation between degrees of freedom, component, and phase, which is known as the phase rule. The phase rule is defined as F = C-P+2. Here, F is degrees of freedom. The number 2 denotes 2 independent variables, *viz.* temperature, pressure. The degree of freedom of a system is defined as the number of independent variables. Thus, in the above example using the phase rule we can say that the number of degrees of freedom is zero, (C = 1, P = 3). Thus, it is an invariant system. So, based on the value of F, we can say invariant (F = 0), univariant (F = 1), bivariant (F = 2), trivariant (F = 3) and so on.

Although, the phase diagram is applicable even for solid solutions (alloys). Here we shall demonstrate only the liquid mixtures.

I. TO STUDY THE CRITICAL SOLUTION TEMPERATURE OF A BINARY MIXTURE

Chemicals and Apparatus

Phenol, distilled water, thermostat/water bath, test tube, thermometer.

Theory

Phenol and water are not miscible completely; rather they are partially miscible at room temperature. When a small quantity of phenol is added to water, the substance will dissolve completely. If the addition of phenol is continued for a certain time it will be observed that no further dissolution takes place and the two liquid layers separate. Each layer is a saturated solution of one in the other. These two layers in equilibrium are known as conjugate solutions. The upper layer is a saturated solution of phenol and water and the lower one is water in phenol.

Mutual solubility of phenol and water increases with an increase in temperature which causes the concentration of phenol as well as that of water in phenol. At a particular temperature, two conjugate solutions convert into a homogeneous solution. The particular temperature is known as the critical solution temperature (CST). This temperature is the characteristic of a particular system and impurities of the system influenced the shift of CST. If pure water and phenol are taken, at 66.4° C the CST is observed. This is known as upper critical solution temperature (UCST). The plot of the composition of phenol added to water *vs.* temperature is plotted as in Fig. (**5.1**).

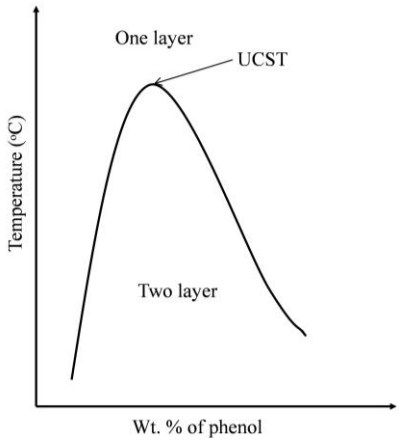

Fig. (5.1). UCST of phenol water system.

At any temperature above UCST, phenol-water is miscible in all proportions. Outside the curve, the system is completely homogeneous, *i.e*., outside the curve, only one layer persists. Below the curve always two layers will separate and the curve gives the composition of the two conjugate solutions consisting of two layers. Throughout the experiment, pressure is kept fixed. Thus, the phase rule has been reduced to F=C-P+1.

For a homogeneous phase of two-component liquids, F = 2 - 2 + 1 = 2, *i.e*., degrees of freedom is 2, implying that the system is bivariant. Thus, for homogeneous solutions both composition and temperature have to be defined.

For the heterogeneous equilibrium with two conjugate solutions, F = 2 - 2 + 1 = 1. This implies that the system would behave as a univariant. So, either temperature or composition is fixed and another parameter will be known automatically from the diagram. At CST composition of the two conjugate solutions be the same, *i.e.*, F = 2 – 2 + 1 – 1 = 0. Thus, the point is fixed. For a particular pair of partially miscible liquids, the value is fixed.

Procedure

1) Note down the room temperature and get the density of water from the table of the variation of density of water with respect to temperature.

2) Weigh ~ 2 g of phenol accurately (Table **5.1**, density of phenol = 1.07 g/cc at 298 K) and transfer it to the hard glass test tube.

3) Fit the hard glass test tube (tt) with a holder fixed to a burette stand. Dip a thermometer inside the tt. Immerse the bottom of the tt into distilled water filled in a 250 ml beaker which is kept on an asbestos board over the tripod stand.

4) Add 1 ml of distilled water into the hard glass tt by using a pipette to the phenol. Stir the phenol-water solution well with the stirrer so that the mixture becomes turbid. Heat the bath slowly until the mixture becomes clear suddenly at a particular temperature. Note the temperature of the disappearance of turbidity. Remove the flame and allow the liquid to cool down slowly. While cooling down, turbidity reappears. Note the temperature. Take the average of two temperatures (Table **5.2**).

