

A
Project Report
on

**Experimental Study on Measuring Diffusion Coefficients of various
Organic Solvents and Solids with varying Geometries in Air**

Submitted by

Durga Prasad Moharana
(Roll No: 110CH0079)

In partial fulfillment of the requirements for the degree in
Bachelor of Technology in Chemical Engineering

Under the guidance of

Dr. Pradip Chowdhury



Department of Chemical Engineering
National Institute of Technology Rourkela
May, 2014



CERTIFICATE

*This is certified that the work contained in the thesis entitled “**Experimental Study on Measuring Diffusion Coefficients of various Organic Solvents and Solids with varying Geometries in Air**” submitted by **Durga Prasad Moharana (110CH0079)**, has been carried out under my supervision and this work has not been submitted elsewhere for a degree.*

Date:

Place:

(Thesis Supervisor)
Dr. Pradip Chowdhury
Assistant Professor, Department of
Chemical Engineering
NIT Rourkela

Acknowledgements

First and the foremost, I would like to offer my sincere gratitude to my thesis supervisor, **Dr. Pradip Chowdhury** for his immense interest and enthusiasm on the project. His technical prowess and vast knowledge on diverse fields left quite an impression on me. He was always accessible and worked for hours with me. Although the journey was beset with complexities but I always found his helping hand. He has been a constant source of inspiration for me.

I am also thankful to all faculties and support staff of Department of Chemical Engineering, National Institute of Technology Rourkela, for their constant help and extending the departmental facilities for carrying out my project work.

I would like to extend my sincere thanks to my friends and colleagues. Last but not the least, I wish to profoundly acknowledge my parents for their constant support.

(Durga Prasad Moharana)

110CH0079

ABSTRACT

Molecular diffusion is fundamental to mass transport and understanding the basic mechanism of this phenomenon and quantitative estimation of the same is critical to mass transfer operations *viz.* distillation, absorption/stripping, liquid-liquid extraction etc. In this project, two contrastingly different cases were selected to experimentally measure binary diffusion coefficients. It is important to highlight the fact that any industrial mass transfer operation involves multi-component system; however, suitable binary system data can be effectively used to estimate the multi-component system. Similarly, for any unit operation involving more than a single-phase (and hence presence of an interphase), it is the local or overall mass transfer co-efficient which explains the mass transfer operation prevailing within the system and can be effectively measured in wetted wall column experiments. However, suitably measured diffusivity data can easily be used in estimating the mass transfer coefficients using fundamental concepts of various predictive theories like (film, penetration, surface renewal and boundary layer). In this work, several organic solvents *viz.* benzene, toluene, acetone, carbon-tetrachloride were used to measure their diffusion coefficients in air at widely different temperatures and at atmospheric pressure. Similarly, solids of different geometries (both spherical as well as cylindrical) were chosen to measure the diffusivity. Naphthalene balls ($C_{10}H_8$) were used to study the diffusion phenomenon in spherical geometry and camphor pellets ($C_{10}H_{16}O$) were used to study the cylindrical system.

CONTENTS

	PAGE NO.
<i>Abstract</i>	IV
<i>List of Tables</i>	VII
<i>List of Figures</i>	VIII
<i>List of Symbols</i>	X
CHAPTER 1: Introduction	1
1.1 Background of research	1
1.2 Objective	2
1.3 Chapter layout	2
CHAPTER 2: Literature Review	3
2.1 Principle of diffusion	3
2.2. Theory of diffusion	4
2.2.1 Fick's law of diffusion	4
2.2.1.1 Fick's first law of diffusion	4
2.2.1.2 Fick's second law of diffusion	4
2.3 Types of diffusion	5
CHAPTER 3: Diffusion in fluids and Solids	6
3.1. Steady State Diffusion	6
3.1.1 Diffusion through a stagnant gas film	6
3.1.2 Pseudo steady state diffusion through a stagnant film	9
3.1.3 Equimolar counter diffusion	10
3.2. Diffusivity of gases	13
3.2.1 Gilliland's correlation for estimating the diffusivity of gases	13
3.3 Diffusivity in liquids	14
3.4 Diffusion in solids	16

CHAPTER 4:	Diffusion setups	18
	4.1 Introduction	18
	4.2 Stefan tube	19
	4.3 Constant temperature water bath	20
	4.3.1 Temperature Control	21
	4.3.2 Safety Control	21
	4.4 Stirrer	21
	4.4 Diffusion pumps	22
CHAPTER 5:	Solids of different geometries diffused in Air	23
	5.1 Objective	23
	5.2 Experimental procedure	23
	5.3 Theory	24
	5.3.1 Diffusion in spherical geometry	25
	5.3.2 Diffusion in cylindrical geometry	27
	5.4 Observation	29
	5.5 Calculation	29
	5.5.1 For spherical naphthalene ball ($C_{10}H_8$)	29
	5.5.2 For cylindrical Camphor ($C_{10}H_{16}O$)	30
	5.6 Result	31
CHAPTER 6:	Organic liquids diffused in air diffusion	32
	6.1 Objective	32
	6.2 Theory	32
	6.3 Description	35
	6.4 Utilities Required	35
	6.5 Experimental Procedure	35
	6.6 Standard data	37
	6.7 Formulae	37
	6.8 Observations and Calculation	38
	6.9 Result	49

CHAPTER 7:	Conclusion and Future work	50
	<i>References</i>	51

LIST OF TABLES

Table	Table Caption	Page Number
Table 3.1	Diffusivity of gases at standard atmospheric pressure.	9
Table 3.2	Liquid diffusivities	15
Table 3.3	Diffusivity of some solid materials	17
Table 5.1	Experimental Data of diffusion of spherical naphthalene ball in air	28
Table 5.2	Experimental Data of diffusion of cylindrical camphor in air	28
Table 6.1	Experimental Data of diffusion of acetone in air	38
Table 6.2	Calculated values of diffusivities of Acetone with temperatures.	39
Table 6.3	Experimental Data of diffusion of CCl ₄ in air at 35°C	40
Table 6.4	Experimental Data of diffusion of CCl ₄ in air at 45°C	40
Table 6.5	Experimental Data of diffusion of CCl ₄ in air at 55°C	41
Table 6.6	Calculated values of diffusivities of CCl ₄ with temperatures	44
Table 6.7	Experimental Data of diffusion of Toluene in air at 40°C	45
Table 6.8	Experimental Data of diffusion of Benzene in air at 40°C	47
Table 6.9	Experimental values of diffusional coefficients of some organic solvents	49

LIST OF FIGURES

Figure Number	Figure Caption	Page Number
Figure 3.1	Diffusion of A through stagnant B	9
Figure 3.2	Equimolar counter diffusion	12
Figure 4.1	A typical diffusion system	18
Figure 4.2	Schematic diagram of a Stefan tube	19
Figure 4.3	Schematic diagram of a water bath	20
Figure 5.1	Diffusion set-up for naphthalene ball	23
Figure 5.2	A sketch indicating shell balance for mass transfer from a sphere	24
Figure 6.1	Diffusion setup for liquids in air	36
Figure 6.2	Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 308.15 K for CCl_4	37
Figure 6.3	Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 318.15 K for CCl_4	43
Figure 6.4	Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 328.15 K for CCl_4	43
Figure 6.5	Temperature vs. $D \times P$ on a log-log graph for CCl_4	44
Figure 6.6	Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 313.15 K for toluene	45
Figure 6.7	Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 313.15K for Benzene	47

LIST OF SYMBOLS

dx_A/dz	Concentration gradient per unit length
D_{AB}	Diffusion constant of diffusing A with non-diffusing B. (in m^2/sec)
J_{AZ}	Diffusional flux of unit (mole/ m^2 .sec)
N_A	Molar flux of A with respect to a stationary observer, $Kmol/m^2sec$
C	Total concentration of A and B in (moles/ m^3)
X_a	Mole fraction of A in concentration of A and B.
ρ_A	Density of substance A (Kg/m^3)
x	Final height from top end of the tube after time Θ .(in cm or mm)
x_0	Initial height from top end of the tube.(in cm or mm)
$x-x_0$	Drop in liquid level in time Θ (in cm or mm)
R	Gas law constant = $8314 m^3Pa/Kg mole-K$ $= 82.057 \times 10^{-3} m^3-atm/Kg mole-K$ $= 82.057 cm^3-atm/Kg mole-K$
T	Operating temperature (in $^{\circ}C$ or K)
M_A	Molecular weight of diffusing substance (in g/g mol)
M_B	Molecular weight of non-diffusing substance (in g/g mol)
P	Total pressure (in atm, Pa)
P_{BM}	Log mean partial pressure of inert component (B, air) (in atm, Pa)
P_{A1}	Partial pressure of the diffusing component A at the liquid-air interface. (position 1) (atm)

P_{A2}	Partial pressure of the diffusing component A in air at the vapor-air interface. (position 2 i.e. top of the tube)
C_A	Molar concentration of A. (k mole/m ³)
C_B	Molar concentration of B. (k mole/m ³)
C_T	Total molar concentration. (k mole/m ³)
C_{BM}	Log mean concentration of B (k mole/m ³)
Θ	Time of evaporation. (in sec.)
δ	Thickness of a stagnant film, (in m or cm.)
P_{AS}	Partial pressure of the substance at surface (atm)
$P_{A\infty}$	Partial pressure of the substance at the bulk (atm)
Z	Distance in the direction of diffusion (in m or cm)
V	Molar volume, (cm ³ /g mol)
M	Molecular weight, (g/g mol)
r_s	Radius of the sphere. (m or cm)

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Mass transfer can either be diffusional or convective. If, there is no external mechanical disturbance then mass transfer occurs due to diffusion mechanism. However, when there is a macroscopic disturbance in the medium, which on the other hand greatly influences the rate of mass transfer, it becomes a convective transport. Thus, the stronger the flow field, creating more mixing and turbulence in the medium, the higher is rate of mass transfer. The concept of molecular diffusion is very important and is widely used in variety of scientific and engineering applications. Whenever there is transport of any gas/liquid/solid molecules occur through a stagnant zone characterized by a laminar flow regime, the importance of molecular diffusion is more evident. Even, when there is a turbulent motion sets into the process, there always remains a laminar zone close to the phase boundary largely influencing the flow mechanism.

Transport in a porous medium is a classical example where molecular diffusion takes place. A typical example is the diffusion of reactants and products in a porous catalyst pellet. Besides normal pore diffusion, Knudsen and surface diffusion as well plays an important role in determining the performance of a catalyst. To be precise, study of molecular diffusion is the fundamental basis to the study of mass transfer in general. Mass transfer is the basis of many chemical and biological processes. Chemical process involve chemical vapour deposition (CVD) of silane (SiH_4) onto a silicon wafer (the doping of silicon wafer lead to the formation of a silicon thin film), the aeration of waste water leading to its purification, the purification of ores and isotopes etc. The biological systems include oxygenation of blood stream and the transport of ions across membrane within the kidney etc.

It is important to highlight the fact that any industrial mass transfer operation involves multi-component system; however, suitable binary system data can be effectively used to estimate the multi-component system. Similarly, for any unit operation involving more than a single-phase (and hence presence of an interphase), it is the local or overall mass transfer coefficient which explains the mass transfer operation prevailing within the system and can be effectively. measured in wetted wall column experiments. However, suitably measured

diffusivity data can easily be used in estimating the mass transfer coefficients using fundamental concepts of various predictive theories like (film, penetration, surface renewal and boundary layer).