5) Add 1 ml of water to the system and repeat step 3 and keep on adding the same volume of water to the system and repeat. Take at least 10-15 readings.

CHAPTER 6

Adsorption

INTRODUCTION

The term Adsorption was first coined in 1881 by a German physicist named Heinrich Kayser. Adsorption is purely a surface phenomenon, where particles are attached to the top layer of material. It normally involves the molecules, atoms, even ions of a gas, liquid, or solid in a dissolved state that is attached to the surface.

Adsorption is mainly a consequence of surface energy. Generally, the surface particles which can be exposed partially tend to attract other particles to their site. Interestingly, adsorption phenomena is widely found in various natural processes and finds its use in many industrial applications. Some examples are summarized below:

1) Air Pollution Masks

These consist of silica gel or activated charcoal powder, when dust or smoke are passed through them, those particles get adsorbed on the surface of these materials. Additionally, these types of masks are effective to protect microbes also.

2) Separation of Noble Gases by Dewar's Flask Process

A mixture of noble gases of second to fourth row (Ne, Ar, Kr) are passed through Dewar's flask in presence of heated coconut charcoal. Argon and Krypton gas get adsorbed leaving Neon.

3) Purification of Water

By the addition of alum stone to the water, impurities get adsorbed on the alum, and water gets purified.

4) Removal of Moisture and Humidity

Moisture in the air can be removed by placing silica gel on which water molecules get adsorbed.

5) Adsorption Chromatography

It is used to separate pigments and hormones.

6) Ion Exchange Method

In this method of removing the hardness of water, calcium and magnesium ions get adsorbed on the surface of the ion exchange resin.

7) In Metallurgy

In the froth floatation process of concentration of ore, the particle gets adsorbed on the froth.

Difference between adsorption and absorption: Absorption is a process in which a fluid is dissolved by liquid or a solid (absorbent). Adsorption is a process in which atoms, ions or molecules from a substance adhere to the surface of adsorbent. So be careful about using these two words. Do not get confused!

I. STUDY THE ADSORPTION OF ACETIC ACID ON CHARCOAL AND PROVE THE VALIDITY OF FREUNDLICH/LANGMUIR ADSORPTION ISOTHERM

Chemicals and Materials Required

0.5 (N) acetic acid (AcOH), 0.1 (N) sodium hydroxide (NaOH), charcoal, phenolphthalein indicator, oxalic acid (Ox), burette, pipette, reagent bottles, conical flask, and shaker.

Theory

Adsorption is a surface phenomenon. Adsorption can take place between any states of matter (gas, liquid, solid) on solid. The substance which gets adsorbed is called adsorbate and the surface of the solid on which it is adsorbed is known as adsorbent. Depending upon the nature of surface forces involved adsorption can be classified as physisorption and chemisorption. Physisorption or physical adsorption mainly arises because of very weak van der Waals' interaction between adsorbent and adsorbate. On the other hand, the interaction between them is much stronger in chemisorption. The heat of adsorption lies in the range of 80-420 kJ/mol with high activation energy for chemisorption. Usually, it is irreversible. While for physical

adsorption, the heat of adsorption is less than 20 kJ/mol, and activation energy is often less than 5 kJ. Physisorption is multilayer, while chemisorption is a monolayer.

The amount adsorbed (a) is dependent on pressure (P) and temperature (T). Hence, a can be expressed as a function of pressure and temperature, a=f (P, T). A plot of P and a, keeping the temperature constant is known as adsorption isotherm.

> In an **isothermal** process, temperature is constant. If pressure is fixed is called **isobaric** and if volume is uniform, then it is known as **isochoric**.

Freundlich Adsorption Isotherm

Freundlich (1909 AD) proposed an empirical relationship: $\frac{x}{m} = kc^{\frac{1}{n}}$. Here, x is the amount of solute adsorbed and m is the amount of adsorbed material. c is the equilibrium concentration of adsorbate in the solution, k is a constant, depends on the nature of adsorbent and adsorbate. n is another constant, dependent on the nature of adsorbate. The value of 1/n lies between 0 to 1. On taking the logarithm of the above equation, we have:

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log c \qquad \textbf{(6.1)}$$

If we plot the left-hand side of the equation along the Y-axis and log c along the X-axis, we get a straight-line having slope 1/n, and log k is the intercept along the x-axis (Fig. **6.1**).

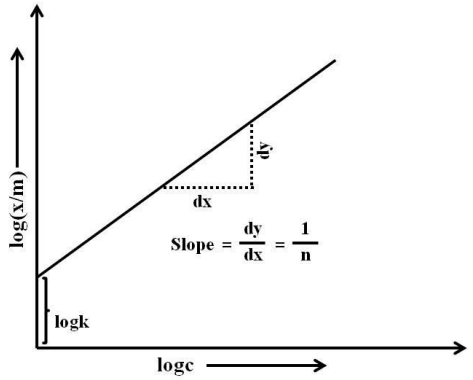

Fig. (6.1). Plot logarithm of concentration *vs.* logarithm of (x/m) (Freundlich adsorption isotherm).

CHAPTER 7

Instruments Based on Optical Measurements

REFRACTOMETRY

Introduction

When a beam of light passes from one medium to another medium it deviates from its path. This phenomenon is known as refraction. If it passes from a less rare medium to a denser medium the beam refracted towards the normal (Fig. **7.1**).

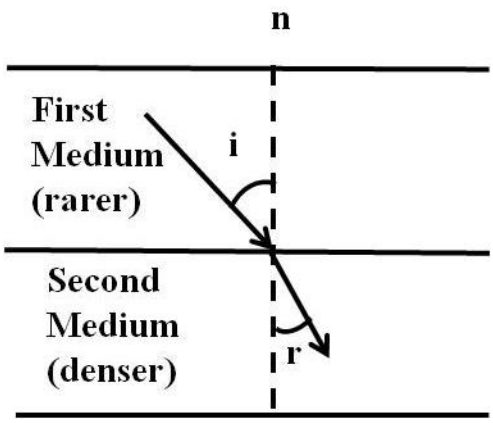

Fig. (7.1). Phenomena of refraction.

In this case the angle of incidence (angle between normal and incident light), i is greater than the angle of refraction (angle between normal and refracted beam), r. The refractive index of the second medium (n) with respect to first can be given by Snell's law of refraction.

$$n = \frac{\sin i}{\sin r} \quad \textbf{(7.1)}$$

The value of the refractive index can also be given by

$$n = \frac{\text{Velocity of light in vacuum}}{\text{velocity of light in the medium}} \quad \textbf{(7.2)}$$

The Refractive index of a liquid depends on temperature as well as the wavelength of light used.

Specific Refractivity

Specific refraction or specific refractivity is expressed as:

$$R = \frac{1}{d} \times \frac{n^2-1}{n^2+2} \quad \textbf{(7.3)}$$

Here R is specific refractivity and it is independent of temperature, d is density.

Molar Refractivity

Molar refractivity can be obtained by multiplying the specific refractivity by the molecular weight of the medium. It can be expressed as:

$$R_M = R \times M = \frac{M}{d} \times \frac{n^2-1}{n^2+2} \quad \textbf{(7.4)}$$

Molar refractivity is the constitutive and additive property and we have refractivity due to atoms (atomic refractivity) as well as refractivity due to structural factors (structural refractivity).

Description of Abbe Refractometer

Many refractometers are available for rapid and accurate determination of the refractive index. For small quantities of liquids, we can easily use the Abbe refractometer (Fig. **7.2**) in the laboratory. It consists of two flint glass prisms, illuminating prism (lower prism), and a measuring prism (Upper prism). The surface of the measuring prism is finely polished while that of the illuminating prism is finely ground. The two prisms are fixed in a metal casing. The prisms are jacketed so that they can be maintained at constant temperature by circulating water. The prisms are rotated using a movable arm that carries reading glass. A thin layer of liquid can be placed between two prisms. The position of the borderline of a total reflection is observed through a telescope and by turning the movable arm, it can be made to coincide with the intersection of the cross wire in the telescope. The arc is graduated in such a way that it gives directly the value of the refractive index with an accuracy of 0.001. Ordinary light can also be used while working with the Abbe refractometer. The telescope is provided with the dispersion compensator, for this purpose. The dispersion compensator consists of an Amici prism mounted one over the other and can be rotated in opposite direction by