1.2 Objective

In this project work, emphasis has been stressed upon to measure the binary diffusion coefficients of some important organic solvents and solids with varying geometries.

In case of organic solvents acetone, benzene, carbon tetrachloride and toluene are chosen to be studied. It is a case of diffusion of A (organic solvent) through stagnant non-diffusing B (air). The experiments are planned to be carried out at widely different temperatures ranging from 25 to 60°C and at atmospheric pressure, using Stefan tube experiment.

Diffusion coefficients of solids (in air) with varying geometries are also planned to be studied. Naphthalene balls are selected for studying the diffusion phenomenon in spherical geometry and Camphor pellets are chosen for studying the diffusion phenomenon in cylindrical geometry.

1.3 Chapter layout

Chapter 2 is highlighted on the literature review which includes the principle and study of diffusion and also describes about the laws of diffusion.

Chapter 3 describes about the theories for diffusion of solid materials and liquid solvents through air and also different data for diffusivities of solids, liquids, and gases also listed.

Chapter 4 is enlighten on the experimental set-ups such as water-bath, stirrer, Stefan tube, diffusion pump etc.

Chapter 5 is about the experimental diffusion of solids of different geometries such as spherical naphthalene ball and cylindrical camphor in air and to find out their binary molecular diffusivities.

Chapter 6 is about the experimental diffusion of different organic liquids (Acetone, CCl₄, Toluene and Benzene) in air and to find out their molecular diffusivities varying with temperature

Chapter 7 is highlighted on the conclusion and future scopes.

CHAPTER 2

LITERATURE REVIEW

2.1 Principles of diffusion

Diffusion is the movement of individual components under the influence of a physical stimulus through a mixture. The most common cause of diffusion is a concentration gradient of the diffusing component. A concentration gradient tends to move the component to the component in such a direction as to equalize concentrations and destroy the gradient. When the gradient is maintained by constantly supplying the diffusing component to the high-concentration end of the gradient and removing it at the low-concentration end, there is a steady-state flux of the diffusing component. This is the characteristic of many mass transfer operations.

For example, when you spray a perfume in a room, the smell of the perfume spread further and further and one can smell the perfume in other side. This is nothing but the concept of the diffusion. The molecules of the perfume when comes in contact with air and forms a concentration gradient and the components of perfume is tend to move from higher concentration to the lower concentration and in this way the molecules of the perfume is being spread and the smell of the perfume can go further and further.

2.2 Theory of diffusion

Molecular diffusion is the thermal motion of liquid or gas particles at temperature above absolute zero. The rate of this movement is a function of temperature viscosity of the fluid and the mass or size of the particle. Diffusion explains the net flux of a molecule from a region of higher concentration to one of lower concentration.

Molecular diffusion or molecular transport can be defined as the transfer or movement of individual molecules through a fluid by means of the random individual movement of molecules. Molecular diffusion is typically described mathematically using Fick's laws of diffusion.

2.2.1 Fick's law of diffusion

Fick's law is only meant for binary diffusion and steady state flow. Fick's laws of diffusion describe diffusion and can be used to solve for the diffusion coefficient, D . They were derived by Adolf Fick in the year 1855.

2.2.1.1 Fick's first law of diffusion

Fick's first law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient. Here only molecules are moving whole bulk of molecules is not in motion.

Hence for this system Fick's law can be defined as

$$J_{AZ} = -CD_{AB} \left(\frac{dx_A}{dz} \right) \text{-----} 2.1$$

Where. dx_A/dz is the concentration gradient per unit length and

D_{AB} is the diffusion constant.

J_{AZ} diffusional flux of unit (mole/m².sec)

C is the total concentration of A and B in (moles/m³)

x_A is mole fraction of A in concentration of A and B.

The negative sign indicates that the diffusion occurs in the direction where there is drop in concentration.

2.2.1.2 Fick's second law of diffusion

Fick's second law predicts how diffusion causes the concentration to change with time. When unsteady state diffusion takes place in one direction in a solid or stagnant fluid, the governing differential equation is called Fick's second law of diffusion.

$$\frac{dC_A}{dt} = D_{AB} \left(\frac{d^2 C_A}{dx^2} \right) \text{-----} 2.2$$

2.3 Types of diffusion

Diffusion is a widespread and important process which occurs in both living and non-living systems. Because diffusion occurs under a variety of conditions, scientists have adopted followings to specify particular types of diffusion:

- (A) Simple diffusion: it refers to diffusion of substances without the help of transport proteins.
- (B) Facilitated diffusion: it refers to diffusion of substances across a cell membrane with the help of transport proteins.
- (C) Dialysis: It refers to the diffusion of solid across a selectively permeable membrane. Selectively permeable membrane is a membrane that some substances pass through easily while other substances pass through very slowly or not at all.
- (D) Osmosis: It refers to the diffusion of the solvent across a selectively permeable membrane. Because water is solvent in all living systems, biologists usually define osmosis as the diffusion of water across a selectively permeable membrane.

Although various types of diffusion have been recognized, all shares following characteristics:

- (i) Net movement of each substance is caused by random molecular motion.
- (ii) Net movement of each substance involves passive transport.
- (iii) Net movement of each substance is down its own concentration gradient.
- (iv) At equilibrium, random molecular motion continues but there is no longer any net movement.

CHAPTER 3

Diffusion in fluids and Solids

3.1. Steady State Diffusion

In this section, steady-state molecular mass transfer through simple systems in which the concentration and molar flux are functions of a single space coordinate will be considered. In a binary system, containing A and B, this molar flux in the direction of z, is given by:

$$N_A = -CD_{AB} \frac{dY_A}{dz} + Y_A (N_A + N_B) \text{ -----3.1}$$

3.1.1 Diffusion through a stagnant gas film

The diffusivity or diffusion coefficient for a gas can be measured, experimentally using Arnold diffusion cell. This cell is illustrated schematically in figure. The narrow tube of uniform cross section which is partially filled with pure liquid A, is maintained at a constant temperature and pressure. Gas B which flows across the open end of the tub, has a negligible solubility in liquid A, and is also chemically inert to A. (i.e. no reaction between A & B). Component A vaporizes and diffuses into the gas phase; the rate of vaporization may be physically measured and may also be mathematically expressed in terms of the molar flux.

Consider the control volume $S \Delta z$, where S is the cross sectional area of the tube. Mass balance on 'A' over this control volume for a steady-state operation yields

[Moles of A leaving at $z + \Delta z$] – [Moles of A entering at z] = 0. i.e.,

$$S N_A|_{z+\Delta z} - S N_A|_z = 0 \text{ ----- 3.2}$$

Dividing through by the volume, $S\Delta z$, and evaluating in the limit as Δz approaches zero, we obtain the differential equation;

$$\frac{dN_A}{dz} = 0$$

This relation stipulates a constant molar flux of A throughout the gas phase from Z_1 to Z_2 . A similar differential equation could also be written for component B as;

$$\frac{dN_B}{dz} = 0$$

And accordingly, the molar flux of B is also constant over the entire diffusion path from z_1 and z_2 .

Considering only at plane z_1 , and since the gas B is insoluble in liquid A, we realize that N_B , the net flux of B, is zero throughout the diffusion path; accordingly B is a stagnant gas.

From equation (3.1)

$$N_A = -CD_{AB} \frac{dY_A}{dz} + Y_A (N_A + N_B)$$

Since $N_B = 0$

$$N_A = -CD_{AB} \frac{dY_A}{dz} + Y_A N_A$$

By rearranging

$$N_A = -CD_{AB} \left(\frac{1}{1-Y_A} \right) \frac{dY_A}{dz} \quad \text{-----3.3}$$

This equation may be integrated between the two boundary conditions:

$$\text{At } z = z_1 \quad Y_A = Y_{A1} \quad \text{and} \quad \text{at } z = z_2 \quad Y_A = Y_{A2}$$

Assuming the diffusivity is to be independent of concentration, and realizing that N_A is constant along the diffusion path, by integrating equation (ii) we obtain

$$N_A \int_{z_1}^{z_2} dz = CD_{AB} \int_{Y_{A1}}^{Y_{A2}} \frac{-dY_A}{1-Y_A}$$

$$N_A = \frac{CD_{AB}}{z_2 - z_1} \ln \left(\frac{1-Y_{A2}}{1-Y_{A1}} \right) \quad \text{----- 3.4}$$

The log mean average concentration of component B is defined as

$$Y_{B,lm} = \frac{Y_{B2} - Y_{B1}}{\ln\left(\frac{Y_{B2}}{Y_{B1}}\right)}$$

Since, $Y_B = 1 - Y_A$

$$Y_{B,lm} = \frac{(1 - Y_{A2}) - (1 - Y_{A1})}{\ln\left(\frac{Y_{A2}}{Y_{A1}}\right)} = \frac{Y_{A1} - Y_{A2}}{\ln\left(\frac{Y_{A2}}{Y_{A1}}\right)} \quad \text{----- 3.5}$$

Substituting from Equation (3.5) in Equation (3.4),

$$N_A = \frac{CD_{AB}}{Z_2 - Z_1} \frac{(Y_{A1} - Y_{A2})}{Y_{B,lm}} \quad \text{----- 3.6}$$

For an ideal gas $C = \frac{n}{V} = \frac{p}{RT}$ and

For mixture of ideal gases $Y_A = \frac{P_A}{P}$

Therefore, for an ideal gas mixture equation. (3.6) Becomes

$$N_A = \frac{D_{AB}}{RT(Z_2 - Z_1)} \frac{(P_{A1} - P_{A2})}{P_{B,lm}} \quad \text{----- 3.7}$$

This is the equation of molar flux for steady state diffusion of one gas through a second stagnant gas.

Where

D_{AB} = molecular diffusivity of A in B

R = universal gas constant

T = temperature of system in absolute scale

z = distance between two planes across the direction of diffusion

P_{A1} = partial pressure of A at plane 1, and

P_{A2} = partial pressure of A at plane 2

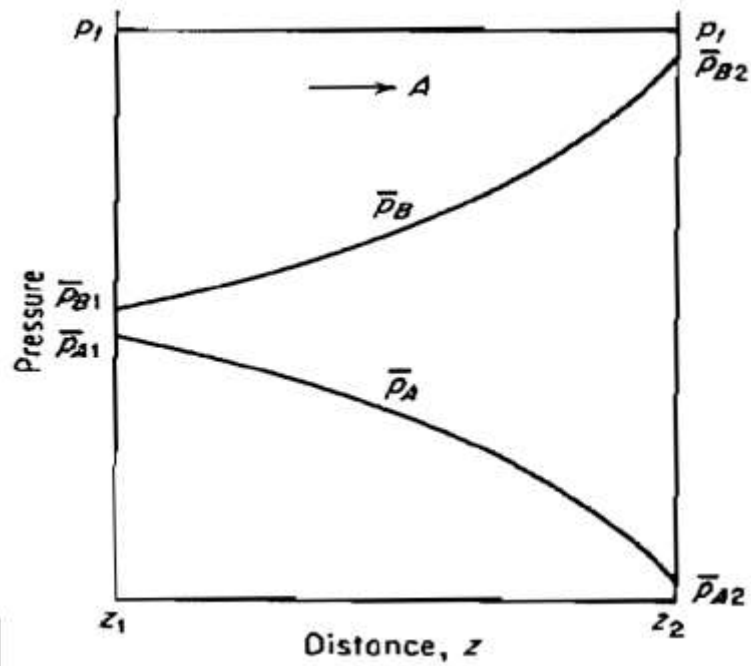


Fig 3.1: Diffusion of A through stagnant B. [3]

3.1.2 Pseudo steady state diffusion through a stagnant film

In many mass transfer operations, one of the boundaries may move with time. If the length of the diffusion path changes a small amount over a long period of time, a pseudo steady state diffusion model may be used. When this condition exists, the equation of steady state diffusion through stagnant gas' can be used to find the flux.

If the difference in the level of liquid A over the time interval considered is only a small fraction of the total diffusion path, and $(t_0 - t)$ is relatively long period of time,

At any given instant in that period, the molar flux in the gas phase may be evaluated by;

$$N_A = \frac{CD_{AB}(Y_{A1} - Y_{A2})}{ZY_{B,lm}} \quad \text{-----} \quad 3.8$$

Where $z = z_2 - z_1$, the length of the diffusion path at time t .

The molar flux N_A is related to the amount of A leaving the liquid by

$$N_A = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt} \quad \text{-----} \quad 3.9$$

Where $\left(\frac{\rho_{A,L}}{M_A}\right)$ is the molar density of A in the liquid phase

Under pseudo steady state conditions, equations (3.8) & (3.9) can be equated to give

$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{CD_{AB}(Y_{A1}-Y_{A2})}{ZY_{B,lm}} \text{-----} 3.10$$

Equation (3.10) may be integrated from $t = 0$ to t and from $z = z_{t0}$ to $z = z_t$ as:

$$\int_{t=0}^t dt = \frac{\rho_{A,L}Y_{B,lm}}{M_A CD_{AB}(Y_{A1} - Y_{A2})} \int_{z_{t0}}^{z_t} z dz$$

Yielding

$$t = \frac{\rho_{A,L}Y_{B,lm}}{M_A CD_{AB}(Y_{A1} - Y_{A2})} \left(\frac{z_t^2 - z_{t0}^2}{2} \right) \text{-----} 3.11$$

This shall be rearranged to evaluate diffusivity D_{AB} as,

$$D_{AB} = \frac{\rho_{A,L}Y_{B,lm}}{M_A C(Y_{A1} - Y_{A2})t} \left(\frac{z_t^2 - z_{t0}^2}{2} \right) \text{-----} 3.12$$

3.1.3 Equimolar counter diffusion

A physical situation which is encountered in the distillation of two constituents If no bulk flow occurs in an element of length dx whose molar latent heats of vaporization are essentially equal, stipulates that the flux of one gaseous component is equal to but acting in the opposite direction from the other gaseous component; that is, $N_A = - N_B$.

The molar flux N_A , for a binary system at constant temperature and pressure is described by

$$N_A = - D_{AB} \frac{dC_A}{dz} + Y_A (N_A + N_B) \text{-----} 3.13$$

With the substitution of $N_B = -N_A$, Equation (1) becomes,

$$N_A = - D_{AB} \frac{dC_A}{dz} \text{-----} 3.14$$

For steady state diffusion Equation. (2) may be integrated, using the boundary conditions:

At $z = z_1$: $C_A = C_{A1}$ and $z = z_2$: $C_A = C_{A2}$

Giving,

$$N_A \int_{z_1}^{z_2} dz = -D_{AB} \int_{C_{A1}}^{C_{A2}} dC_A$$

From which

$$N_A = -\frac{D_{AB}}{z_2 - z_1} (C_{A1} - C_{A2}) \text{-----} 3.15$$

For ideal gases, $C_A = \frac{n_A}{V} = \frac{P_A}{RT}$.

Therefore equation (3.14) becomes:

$$N_A = -\frac{D_{AB}}{RT(z_2 - z_1)} (P_{A1} - P_{A2}) \text{-----} 3.16$$

This is the equation of molar flux for steady-state equimolar counter diffusion.

Concentration profile in this equimolar counter diffusion may be obtained from,

$$\frac{d}{dz} (N_A) = 0 \text{ (Since } N_A \text{ is constant over the diffusion path)}$$

And from equation (3.14)

$$N_A = -D_{AB} \frac{dC_A}{dz}$$

Therefore

$$\frac{d}{dz} \left(-D_{AB} \frac{dC_A}{dz} \right) = 0 \Rightarrow \frac{d^2 C_A}{dz^2} = 0$$

This equation may be solved using the boundary conditions to give

$$\frac{C_A - C_{A1}}{C_A - C_{A2}} = \frac{z - z_1}{z_1 - z_2} \text{-----} 3.17$$

Equation (3.17) indicates a linear concentration profile for equimolar counter diffusion.

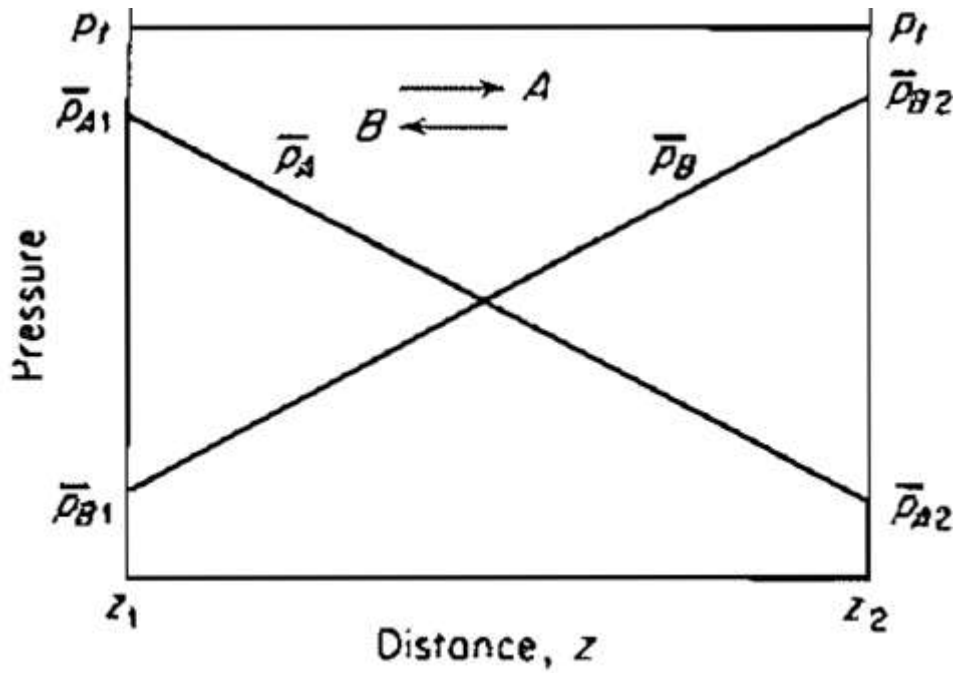


Fig 3.2: Equimolar counter diffusion. [3]

3.2 Diffusivity of gases

The diffusivity or diffusion coefficient, D is a property of the system dependent upon temperature, pressure and nature of the components. An advanced kinetic theory predicts that in binary mixtures there will be only a small effect of composition. The dimensions of diffusivity can be established as $\text{length}^2/\text{time}$ and the SI dimensions are m^2/sec .

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{p} \quad (\text{For moderate ranges of pressures, up to 25 atm})$$

And temperature dependency is according to

$$D_{AB} \propto T^{\frac{3}{2}}$$

3.2.1 Gilliland's correlation for estimating the diffusivity of gases

$$D = \frac{0.0043 \sqrt{T^3 \left[\frac{1}{M_A} + \frac{1}{M_B} \right]}}{P \left(V_A^{1/3} + V_B^{1/3} \right)^2} \quad \text{----- 3.17}$$

Where,

V_A, V_B = Molar volume of A and B, $\text{cm}^3/\text{g mol}$.

M = molecular weight, g/g mol .

T = Temperature in K

P = Ambient pressure, atm.

D = diffusivity in cm^2/sec .

Table 3.1: Diffusivity of gases at standard atmospheric pressure.[3]

System	temperature($^{\circ}\text{C}$)	Diffusivity ($\text{m}^2/\text{s} \times 10^5$)
$\text{H}_2\text{-CH}_4$	0	6.25
$\text{O}_2\text{-N}_2$	0	1.81
CO-O_2	0	1.85
$\text{CO}_2\text{-O}_2$	0	1.39
Air- NH_3	0	1.98
Air- H_2O	25.9	2.58
	59.0	3.05
Air-ethanol	0	1.02
Air-n-butanol	25.9	0.87
	59.0	1.04
Air-ethyl acetate	25.9	0.87
	59.0	1.06
Air-aniline	25.9	0.74
	59.0	0.90
Air-toluene	25.9	0.86
	59.0	0.92

3.3 Diffusivity in liquids

Diffusivity in liquid are exemplified by the values, most of these are nearer to 10^{-5} cm²/sec, and about ten thousand times slower than those in dilute gases. This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids such as reaction between two components in liquids. In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction.

Diffusion in liquids is important because it is slow. Certain molecules diffuse as molecules, while others which are designated as electrolytes ionize in solutions and diffuse as ions. For example, sodium chloride (NaCl), diffuses in water as ions Na⁺ and Cl⁻. Though each ion has a different mobility, the electrical neutrality of the solution indicates the ions must diffuse at the same rate; accordingly it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl. However, if several ions are present, the diffusion rates of the individual cations and anions must be considered, and molecular diffusion coefficients have no meaning. Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five. In extremely high viscosity materials, diffusion becomes independent of viscosity.

Table 3.2: Liquid diffusivities.[3]

Solute	solvent	Concentration	D, m ² s ⁻¹
HCl	Water	0.1 M	3.05×10^{-9}
NaCl	Water	0.1M	1.48×10^{-9}
CaCl ₂	Water	0.1M	1.10×10^{-9}
H ₂	Water	Dilute	5.0×10^{-9}
O ₂	Water	Dilute	2.5×10^{-9}
H ₂ SO ₄	Water	Dilute	1.97×10^{-9}
Na ₂ SO ₄	Water	Dilute	1.12×10^{-9}
K ₄ Fe(CN) ₆	Water	0.01M	1.18×10^{-9}
Ethanol	Water	X=0.05	1.13×10^{-9}
Glucose	Water	0.39%	0.67×10^{-9}
Benzene	CCl ₄	Dilute	1.53×10^{-9}
CCl ₄	Benzene	Dilute	2.04×10^{-9}
Br ₂	Benzene	Dilute	2.7×10^{-9}
CCl ₄	Kerosene	Dilute	0.96×10^{-9}

3.4 Diffusion in solids

In certain unit operation of chemical engineering such as in drying or in absorption, mass transfer takes place between a solid and a fluid phase. If the transferred species is distributed uniformly in the solid phase and forms a homogeneous medium, the diffusion of the species in the solid phase is said to be structure independent. In these cases diffusivity or diffusion coefficient is direction independent.