turning the milled head. When we put a drop of liquid on the surface of the illuminating prism and clamp it with a measuring prism, a thin film of liquid spreads between them. Light reflected by the mirror enters the lower prism and passes into the upper prism. The deviation of the ray of light depends upon the angle of incidence. At an angle near 90° to its surface, the rays will deviate the least on entering the prism and rays entering the measuring prism at angles less than 90° bent more and form the edge of the field. The line of demarcation between the dark and light fields will be coloured and cannot be visualized because when white light is used it will be refracted to a different extent by the measuring prism and the liquid. Light of different wavelengths is dispersed by the liquid, measuring prism, and by the Amici prism A_1. As different liquids produce different dispersion, therefore the second Amici prism A_2 is so adjusted that its dispersion is equal and opposite to that produced by the liquid in measuring prism and A_1. The Amici prism can be adjusted by turning the Milled head until the colour fringe disappears and a sharp light-dark boundary is observed by the eye-piece (Completion of compensation).

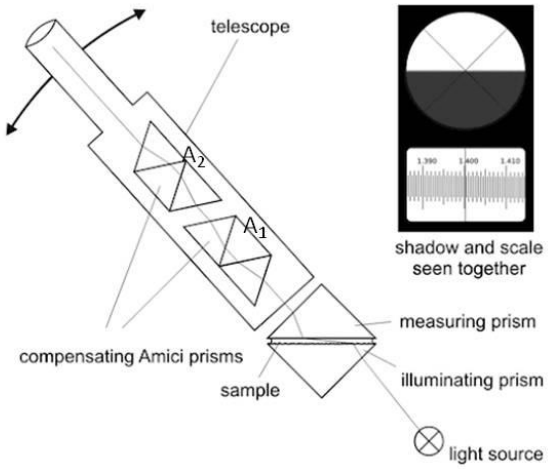

Fig. (7.2). Schematic representation for Abbe Refractometer.

Working Principle of Abbe Refractometer

The instrument is kept on a working table in such a manner that the light from the source is reflected by the mirror. The mirror is adjusted to get the maximum illumination. The prism box is opened using a clamp. The surfaces of the two prisms are cleaned with acetone and dried with soft tissue paper. The polished upper surface should never be scratched. Water is circulated at room temperature through

CHAPTER 8

Measurements Based on Electrode

pH-METRY

Introduction

Determination of pH is a very common measurement in laboratories, industry, hospitals, soil and water testing, and a wide variety of other analytical, control, and monitoring operations. Therefore, a large variety of instruments are available commercially to measure, control, and monitoring pH operations. Measurement of pH gives a quantitative idea of the degree of acidity (or basicity)- concentration of H^+ - in a stationary or flowing sample fluid. This is often very crucial in decision making in quality control, process industries, food, beverages and fermentation industry, biological and microbiological operations, *etc.*

Sensing of pH is accomplished by a pH-sensitive glass in contact with the internal fill, a 7-pH buffer, and the external sample. The pH-sensitive glass develops potential as per Equations (8.1) and (8.3), by proton exchange between H_3O^+ in the aqueous solution and the hydrated gel layer of the glass. The protons enter the sites vacated by Na^+ and recombine with H_3O^+ in the hydrated gel layer.

The potential developed is proportional to the difference in logarithms of activity of H_3O^+ in solution and gel layer on both sides of the glass membrane. The log of hydrogen ion activity can be converted to pH using the definition of pH, to give Equation (8.6):

$$E_1 = K_g^1 + 0.1984(T + 273.16)\log\frac{a_1}{a_g^1}$$

$$E_1 = K_g^1 + 0.1984\,(T + 273.16)\log\left(\frac{a_1}{a_g}\right) \quad \textbf{(8.1)}$$

$$E_1 = K_g^1 + 0.1984(T + 273.16)\,[\log a_1 - \log a_g^1]$$

$$E_1 = K_g^1 + 0.1984\,(T + 273.16)\log(a_1 - a_g) \quad \textbf{(8.2)}$$

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$$E_2 = K_g^2 + 0.1984(T + 273.16)\log\frac{a_2}{a_g^2}$$

$$E_1 = K_g^2 + 0.1984\,(T + 273.16)\log\left(\frac{a_2}{a_g^2}\right) \quad \textbf{(8.3)}$$