At steady state, and for mass diffusion which is independent of the solid matrix structure, the molar flux in the z direction is:

$$N_A = -D_{AB} \frac{dc_A}{dz} = \text{constant, as given by Fick's law.}$$

$$N_A = \frac{D_{AB}(C_{A1}-C_{A2})}{z}$$

Which is similar to the expression obtained for diffusion in a stagnant fluid with no bulk motion (i.e. $N = 0$).

Typical values for diffusivity in solids are shown in table. One outstanding characteristic of these values is their small size, usually thousands of times less than those in a liquid, which are in turn 10,000 times less than those in a gas.

Diffusion plays a major role in catalysis and is important to the chemical engineer. For metallurgists, diffusion of atoms within the solids is of more importance.

Table 3.3: Diffusivity of some solid materials.[3]

Diffusing ion	Crystal in which diffusion takes place	$D_0(\text{m}^2\text{sec}^{-1})$	$Q(\text{J mol}^{-1})$
Ag^+	$\alpha\text{-Cu}_2\text{S}$	38×10^{-9}	19100
Cu^+	$\alpha\text{-Ag}_2\text{S}$	12×10^{-9}	13300
Ag^+	$\alpha\text{-Cu}_2\text{Te}$	2.4×10^{-9}	87300
Cu^+	$\alpha\text{-AgI}$	16×10^{-9}	9420
Li^+	$\alpha\text{-AgI}$	50×10^{-9}	19100
Se^{2-}	$\alpha\text{-Ag}_2\text{S}$	17×10^{-9}	83850
Pb^{2+}	PbCl_2	7.8×10^{-4}	150000
Pb^{2+}	PbI_2	10.6×10^{-4}	126000
O^{2-}	Fe_2O_3	1×10^{-7}	611000
Fe^{3+}	Fe_2O_3	4×10^{-1}	469000
Co^{2+}	CoO	2.15×10^{-7}	144000
Ni^{2+}	NiO	1.83×10^{-7}	192000

CHAPTER 4

Diffusion setups

4.1 Introduction

Diffusion setup consists of glass Stefan T-tube, constant temperature water bath, air pump, Stirrer, heater, air blower, temperature sensor device for measuring temperature, diffusing cylinder for diffusing solid materials, Rota meter for measuring variable pressure, bench area for fixing whole diffusion set-up, pipe which is connect to T-tube for flowing air in which one end of pipe is connected to air blower.



Fig 4.1: A typical diffusion system

4.2 Stefan tube

The Stefan tube is a simple device used for measuring diffusion coefficients in binary vapors. At the bottom of the tube is a pool of mixture. The vapor that evaporates from this pool diffuses to the top of the tube, where a stream of air, flowing across the top of the tube, keeps the mole fraction of diffusing vapor there to be zero. The mole fraction of vapor above the liquid interface is at equilibrium. Because there is no horizontal flux inside the tube, one can analyze the problem using a 1 Dimensional model. The system composition of acetone, methanol, and air has been extensively investigated.

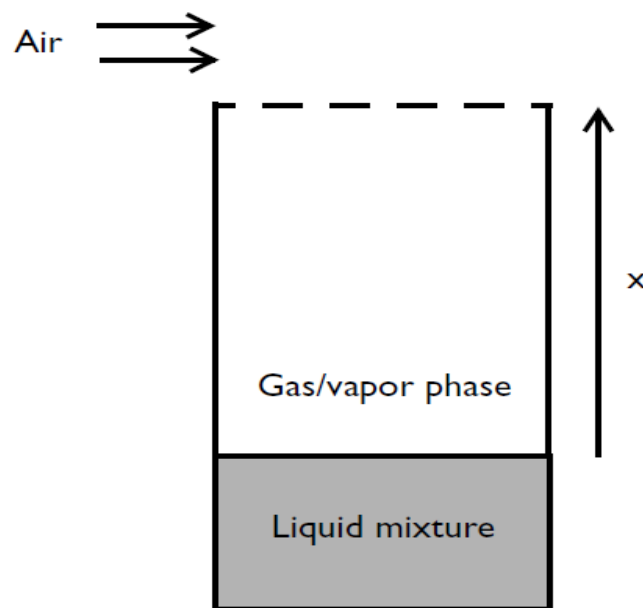


Fig 4.2: Schematic diagram of a Stefan tube

In the method of diffusion, the Stefan tube under which the set of experiments occur, one of the components assuming 'A' is available as a volatile liquid and other component 'B' is a gas which is insoluble in 'A'. Stefan tube consists of a vertical glass tube sealed at the bottom is joined to a larger diameter horizontal tube to form a 'T shaped structure.'

The liquid 'A' is taken in the narrow vertical tube and the gas 'B' is ejected to the horizontal tube. Evaporated 'A' diffused through mixture of 'A' and 'B' in the vertical tube, flow towards the top and swept away by the flowing stream of 'B'. As 'B' is not soluble in 'A', it will not diffuse and

the statement is confirmed to be “Diffusion of ‘A’ through non-diffusing ‘B’. The liquid tube level will gradually drop slowly and pseudo-steady state assumption is reached.

4.3 Constant temperature water bath

A water bath is a device that maintains water at a constant temperature. It is used in the microbiological laboratory for incubations also used in a diffusion setup to heat the tube.

At the beginning of the experiment, one should check the water bath to see if it is turned on, then set at the right temperature, and filled with water. Water baths should be filled with distilled water. If someone using the water bath for an experiment then the temperature is to be checked frequently to make sure that the water bath is maintaining the proper temperature.

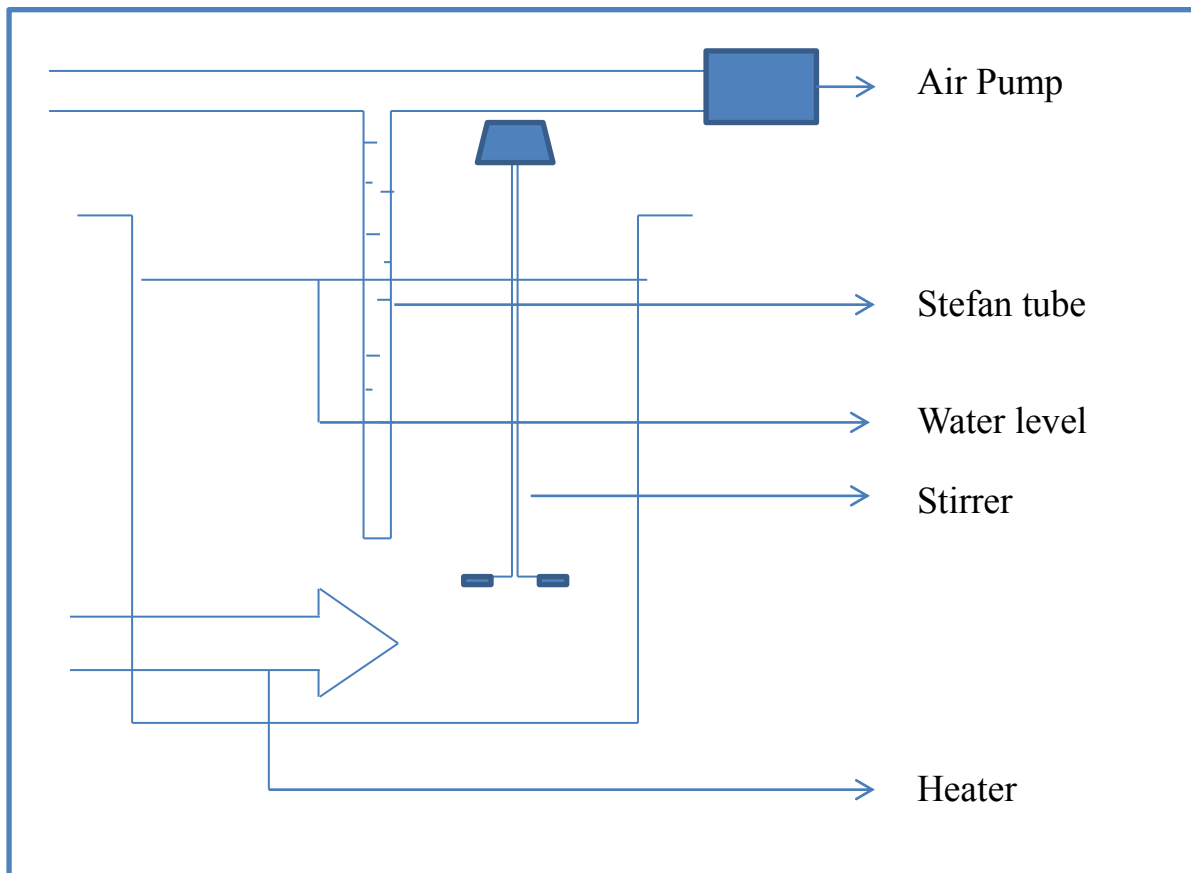


Fig 4.3: Schematic diagram of water bath.

4.3.1 Temperature Control

All water baths have a control to set temperature. This control can be digital or a dial. Often there is an indicator light associated with this control. When the light is on the water bath is heating. When the water bath reaches the set temperature, it will cycle on and off to maintain constant temperature.

4.3.2 Safety Control

Most water baths have a second control called the safety. This control is set at the maximum temperature the water bath should attain. It is usually set just above the temperature control. Often an indicator light is associated with the safety control. If the water bath reaches the temperature that the safety control is set at, the light will go on. It will be impossible for the water bath to heat higher than the safety setting even when the temperature setting is higher. If your water bath stays a temperature lower than the temperature control setting, try increasing the safety control setting.

4.4 Stirrer

A stirrer is a laboratory device that employs a rotating rod to cause a stir bar submerged in a liquid to spin very quickly. The rotating field may be created either by a motor or a set of stationary electromagnets, placed in the vessel with the liquid. Since glass does not affect a magnetic field affectively , and most chemical reactions take place in glass vessels such as beaker (glassware) or laboratory flasks, magnetic stir bars work well in glass vessels. They also have difficulty dealing with viscous liquids or thick suspensions. For larger volumes or more viscous liquids, some sort of mechanical stirring is typically needed.

The stirrers are distinguished according to the type of flow they generate in the stirred material, the speed-depending applications and the various designs for different viscosities. Stirrers are often used in chemistry and biology. They are preferred over gear-driven motorized stirrers because they are quieter, more efficient, and have no moving external parts to break or wear out. Because of its small size, a stirring bar is more easily cleaned and sterilized than other stirring devices. They do not require lubricants which could contaminate the reaction vessel and the product. They can be used inside tightly closed vessels or systems, without the need for complicated rotary seals.

4.4 Diffusion pumps

Diffusion pumps use a high speed jet of vapor to direct gas molecules in the pump throat down into the bottom of the pump and out the exhaust. Invented in 1915 by Wolfgang Gaede using mercury vapor, and improved by Irving Langmuir and W. Crawford, they were the first type of high vacuum pumps operating in the regime of free molecular flow, where the movement of the gas molecules can be better understood as diffusion than by conventional fluid dynamics. Gaede used the name diffusion pump since his design was based on the finding that gas cannot diffuse against the vapor stream, but will be carried with it to the exhaust. However, the principle of operation might be more precisely described as gas-jet pump, since diffusion plays a role also in other high vacuum pumps. An air pump is a device for pushing air.

CHAPTER 5

Solids of different geometries diffused in Air

5.1 Objective

To study the diffusion of spherical naphthalene ball and cylindrical camphor in air and to determine their diffusivities.