$$E_2 = K_g^2 + 0.1984(T + 273.16)[\log a_2 - \log a_g^2]$$

$$E_1 = K_g^2 + 0.1984\,(T + 273.16)\log(a_2 - a_g^2) \quad \textbf{(8.4)}$$

$$\text{If } K_g^1 = K_g^2; a_g^1 = a_g^2 K_g^1 = K_g^2; a_g^1 = a_g^2$$

$$E_2 - E_1 = 0.1984(T + 273.16)[\log a_1 - \log a_2]$$

$$E_2 - E_1 = 0.1984\,(T + 273.16)[\log a_1 - \log a_2] \quad \textbf{(8.5a)}$$

$$= 0.1984(T + 273.16)(pH_2 - pH_1)$$

$$= 0.1984\,(T + 273.16)(pH_2 - pH_1) \quad \textbf{(8.5b)}$$

$$= 0.1984(T + 273.16)(7 - pH_1)$$

$$= 0.1984\,(T + 273.16)(7 - pH_1) \quad \textbf{(8.6)}$$

The above series of equations also indicate that:

1. mV output of electrode decreases as the pH increases

2. mV output is zero at pH = 7.

3. mV output is (+)-ve below pH 7 and (–)-ve above pH 7.

4. Effect of temperature on mV output approaches zero as pH approaches 7.

5. At 25^0 C the output changes by 59.16 mV per pH unit (0.198 x 298.16)

The pH values of various foodstuffs have been represented in Fig. (**8.1**). The pH and corresponding acidic, basic, and neutral substances along with H^+ and OH^- ion concentration are given in Table **8.1**.

In laboratories, pH is measured with the help of a pH meter consisting of an electrode and microprocessor. Detail of various types of measurement electrodes is given in Table **8.2**. The Source of errors in measurement and their symptoms are summarised in Table **8.3**.

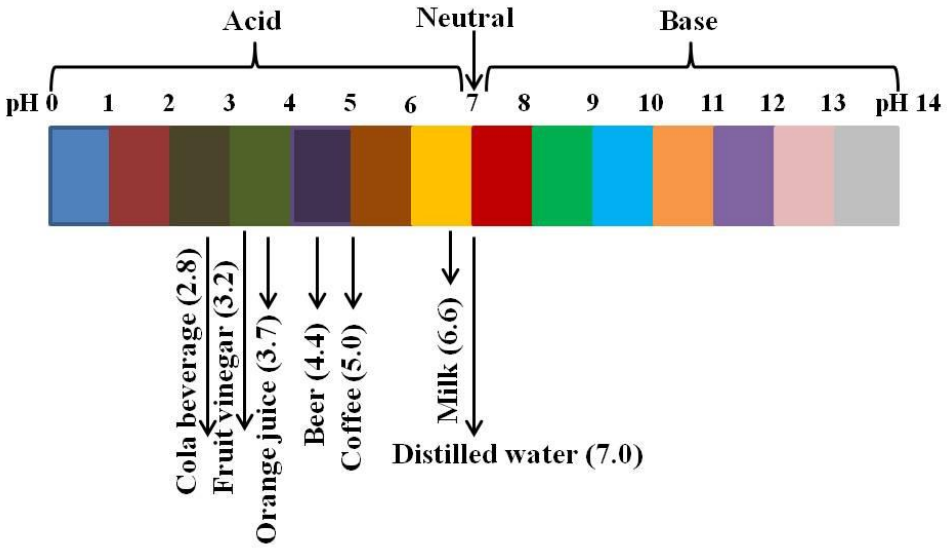

Fig (8.1). pH range of various food products.

Table 8.1. pH values of acidic, neutral and basic stuff.

Range	pH	H^+ Concentration (mol/L)	OH Concentration (mol/L)
Acid	0	1	0.00000000000001
	1	0.1	0.0000000000001
	2	0.01	0.000000000001
	3	0.001	0.00000000001
	4	0.0001	0.0000000001
	5	0.00001	0.000000001

CHAPTER 9

Some Advanced Physical Chemistry Experiments

STUDY OF CORROSION KINETICS OF IRON IN ACID MEDIUM (CONC. HCl)

Chemicals and Apparatus Required

Iron bar, Conc. HCl, four beakers.