5.2 Experimental procedure

Diameter and weight of the naphthalene ball is measured before putting in the diffusing cylinder. The flow rate of the Rota meter at the rate 30 lpm is set after putting naphthalene ball in diffusing cylinder. The setup is leave for 30 minutes and the weight and diameter of the naphthalene balls were measured.



Fig 5.1: Diffusion set-up for solid geometries.

5.3 Theory

5.3.1 Diffusion in spherical geometry

In case of diffusion in spherical geometry let us consider an evaporating drop that has radius ' r_s ' at any instant ' t '. Imagine a thin spherical shell of inner radius ' r ' and thickness Δr around the drop. This is a binary system involving diffusion of molecule 'A' through air 'B'. Then,

Rate of input of A into the thin shell (at $r = r$) : $(4\pi r^2)N_{A|r}$

Rate of output of A from the thin shell (at $r = r + \Delta r$) : $(4\pi r^2)N_{A|r+\Delta r}$

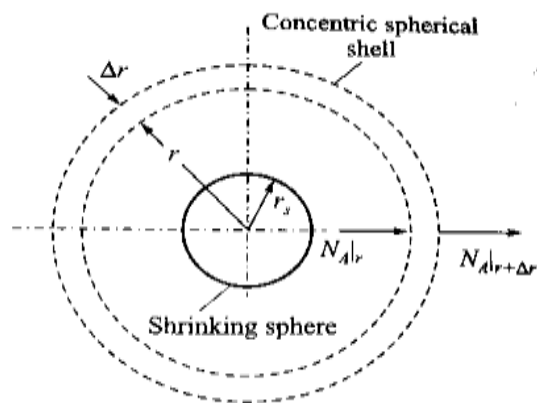


Fig 5.2 A sketch indicating shell balance for mass transfer from a sphere

The notation $|_r$ means that the quantity is evaluated at the position r .

The rate of accumulation = 0

By a steady state mass balance,

$$\text{Input} - \text{output} = \text{accumulation}$$

$$(4\pi r^2)N_{A|r} - (4\pi r^2)N_{A|r+\Delta r} = 0$$

Dividing both sides by Δr and taking the limit $\Delta r \rightarrow 0$,

$$\lim_{\Delta r \rightarrow 0} \frac{(4\pi r^2)N_{A|r} - (4\pi r^2)N_{A|r+\Delta r}}{\Delta r} = 0$$

$$\Rightarrow -\frac{d}{dr}(4\pi r^2 N_A) = 0$$

$$\Rightarrow 4\pi r^2 N_A = \text{constant} = W \text{ (say)} \text{-----} 5.1$$

Equation 5.1 is a very important result for steady state diffusion through a variable area and can be generalized as

$$\text{(Area)(Flux)} = \text{Constant} \text{-----} 5.2$$

In this case molecule A diffuses, but air does not diffuse because it is not soluble in the molecule. So, the case corresponds to diffusion of A through non diffusing B. Since diffusion occurs in radial condition, we get

$$N_A = (N_A + N_B) \frac{P_A}{P} - \frac{D_{AB}}{RT} \frac{dP_A}{dr}$$

Putting $N_B = 0$ and rearranging,

$$N_A = -\frac{D_{AB}P}{RT(P-P_A)} \frac{dP_A}{dr} \text{-----} 5.3$$

From equation 5.1 and 5.3,

$$-\frac{dP_A}{P-P_A} = \frac{WRT}{4\pi D_{AB}P} \frac{dr}{r^2} \text{-----} 5.4$$

Equation 5.4 can be integrated from $r = r_s$ (i.e. the surface of the molecule) to $r = \infty$ (i.e. far away from the drop) where $P_A = P_{A\infty}$

Here P_{As} is the vapour pressure of the molecule at the temperature of the surface and $P_{A\infty}$ is the partial pressure of the molecule in the bulk air.

$$-\int_{P_{As}}^{P_{A\infty}} \frac{dP_A}{P-P_A} = \frac{WRT}{4\pi D_{AB}P} \int_{r_s}^{\infty} \frac{dr}{r^2}$$

$$\Rightarrow \ln \frac{P - P_{A\infty}}{P - P_{As}} = \frac{WRT}{4\pi D_{AB}P} \frac{1}{r_s}$$

$$\Rightarrow W = \frac{4\pi D_{AB}P r_s}{RT} \ln \frac{P - P_{A\infty}}{P - P_{As}} \text{-----} 5.5$$

Since W is the constant molar rate of mass transfer, it is equal to the rate of vaporization of the molecule at any instant.

This rate can be related to the change in the molecule radius by the following equation.

$$W = -\frac{d}{dt} \left(\frac{4}{3} \pi r_s^3 \frac{\rho_A}{M_A} \right) = -4\pi \frac{\rho_A}{M_A} r_s^2 \frac{dr_s}{dt} \text{-----5.6}$$

The negative sign is incorporated because the size of the molecule decreases with time. Equating equations 5.5 and 5.6,

$$-4\pi \frac{\rho_A}{M_A} r_s^2 \frac{dr_s}{dt} = \frac{4\pi D_{AB} P r_s}{RT} \ln \frac{P - P_{A\infty}}{P - P_{As}}$$

Here again we have made use of the ‘pseudo-steady state’ assumption, that the molecule size changes so slowly that the diffusion of the substance through the surrounding air occurs virtually at steady state all time. The change in the molecule size over considerable period of time can be determined by integrating the above equation.

If at time $t = 0$, the radius of the molecule is r_{s0} and at time t it is r_s . Then,

$$\begin{aligned} -\int_{r_{s0}}^{r_s} r_s dr_s &= \frac{D_{AB} P M_A}{RT \rho_A} \ln \frac{P - P_{A\infty}}{P - P_{As}} \int_0^t dt \\ \Rightarrow r_{s0}^2 - r_s^2 &= \frac{2D_{AB} P M_A t}{RT \rho_A} \ln \frac{P - P_{A\infty}}{P - P_{As}} \text{-----5.7} \end{aligned}$$

Hence diffusivity of the molecule in the spherical geometry is calculated as

$$D_{AB} = \frac{RT \rho_A (r_{s0}^2 - r_s^2)}{2t P M_A \ln \left(\frac{P - P_{A\infty}}{P - P_{As}} \right)} \text{-----5.8}$$

5.3.2 Diffusion in cylindrical geometry

This is the case of diffusion of A (cylindrical substance) through non-diffusing B (air) through a variable area. Taking the help of equation 5.2 and 5.3, we may write

$$(2\pi rL)N_A = (2\pi rL) \left(-\frac{D_{AB} P}{RT(P - P_A)} \right) \frac{dP_A}{dr} = W \text{ (Constant) ----- 5.9}$$

L = length of the cylinder

Here r is the radial distance of any point within surrounding air film from the axis of the cylinder.

W is the molar rate of sublimation

Distance r varies from radius of the cylinder (r_c) to the outer edge of the air-film ($r_c + \delta$) where δ is the thickness of the film.

The corresponding values of the partial pressure of cylindrical substance are,

At $r = r_c$, $P_A = P_{As}$ (sublimation pressure)

At $r = r_c + \delta$, $P_A = 0$, as there is no molecules of the substance in bulk air.

To calculate the rate of sublimation, we have to integrate the equation 5.9.

$$\begin{aligned}
 - \int_{P_{As}}^0 \frac{dP_A}{P - P_A} &= \frac{WRT}{2\pi D_{AB}PL} \int_{r_c}^{r_c + \delta} \frac{dr}{r} \\
 \Rightarrow W &= \frac{2\pi D_{AB}PL \ln\left(\frac{P}{P - P_{As}}\right)}{RT \ln\left(1 + \frac{\delta}{r_c}\right)} \dots\dots\dots 5.10
 \end{aligned}$$

In order to calculate the required time of sublimation, we make the usual pseudo-steady state approximation.

If at any time t the mass of the cylinder, $m = \pi r_c^2 L \rho_A$

Then the rate of sublimation neglecting the end losses can be expressed as

$$W = - \frac{d(m/M_A)}{dt} = - \frac{d}{dt} \left(\frac{\pi r_c^2 L \rho_A}{M_A} \right) = - 2\pi L \left(\frac{\rho_A}{M_A} \right) r_c \frac{dr_c}{dt} \dots\dots\dots 5.11$$

M_A is the molecular weight.

From equations 5.10 and 5.11,

$$\frac{2\pi D_{AB} PL \ln\left(\frac{P}{P-P_{As}}\right)}{RT \ln\left(1 + \frac{\delta}{r_c}\right)} = -2\pi L \left(\frac{\rho_A}{M_A}\right) r_c \frac{dr_c}{dt}$$

By integrating,

$$\begin{aligned} - \int_{r_c^1}^{r_c^2} r_c \ln\left(1 + \frac{\delta}{r_c}\right) dr_c &= \frac{D_{AB} P M_A}{RT \rho_A} \ln\left(\frac{P}{P-P_{As}}\right) \int_0^t dt \\ \Rightarrow \frac{1}{2} r_{c1}^2 \ln\left(1 + \frac{\delta}{r_{c1}}\right) - \frac{1}{2} r_{c2}^2 \ln\left(1 + \frac{\delta}{r_{c2}}\right) + \frac{\delta}{2} \left[(r_{c1} - r_{c2}) - \delta \ln\left(\frac{r_{c1} + \delta}{r_{c2} + \delta}\right) \right] \\ &= \frac{D_{AB} P M_A}{RT \rho_A} \ln\left(\frac{P}{P-P_{As}}\right) t \quad \text{----- 5.12} \end{aligned}$$

Equation 5.22 is the desired equation for finding the diffusivity of cylindrical geometries.

5.4 Observation

Table 5.1: Experimental Data of diffusion of spherical naphthalene ball in air

SL NO.	Diameter of the ball before diffusion (cm)	Diameter of the ball after diffusion (cm)
1	1.90	1.89
2	1.88	1.87
3	1.86	1.855

Table 5.2: Experimental Data of diffusion of cylindrical camphor in air

SL NO.	Diameter of the ball before diffusion (cm)	Diameter of the ball after diffusion (cm)	Height of the ball before diffusion (cm)	Height of the ball before diffusion (cm)
1	1.0	0.88	0.9	0.85
2	0.98	0.85	0.83	0.8
3	1.0	0.9	0.91	0.85

5.5 Calculation

5.5.1 For spherical naphthalene ball ($C_{10}H_8$)

Weight of the bulk of naphthalene ball before sublimation=106.6 gm.

Weight of the bulk of naphthalene ball after sublimation=105.916 gm.

Number of naphthalene ball = 33

Average weight of one ball before diffusion= $\frac{106.6}{33} = 3.23$ gm.

Average weight of one ball after diffusion = $\frac{105.916}{33} = 3.21$ gm.

From the table 5.1 data for naphthalene ball:

The average radius before diffusion = $\frac{1.90+1.88+1.86}{2 \times 3} = 0.94$ cm.

The average radius after diffusion = $\frac{1.89+1.87+1.855}{2 \times 3} = 0.9367$ cm

Time (t) = 30 minutes = (30×60) seconds =1800 seconds.

Density ($\rho_{naphtha}$) = $1.14 \frac{gm}{cm^3}$

Partial pressure of naphthalene ball at surface (P_{AS}) = 0.087 mmHg = 1.145×10^{-4} atm

From equation 5.8 we can calculate D_{AB} value as,

$$D_{AB} = \frac{RT\rho_A (r_{S0}^2 - r_S^2)}{2tPM_A \ln\left\{\frac{P-P_\infty}{P-P_{AS}}\right\}}$$

$$= \frac{0.08206 \times 313.15 \times 1.14 \times (0.94^2 - 0.9367^2)}{2 \times 1800 \times 128 \ln\left\{\frac{1-0}{1-1.145 \times 10^{-4}}\right\}} = 3.438 \times 10^{-3} \text{ cm}^2/\text{sec.}$$

5.5.2 for cylindrical Camphor ($C_{10}H_{16}O$)

Weight of the bulk of camphor before sublimation = 6.61 gm.

Weight of the bulk of camphor after sublimation = 6.108 gm.

Number of camphor = 10

Average weight of one ball before diffusion = $\frac{6.61}{10} = 0.661$ gm.

Average weight of one ball after diffusion = $\frac{6.108}{10} = 0.6108$ gm.

From the table 5.2 data for camphor:

The average radius before diffusion, $r_{C1} = \frac{1+0.98+1}{2 \times 3} = 0.496$ cm.

The average radius after diffusion, $r_{C2} = \frac{0.9+0.85+0.9}{2 \times 3} = 0.442$ cm

The average height before diffusion = $\frac{0.9+0.83+0.91}{3} = 0.88$ cm

The average height after diffusion = $\frac{0.85+0.8+0.85}{3} = 0.83$ cm

Thickness, $\delta = 0.88 - 0.83 = 0.05$ cm

Time (t) = 30 minutes = (30 × 60) seconds = 1800 seconds.

Density ($\rho_{camphor}$) = $0.99 \frac{\text{gm}}{\text{cm}^3}$

Partial pressure of camphor at surface (P_S) = 0.66 mmHg = 8.68×10^{-4} atm

D_{AB} value can be calculated from the equation 5.12

$$D_{AB} = \frac{RT\rho_A}{PtM_A \ln\left(\frac{P}{P-P_{As}}\right)} \left[\frac{1}{2} r_{c1}^2 \ln\left(1 + \frac{\delta}{r_{c1}}\right) - \frac{1}{2} r_{c2}^2 \ln\left(1 + \frac{\delta}{r_{c2}}\right) + \frac{\delta}{2} \left[(r_{c1} - r_{c2}) - \delta \ln\left(\frac{r_{c1} + \delta}{r_{c2} + \delta}\right) \right] \right]$$

$$= 3.8 \times 10^{-3} \text{ cm}^2/\text{sec} = 3.8 \times 10^{-7} \text{ m}^2/\text{sec}$$

5.6 Result

Binary molecular diffusivity of spherical naphthalene ball and cylindrical camphor is calculated and found to be $3.43 \times 10^{-7} \text{ m}^2/\text{sec}$ and $3.8 \times 10^{-7} \text{ m}^2/\text{sec}$.

CHAPTER 6

Organic liquids diffused in air

6.1 Objective

- Determination of the diffusion co-efficient of an organic vapor in air.
- To study the effect of temperature on the diffusion co-efficient.

6.2 Theory

If two gases are inter-diffusing with continual supply of fresh gas and removal of the products of diffusion, this diffusion reaches an equilibrium state with constant concentration gradients. This is known as steady state diffusion. If also there is no total flow in either direction of rates of diffusion of A and B. N_A and N_B are equal but have opposite sign.

According to Dalton's law the total concentration of the two components C_A and C_B is constant.

$$\frac{dC_A}{dx} = - \frac{dC_B}{dx} \text{ ----- 6.1}$$

Then using the integrated form of the Fick Diffusion equation with appropriate constants:

$$N_A = -D_{AB} \frac{dC_A}{dx} \text{ ----- 6.2}$$

$$N_B = -D_{BA} \frac{dC_B}{dx} \text{ ----- 6.3}$$

Where $D_{AB} = D_{BA}$ = Diffusivity coefficient of A/B.

Molar concentration of a perfect gas C_A is related to partial pressure P_A by the gas law:

$$C_A = \frac{P_A}{RT}$$

Then,

$$N_A = \frac{D}{RT} \frac{dP_A}{dx} \text{ ----- 6.4}$$

Integration of equation-7.4 yields,

$$N_A = \frac{D}{RTx} (P_{A1} - P_{A2}) = N_B = \frac{D}{RTx} (P_{B2} - P_{B1}) \text{ ----- 6.5}$$

Where P_{A1} and P_{A2} are the partial pressures of A at the boundaries of the zone of diffusion and x is the distance over which diffusion occurs.

In case where gas A is diffusing through stagnant gas non-diffusing B, the flow carries both components in proportions to their partial pressure $\frac{N_A P_A}{P} + \frac{N_B P_B}{P}$.

The total transfer of A is the sum of this proportion of the flow and the transfer by diffusion.

$$N_A = N_A \frac{P_A}{P} - \frac{D}{RT} \frac{dP_A}{dx} \text{-----} 6.6$$

Or

$$N_A = N_A \left(1 - \frac{P_B}{RT}\right) + \frac{D}{RT} \frac{dP_B}{dx} \text{-----} 6.7$$

Or

$$N_A \int_0^x dx = \frac{DP}{RT} \int_{P_{B1}}^{P_{B2}} \frac{dP_B}{P_B} \text{-----} 6.8$$

And

$$N_A = \frac{DP}{RTx} \ln \frac{P_{B2}}{P_{B1}} \text{-----} 6.9$$

Equation 7.9 is the expression used for the determination of vapour diffusion coefficients in gases by evaporation from a surface of liquid in a thinner bore tube and measuring the level of the falling liquid surface.

The distance of the liquid surface below the open end of the tube is measured before and after evaporation over a particular period of time. If the change in level is small then the arithmetic mean of these two readings is taken as the value of x.

In case there is some change of level, the value of x is determined by integration between the initial and final readings of level.

Thus, the rate of evaporation is given by,

$$N_A = \frac{DP}{RTx} \ln \frac{P_{B2}}{P_{B1}} = \frac{\rho_1 dx}{M d\theta} \text{-----} 6.10$$

Where

M= molecular weight of evaporating liquid

ρ_1 =density of evaporating liquid

Integration of this expression yields:

$$\frac{DP}{RT} \ln \left(\frac{P_{B2}}{P_{B1}} \right) \frac{M}{\rho_1} \int_0^\theta d\theta = \int_{x_1}^{x_2} x dx \quad \text{-----} \quad 6.11$$

$$\frac{DP}{RT} \ln \left(\frac{P_{B2}}{P_{B1}} \right) \frac{M\theta}{\rho_1} = \frac{x_2^2 - x_1^2}{2} \quad \text{-----} \quad 6.12$$

Therefore,

$$D = \frac{RT}{P \ln \left(\frac{P_{B2}}{P_{B1}} \right)} \frac{\rho_1}{M} \frac{x_2^2 - x_1^2}{2\theta} \quad \text{-----} \quad 6.13$$

θ is the time of evaporation.

Other form of equation which is convenient to use is:

$$D_{AB} = \frac{\rho_A (x^2 - x_0^2) R T P_{BM}}{2P (P_{A1} - P_{A2}) M_A \theta} \quad \text{-----} \quad 6.14$$

In terms of concentration terms the expression for D is:

$$x^2 - x_0^2 = \frac{2\theta M_A D_{AB} C_A C_T}{\rho_1 C_{BM}} \quad \text{-----} \quad 6.15$$

$$C_{BM} = \frac{C_{B1} - C_{B2}}{\ln \left(\frac{C_{B1}}{C_{B2}} \right)} \quad \text{-----} \quad 6.16$$

Usually, x_0 will not be measured accurately nor is the effective distance for diffusion, x at time θ . Accurate value of $(x-x_0)$ is available.

Rewriting eq-7.15 as,

$$\frac{\theta}{x-x_0} = \frac{\rho_1 C_{BM}}{2M_A D_{AB} C_A C_T} (x - x_0) + \frac{\rho_1 C_{BM}}{M_A D_{AB} C_A C_T} x_0 \quad \text{-----} \quad 6.17$$

A graph between $\frac{\theta}{x-x_0}$ against $(x-x_0)$ should yield a straight line with slope

$$S = \frac{\rho_1 C_{BM}}{2M_A D_{AB} C_A C_T} \quad \text{-----} \quad 6.18$$

$$\Rightarrow D_{AB} = \frac{\rho_1 C_{BM}}{2M_A S C_A C_T} \quad \text{-----} \quad 6.19$$

If we take kilogram molecular volume of a gas as 22.4 m^3 , then

$$C_T = \frac{273.15}{22.4T} \text{-----} 6.20$$

If the vapour pressure of evaporating liquid A is vapour pressure (KN/m^2) at the operating temperature of $^{\circ}\text{K}$. Then,

$$C_A = \frac{(V.P)_A}{(P)\text{total pressure in KN/m}^2} \cdot C_T \text{-----} 6.21$$

Effect of temperature and pressure on co-efficient of diffusion, D is expressed as:

$$D = \text{Const. } T^{1.5}/P \text{-----} 6.22$$

6.3 Description

The main components of the experimental set-up are:

Glass T-tube, constant temperature water bath, Air pump, Scale for measurement,

Volatile component is filled in the T-tube and air is passed over it by the pump and changes in the level are measured by the measuring centimeter scale.

6.4 Utilities Required

Electricity supply: 1 phase, 220 V AC and 0.6 KW

Required chemicals such as Acetone, CCl_4 , toluene, and benzene and laboratory glassware.

Bench area $1.2 \text{ m} \times 0.75 \text{ m}$

6.5 Experimental Procedure

1. The water bath temperature is set at the desired level between 25°C to 60°C and to wait till the bath attains the set temperature. Steady temperature of the bath is noted down.
2. The T-tube is filled with CCl_4 to within 2 centimeters of the top of capillary leg. The initial diffusion height of the liquid in the capillary from the top is noted down (x_0).
3. Then the connection with the air of vacuum pump is made and a gentle current of air is allowed to flow over the capillary.

4. The height of liquid (x) from the top of the capillary bore is recorded after every 30 minutes. Then the complete variation of x with Θ is recorded and the diffusivity D_{AB} is calculated corresponding to its bath temperature using equation (6.14).
5. Steps from 1 to 4 are repeated for other different temperatures 45 and 55 °C. Then D_{AB} at each temperature is calculated using eqⁿ. 6.17, 6.18, 6.19
6. Experimental values with the Gilliland's correlation is compared.
7. Different organic liquids like toluene, benzene is used and the results were tabulated and discussed.



Fig 6.1: Diffusion setup for liquids in air

6.6 Standard data

Capillary: Material Borosilicate glass.

Water bath: Material Stainless steel 304 grade, capacity 8 liters fitted with heater and stirrer.

Heater: Nichrome wire heater

Stirrer: Stainless steel 304 grade impeller and shaft coupled with FHP motor.

Air circulation: FHP motor.

Temperature sensor: RTD PT-100 type

Control panel comprising of:

Digital temperature controller cum-indicator, standard make on-off switch, mains indicator etc.

The whole set-up is fixed on a powder coated base plate.