Theory

Corrosive environments have received a considerable amount of attention because of their destruction of materials. One of these environments is the acid solutions which are often used in industry for washing, descaling, and pilling of steel structures, processes which are generally accompanied by considerable digestion of the metal. The information about corrosion rate and kinetic parameters may be helpful in the counted. Activation parameters for some systems can be estimated either from the Arrhenius equation or from the transition state theory.

Chemical kinetics study deals with the rates of chemical processes. Chemical kinetics include an investigation of how different experimental conditions can influence the rate of a chemical reaction and yield information about the reaction mechanism as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Iron is widely used in many industries. During industrial processes, such as pickling, etching, acid cleaning, acid descaling, iron is often made to meet aggressive solutions such as acidic, basic solutions. Hence metal is prone to corrosion attacks. The magnitude of corrosion of a metal depends on the concentration of the acidic and basic medium, operating temperature and period of contact, *etc.* various works have the interaction of this medium on the surface of the iron.

Procedure

1) An iron bar was purchased from the local market for weight loss measurement. The specimen surface was polished with sandpaper and then dipped in an acid solution of different concentrations.

2) 1 (N), 2 (N), and 3 (N) solutions of hydrochloric acid solutions were prepared from the concentrated HCl solution.

3) The iron bar of known mass was immersed in the prepared solution**.** The iron bar was immersed in different concentrations of one kind of acid solution for an equal time interval. It was then recovered from the test solution and washed with distilled water, and dried in a hot oven. Finally, the mass of the bar was measured very accurately (Table **9.1**). The difference in weight for each variation was recorded, and from that, corrosion rates and specific reaction rates were calculated.

Observation Table

Experimental Temperature = …°C.

Table 9.1. Effect of hydrochloric acid concentration.

HCl Concentration (N)	Initial Weight (g)	Final Weight (g)	Period (min)	Weight loss (g)
1 (N)			60	
2 (N)			60	
3 (N)			60	

Kinetics Study

The initial weight of iron specimen and change in weight of specimen at the various instant of time in hydrochloric acid were calculated using first-order rate expression:

$$k = 2.303 \log\left(\frac{\text{Initial weight of specimen}}{\text{Weight of specimen at time t}}\right) \quad \textbf{(9.1)}$$

The half-life time value was calculated by using the formula $t_{1/2} = \frac{0.693}{k}$. It was observed that the concentration of the hydrochloric acid solution was from 1 (N) to 3 (N). The values of the specific rate constant and the half-life are given in the following Table **9.2**. Based on the results, we may say that the corrosion of iron in an acidic medium follows first-order kinetics.

Observation Tables

Table 9.2. Kinetics of corrosion reaction.

Conc. of HCl (N)	Initial Weight w_1 (g)	Final Weight W_2 (g)	Weight Loss $(w_1 - w_2)$ g	Time Dipped in soln. (min)	Specific Rate Constant (c/s)	Half-Life (min)
1 (N)				60		
2 (N)				60		
3 (N)				60		

Conclusion

From the corrosion study of the iron specimen in 1 (N), 2 (N), and 3 (N) HCl acid solution, it is found that as the concentration of the HNO_3 increases, the weight loss of the iron specimen also increases vigorously. As a result, the specific rate constant also increases rapidly with the increasing concentration of the HCl acid, and the half-life period of the specimen of iron decreases abruptly with an increase in the concentration of the acid.

II. PREPARATION AND CHARACTERIZATION OF SILVER NANOPARTICLES

Chemicals and Apparatus Required

Silver Nitrate, Sodium citrate (capping agent), Sodium borohydride (0.025M), Volumetric flask (100 ml), Beaker (100 ml, 250 ml), Graduated pipette, Burette, Weighing balance, Spatula, UV- vis spectrophotometer.

CHAPTER 10

General Introduction of Making Structure of Molecules using Computer

INTRODUCTION

In this chapter, we shall execute some experiments without consuming any chemicals, we will be using a computer and necessary software (S/W) instead. We can calculate various properties of atoms, molecules, polymer, periodic systems, *etc.* Although the calculation of properties of molecules is discussed here, computational studies of the rest of the mentioned systems are beyond the scope of the book.