6.7 Formulae

1. Diffusivity for acetone, $D_{AB} = \frac{RT\rho_A (Z_i^2 - Z_f^2)}{2tPM_A \ln\left\{\frac{P-P_{A2}}{P-P_{A1}}\right\}}$ ----- 6.23

Where Z_i is the initial height and Z_f is the final height of acetone in the tube.

2. Vapour pressure can be obtained from the equation:

$$VP = \exp\left[C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5}\right] \text{----- 6.24}$$

2. $C_T = \frac{1 \times 273.15}{22.4 \times T} = \frac{12.19}{T} \text{ Kmole/m}^3$

3. $D_{AB} = \frac{\rho_1 C_{BM}}{2M_A S C_A C_T}$

4. $C_{BM} = \frac{C_{B1} - C_{B2}}{\ln\left(\frac{C_{B1}}{C_{B2}}\right)}$

6.8 Observations and Calculation

6.8.1 Diffusing component Acetone (A) and Non-diffusing component is Air(B)

Table 6.1: Experimental Data of diffusion of acetone in air

SL NO.	Temperature (°C)	Height (cm)		Change in height (Z _i -Z _f) (cm)	Time (sec)
		Before (Z _i)	After (Z _f)		
1	40	11.8	11.78	0.02	1200
2	50	11.78	11.70	0.08	1200
3	60	11.70	11.60	0.1	1200

6.8.1.1 At operating temperature = 40°C

$$M_A = 58.08 \text{ gm.}$$

$$\rho_A = 0.791 \text{ gm/cm}^3$$

$$P_{A1} = 428.2 \text{ mmHg} = 0.563 \text{ atm.}$$

$$P_{A2} = 0$$

$$Z_i = 11.8 \text{ cm and } Z_f = 11.78 \text{ cm}$$

$$D_{AB} = \frac{RT\rho_A(Z_f^2 - Z_i^2)}{2tPM_A \ln\left\{\frac{P - P_{A2}}{P - P_{A1}}\right\}}$$

$$= \frac{82.06 \times 313.15 \times 0.791 \times (11.8^2 - 11.78^2)}{2 \times 58.08 \times 1200 \times \ln\left(\frac{1-0}{1-0.563}\right)}$$

$$= 10.3 \times 10^{-2} \text{ cm}^2/\text{sec.} = 10.3 \times 10^{-6} \text{ m}^2/\text{sec}$$

6.8.1.2 At operating temperature = 50°C

$$M_A = 58.08 \text{ gm.}$$

$$\rho_A = 0.785 \text{ gm/cm}^3$$

$$P_{A1} = 619.22 \text{ mmHg} = 0.8147 \text{ atm.}$$

$$P_{A2} = 0$$

$$Z_i = 11.78 \text{ cm and } Z_f = 11.70 \text{ cm}$$

$$D_{AB} = \frac{RT\rho_A (Z_f^2 - Z_i^2)}{2tPM_A \ln\left\{\frac{P-P_{A2}}{P-P_{A1}}\right\}}$$

$$= \frac{0.08206 \times 323.15 \times 0.785 \times (11.78^2 - 11.7^2)}{2 \times 58.08 \times 600 \times \ln\left(\frac{1-0}{1-0.8147}\right)}$$

$$= 10.68 \times 10^{-2} \text{ cm}^2/\text{sec} = 10.68 \times 10^{-6} \text{ m}^2/\text{sec}$$

6.8.1.3 At operating temperature = 60°C

$$M_A = 58.08 \text{ gm.}$$

$$\rho_A = 0.791 \text{ gm/cm}^3$$

$$P_{A1} = 415.62 \text{ mmHg} = 0.925 \text{ atm.}$$

$$P_{A2} = 0$$

$$Z_i = 11.7 \text{ cm and } Z_f = 11.6 \text{ cm}$$

$$D_{AB} = \frac{RT\rho_A (Z_f^2 - Z_i^2)}{2tPM_A \ln\left\{\frac{P-P_{A2}}{P-P_{A1}}\right\}}$$

$$= \frac{82.06 \times 333.15 \times 0.791 \times (11.7^2 - 11.6^2)}{2 \times 58.08 \times 1200 \times \ln\left(\frac{1-0}{1-0.5468}\right)}$$

$$= 12.54 \times 10^{-2} \text{ cm}^2/\text{sec} = 12.54 \times 10^{-6} \text{ m}^2/\text{sec}$$

Table 6.2: Calculated values of diffusivities of Acetone with temperatures.

Temperature T, K	Diffusivity D_{AB} , m^2/sec
313.15	10.3×10^{-6}
323.15	10.68×10^{-6}
333.15	12.54×10^{-6}

6.8.2 Diffusing component CCl_4 (A) and Non-diffusing component is Air (B)

(1) Bath temperature = $35^\circ\text{C} = 308.15\text{K}$

Total pressure = $P = 101.3 \text{ KN/m}^2$

Table 6.3: Experimental Data of diffusion of CCl_4 in air at 35°C

SL NO	Time(Θ) ($\text{sec} \times 10^3$)	X, mm	($x-x_0$), mm	$\Theta/(x-x_0)$, $\text{Sec} \times 10^3/\text{mm}$
1	0	10	0	-
2	1.8	10.5	0.5	3.6
3	3.6	10.95	0.95	3.78
4	5.4	11.30	1.30	4.15
5	7.2	11.65	1.65	4.36
6	9.0	12.10	2.10	4.28
7	10.8	12.42	2.42	4.46

(2) Bath temperature = $45^\circ\text{C} = 318.15\text{K}$

Total pressure = $P = 101.3 \text{ KN/m}^2$

Table 6.4: Experimental Data of diffusion of CCl_4 in air at 45°C

SL NO	Time(Θ) ($\text{sec} \times 10^3$)	X, mm	($x-x_0$), mm	$\Theta/(x-x_0)$, $\text{Sec} \times 10^3/\text{mm}$
1	0	10	0	-
2	1.8	10.55	0.55	3.27
3	3.6	11.2	1.2	3.0
4	5.4	11.7	1.7	3.18
5	7.2	12.15	2.15	3.35
6	9.0	12.5	2.5	3.6
7	10.8	13.05	3.05	3.54

(3) Bath temperature = 55°C = 328.15K

Total pressure = P = 101.3 KN/m²

Table 6.5: Experimental Data of diffusion of CCl₄ in air at 55°C

SL NO	Time(Θ) (sec×10 ³)	X, mm	(x-x ₀), mm	Θ/(x-x ₀), Sec×10 ³ /mm
1	0	10	0	-
2	1.8	11.2	1.2	1.5
3	3.6	12.0	2.0	1.8
4	5.4	12.95	2.95	1.83
5	7.2	13.8	3.8	1.895
6	9.0	14.55	4.55	1.978
7	10.8	15.45	5.45	1.982

6.8.2.1 Sample calculation

Vapour pressure of CCl₄ can be obtained from the equation 6.23

$$VP = \exp \left[C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5} \right]$$

Where T is in K and VP in Pa.

For CCl₄

$$C_1=78.441, C_2= -6128.1, C_3= -8.5766, C_4=6.8465 \times 10^{-6}, C_5=2$$

With these values of constants the vapour pressure of CCl₄ at 308.15 K is

$$\begin{aligned} VP &= \exp \left[78.441 + \frac{-6128.1}{308.15} + -8.5766 \times \ln(308.15) + 6.8465 \times 10^{-6} \times 308.15^2 \right] \text{KPa} \\ &= 23.14 \text{ KPa} = 23.14 \text{ KN/m}^2 \end{aligned}$$

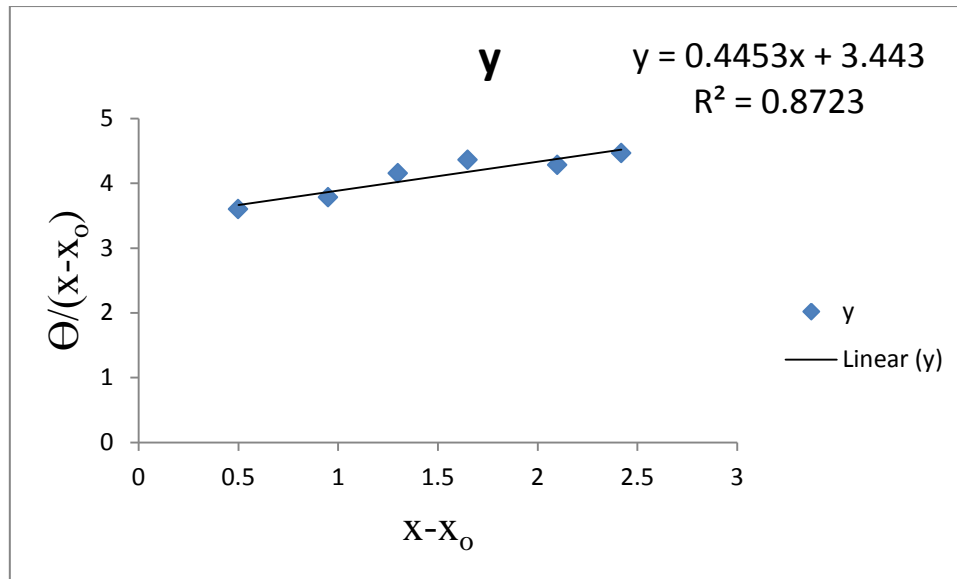


Fig: 6.2 Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 308.15 K for CCl_4

This graph yields a slope 0.4453

Least square equation of this line is

$$y = mx + C$$

i.e. $y = 0.4453x + 3.443$ and $R^2 = 0.8723$

From the graph, slope, $s = 0.4453 \text{ sec} \times 10^3 / \text{mm}^2 = 4.453 \times 10^8 \text{ sec/m}^2$

Total pressure = 101.3 KN/m^2

Kilogram molecular volume of a gas = 22.4 m^3 at 273.15 K

$$\text{Total concentration} = C_T = \frac{1 \times 273.15}{22.4 \times T} = \frac{12.19}{T} = \frac{12.19}{308.15} = 0.04 \text{ Kmole/m}^3$$

Molecular weight of $\text{CCl}_4 = M_A = 154 \text{ Kg/mole}$

$$C_A = \text{concentration of } \text{CCl}_4 = C_A = \frac{(V.P)_A}{(P) \text{ total pressure in KN/m}^2} \cdot C_T = 9.14 \times 10^{-3} \text{ Kmole/m}^3$$

Density of $\text{CCl}_4 = \rho_1 = 1540 \text{ Kg/m}^3$

$$C_{B1} = \frac{273.15}{22.4 \times 308.15} = 0.04 \text{ Kmole/m}^3$$

$$C_{B2} = \frac{C_{B1} \times (P - (V.P)_A)}{P} = \frac{0.04 \times (101.3 - 23.14)}{101.3} = 0.031 \text{ Kmole/m}^3$$

$$C_{BM} = \frac{C_{B1} - C_{B2}}{\ln\left(\frac{C_{B1}}{C_{B2}}\right)} = \frac{0.04 - 0.031}{\ln\left(\frac{0.04}{0.031}\right)} = 0.035 \text{ Kmole/m}^3$$

Now,

$$D_{AB} = \frac{\rho_1 C_{BM}}{2 M_A S C_A C_T} = \frac{1540 \times 0.035}{2 \times 154 \times 9.14 \times 10^{-3} \times 0.04 \times 4.453 \times 10^8} = 1.07 \times 10^{-6} \text{ m}^2/\text{sec at } 35^\circ \text{C}$$