In the last two decades, computational chemistry has become a very demanding tool for experimental chemists to corroborate several chemical phenomena at the molecular level. Using computational chemistry, one can predict several properties of chemical systems, like *in silico* (Since computer chips consist of silicon semiconductors, so computational jobs are often known as *in silico* work) prediction of spectroscopic properties, response properties (optimized structure, electrical properties, magnetic properties), excited-state properties, adsorption, *etc.*

Here, we shall present a brief introduction to drawing the structure of small molecules using standard software and some preliminary quantum chemical calculations of some small molecules. We have also discussed how to study the geometry of a crystal from a Crystallographic Information File (CIF).

Nowadays, several software packages are available to compute energy accurately and various properties of molecules that involve energy. Among several available software packages to design molecular structures, ChemDraw [1], GaussView [2], Molden [3] are frequently used. Among these software packages, the first two are paid software (One has to purchase), while the last one is free to use. Similarly, to calculate energy and response properties of molecules using quantum chemical methods, Gaussian 09 [4], TURBOMOLE [5], GAMESS [6], ORCA [7], *etc.*, are widely used. Among these software packages Gaussian, TURBOMOLE are not free, but the GAMESS and ORCA, *etc.*, software suits are free to use for academic purposes. It is necessary to mention that all the software packages are not available in Windows Operating Systems (OS). To the best of our knowledge, Gaussian,

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GAMESS, and TURBOMOLE are available in both Windows and UNIX OS, but the rest are available in UNIX OS.

To calculate the energy and properties of molecules using quantum chemical methods, the Hartree-Fock (HF) [8] method is widely used. However, the Hartree-Fock method can give exact energy up to 95% accuracy [8] because the correlation energy is not taken into account properly. To get very accurate results, one has to adopt several correlated methods, like Configuration Interaction (CI) [8], Many-Body Perturbation Theory (MBPT) [8], coupled cluster (CC) [9], Density Functional Theory (DFT) [10], *etc.*

In this chapter, we shall discuss a brief outline of the HF method and the basis set. Using ChemDraw and GaussView how one can draw structures of molecules, and finally, we shall show how to calculate the energy of small molecules using the Gaussian software package (g09).

Hartree-Fock Method and Basis Set

To evaluate the energy of an atom or a molecule using quantum mechanics, solving the equivalent time-independent Schrödinger equation is required to determine wave-function (Ψ) of the system, which is:

$$\hat{H}|\Psi\rangle=\varepsilon|\Psi\rangle \qquad \textbf{(10.1)}$$

$\hat{H}$ is the Hamiltonian or total energy operator. $\hat{H}$ consists of the kinetic energy of constituent particles and potential energy resulted out from various interactions among them. The potential energy can be of attractive interaction, which arises because of interaction between oppositely charged particles, like attractive interaction between electron and nucleus or repulsive interaction which arises because of interaction between same charged particles, *e.g.*, electron-electron repulsion, nucleus-nucleus repulsion. Notably, the operators are represented by the symbol '^', but to simplify notation, we drop the symbol.

To represent the Hamiltonian (total energy) operator for a molecule, let us assume a molecule consists of M number of protons and N number of electrons. The Hamiltonian can be expressed as:

$$H=-\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\|r_i-R_A\|}+\sum_{\substack{i,j\\ i<j}}^{N}\frac{1}{\|r_i-r_j\|}+\sum_{\substack{A,B\\ A<B}}^{N}\frac{Z_AZ_B}{\|R_A-R_B\|} \qquad \textbf{(10.2)}$$

The successive first two terms of the right-hand side of Equation (10.2) are the kinetic energy of the nuclei and electron, respectively. R_A and r_i are the spatial coordinates of nuclei A and electron *i*, respectively. The third term is electrostatic energy of attraction between electron i and nucleus A, Z_A is the charge of nucleus A. Among the five terms, the first three terms represent attractive force. On the other hand, the last two terms are the repulsive force. Between the last two terms, the first one is repulsive electrostatic force between electron *i* and *j*, the restriction i<j is imposed to avoid double counting; another option is to multiply by a factor 1/2. The same logic is imposed for the last term also, which arises because of electrostatic repulsion between nucleus A and B of charge Z_A and Z_B. Ψ is the wave function of the system and is a function of space and spin coordinates of nuclei, denoting the combined space-spin coordinate of i^{th} electron by $x_i = (r_i,\xi_i)$. Where, ξ_i, is the spin of i^{th} electron. The N electron-M nuclear system wave function (Ψ) can be represented as:

$$\Psi(R_A,....,R_M,x_1,....,x_N)$$

Solution of the eigenvalue Equation (10.1) gives stationary state energies (When the first derivative of energy with respect to time is zero, the state is considered as a stationary state) and wave-functions.

Solution of Equation (10.1) is exactly solvable only for the hydrogen atom, but it is impossible for many-electron systems because of the repulsion terms. Hence, to solve Equation (10.1) for many-electron systems, we should adopt approximation techniques.

The nucleus is almost 1836 times heavier compared to electrons, so the velocity of the nuclei should be much lower than that of electrons. Thus, the motion of the nuclei can be frozen when we are interested in studying the electronic structure. This approximation is popularly known as the Born-Oppenheimer (BO) approximation [11]. Thus, by using BO approximation, we can drop the first and last terms of Equation (10.2). The rest term of the total Hamiltonian can be considered as electronic Hamiltonian (H_{el}), and can be expressed as:

$$H= -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{\|r_i-R_A\|} + \sum_{\substack{i,j \\ i<j}}^{N}\frac{1}{\|r_i-r_j\|} \qquad \textbf{(10.3A)}$$

$$H_{el} = \sum_{i=1}^{N} h(r_i) + \sum_{i<j}^{N} g\left(\|r_i-r_j\|\right) \qquad \textbf{(10.3B)}$$

Where $h(r_i)$ and $g\left(\|r_i-r_j\|\right)$ are represented as:

SUBJECT INDEX

A

B

C

D

E

F

G

H

I

K

L

M

N

O

P

Q

R

S

T

U

W

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CHARU ARORA

Dr. Charu Arora is a Professor (Associate) of Physical Chemistry at Guru Ghasidas University (A Central University), Bilaspur, C.G., India, and has 19 years of teaching and research experience. She has served as the Head of the Department of Chemistry at Guru Ghasidas University and as Division Chair at the Division of Nanochemistry at Galgotias University, Greater Noida, and several other reputed institutes and universities. Her areas of interest and research are Environmental Chemistry, Kinetics and Natural Product Chemistry. She has completed her Ph.D. and postgraduation in Chemistry from GK University, Haridwar, and Indian Institute of Technology, Roorkee, in 2003 and 1995, respectively. She is the recipient of the SERS Fellow Award 2017 for contribution in the field of Chemistry during the International Conference on Innovative Approaches in Applied Sciences and Technologies, organized at Nanyang Technological University, Singapore, in 2017. She is the recipient of the Gold Medal Award of the Hi-Tech Horticulture Society for outstanding contribution in Chemistry, during Global Agriculture & Innovation Conference (27th -29th Nov 2016) at Noida International University, Noida, and Science Initiator Award by Scientific Educational Research Society during International Conference on Innovative Approaches in Applied Sciences and Technologies, organized at Faculty of Science, Kasetsart University, Bangkok, during 1-5 Feb 2016. She received the SARC Gold Medal Award 2011 conferred by Scientific and Applied Research Centre, CCS University, Meerut, for outstanding contribution in the field of Chemistry Research. She has published more than 50 research papers and 15 book chapters with reputed publishers viz. Elsevier, Bentham Science, Wiley, Academic Excellence, Springer, etc.

SUMANTRA BHATTACHARYA

Dr. Sumantra Bhattacharya obtained his Ph.D. degree from CSIR-National Chemical Laboratory, Pune, India, in 2013. The title of thesis is “Study of Response Properties using Coupled Cluster Method”. After obtaining his Ph. D., He worked as Research Fellow at the Indian Association for the Cultivation of Science, Kolkata, India, South Korea and USA as well as served as an Assistant Professor (Ad-hoc) at Guru Ghasidas University, Bilaspur, India. Presently he is working as an Assistant Professor (Temporary) in the National Institute of Technology Sikkim, India, which is an institute of National Importance. He is a computational chemist. Still, now he has published thirteen scientific publications in peer-reviewed journals and one book. His research is mainly focused on the development of highly accurate quantum chemical methods to study the response properties of molecules in their low-lying excited state., The application of quantum chemical methods to study the excited state properties and their applications as well as in silico designing of homogeneous reactions were examined.