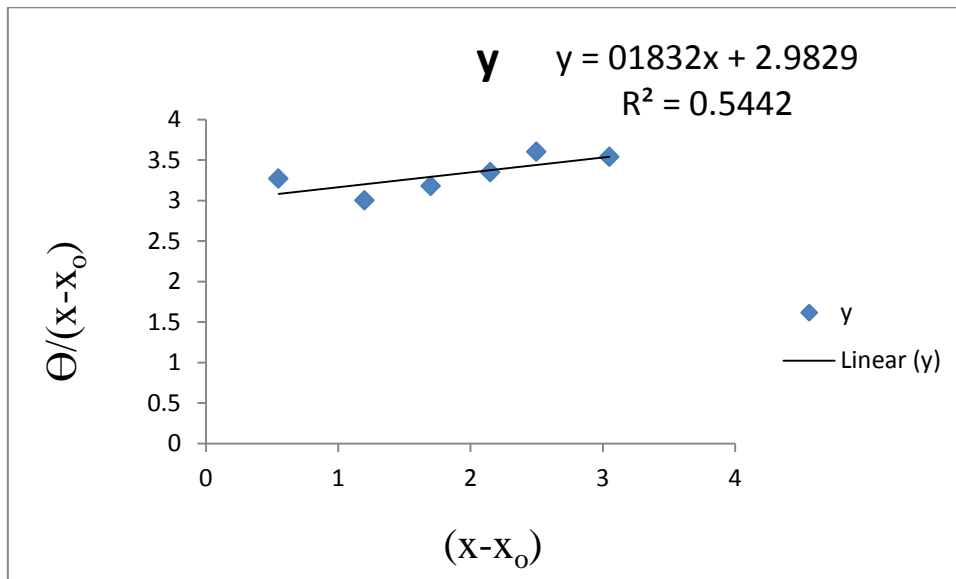


Fig: 6.3 Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 318.15 K for CCl_4

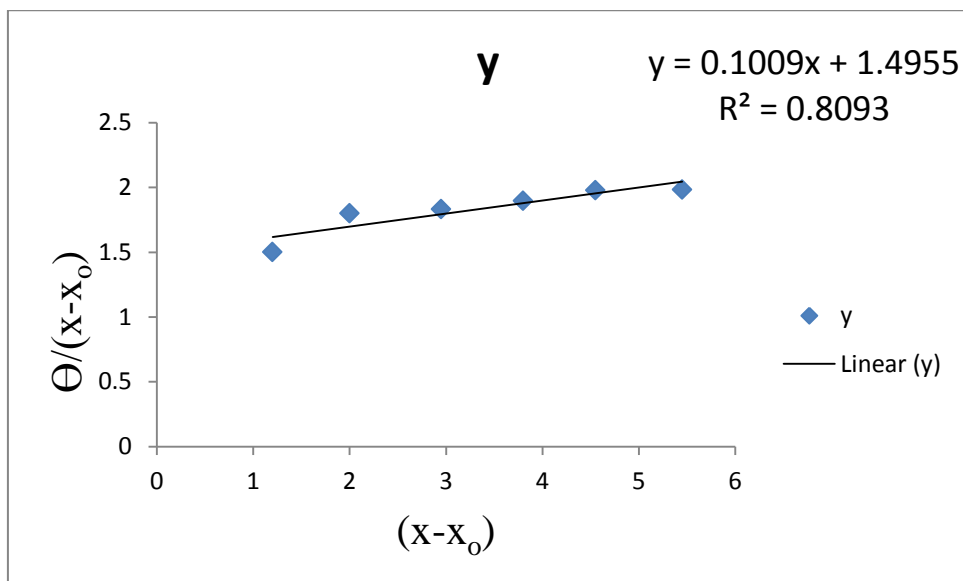


Fig: 6.4 Plot of $(X-X_0)$ vs. $\Theta/(X-X_0)$ at 328.15 K for CCl_4

Table 6.6: Calculated values of diffusivities of CCl₄ with temperatures.

Temperature T, K	Diffusivity D _{AB} , m ² /sec	D _{AB} ×P
308.15	8.87×10 ⁻⁶	0.898531
318.15	8.986×10 ⁻⁶	0.9102818
328.15	9.16×10 ⁻⁶	0.927908

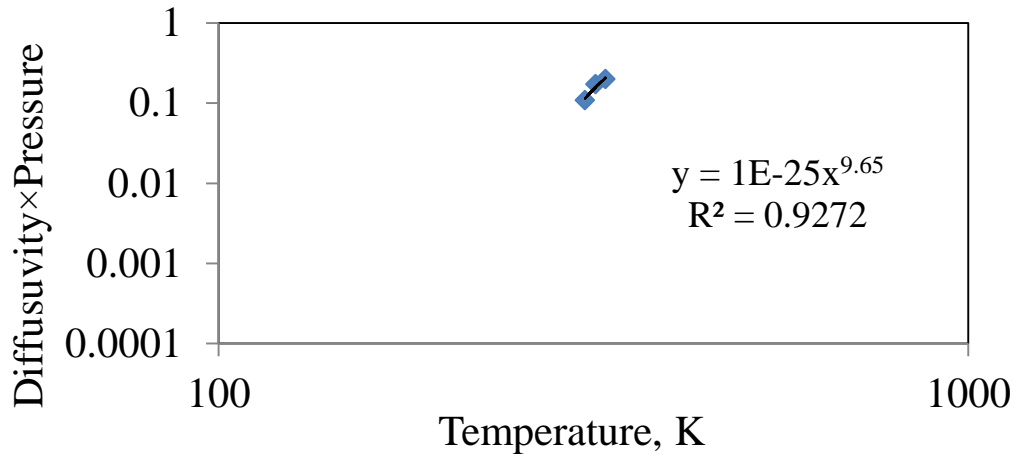


Fig:6.5 Temperature vs. D×P on a log-log graph for CCl₄

The equation from this graph is

$$D = 1 \times 10^{-25} T^{9.65} / P$$

From Gilliland's correlation,

$$\begin{aligned}
 \text{For temperature} = 308.15 \text{ K} \quad D &= \frac{0.0043 \sqrt{T^3 \left[\frac{1}{M_A} + \frac{1}{M_B} \right]}}{P \left(V_A^{1/3} + V_B^{1/3} \right)^2} \\
 &= \frac{0.0043 \sqrt{308.15 \left(\frac{1}{154} + \frac{1}{29} \right)}}{1 \times (101.2^{1/3} + 29.9^{1/3})^2} \\
 &= 8.49 \times 10^{-2} \text{ cm}^2/\text{sec} \\
 &= 8.49 \times 10^{-6} \text{ m}^2/\text{sec}
 \end{aligned}$$

Similarly,

$$\text{For } T=318.15 \text{ K} \quad D = 8.68 \times 10^{-6} \text{ m}^2/\text{sec}$$

$$\text{For } T=328.15 \text{ K} \quad D = 8.95 \times 10^{-6} \text{ m}^2/\text{sec}$$

6.8.2 Diffusing component Toluene (A) and Non-diffusing component is Air (B)

Operating temperature = 40°C = 313.15 K

Pressure = 101.3 KN/m²

Table 6.7: Experimental Data of diffusion of Toluene in air at 40°C

SL NO	Time(Θ) (sec $\times 10^3$)	X, mm	(x-x ₀), mm	$\Theta/(x-x_0)$, Sec $\times 10^3$ /mm
1	0	0	0	-
2	1.8	1.2	1.2	1.5
3	3.6	2.8	2.8	1.285
4	5.4	4.0	4.0	1.35
5	7.2	4.9	4.9	1.469

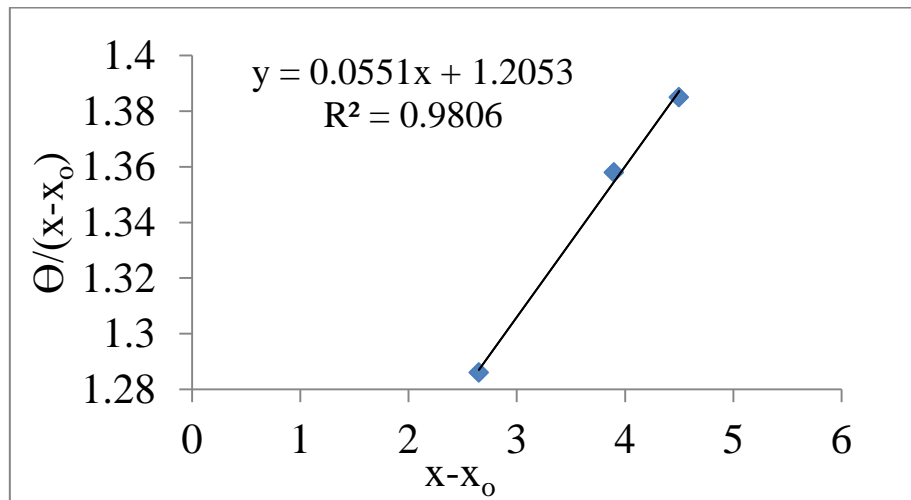


Fig 6.6 Plot of (X-X₀) vs. $\Theta/(X-X_0)$ at 313.15 K for toluene

Vapour pressure of Toluene can be obtained from the equation 6.23

$$VP = \exp \left[C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5} \right]$$

Where T is in K and VP in KPa.

For Toluene

$C_1 = 74.1358$, $C_2 = -6918.798$, $C_3 = -8.79548$, $C_4 = 5.754912 \times 10^{-6}$, $C_5 = 2$

With these values of constants the vapour pressure of Toluene at 313.15 K is

$$VP = \exp \left[74.1358 - \frac{6918.798}{313.15} - 8.79548 \times \ln(313.15) + 5.754912 \times 10^{-6} \times 313.15^2 \right]$$

$$= 7.895 \text{ KPa}$$

Fig 6.5 yields a slope 0.0551

Least square equation of this line is

$$y = mx + C$$

$$\text{i.e. } y = 0.0551x + 1.2053 \text{ and } R^2 = 0.9806$$

From the graph, slope, $s = 0.0551 \text{ sec} \times 10^3 / \text{mm}^2 = 0.551 \times 10^8 \text{ sec/m}^2$

Total pressure = 101.3 KN/m²

Kilogram molecular volume of a gas = 22.4 m² at 273.15 °K

$$\text{Total concentration} = C_T = \frac{1 \times 273.15}{22.4 \times T} = \frac{12.19}{T} = \frac{12.19}{313.15} = 0.038 \text{ Kmol/m}^3$$

Molecular weight of Toluene = $M_A = 92 \text{ Kg/mol}$

$$C_A = \text{concentration of } CCl_4 = C_A = \frac{(V.P)_A}{(P)_{\text{total pressure in KN/m}^2}} \cdot C_T = 2.96 \times 10^{-3} \text{ Kmol/m}^3$$

Density of Toluene = $\rho_1 = 866.9 \text{ Kg/m}^3$

$$C_{B1} = \frac{273.15}{22.4 \times 313.15} = 0.038 \text{ Kmol/m}^3$$

$$C_{B2} = \frac{C_{B1} \times (P - (V.P)_A)}{P} = \frac{0.038 \times (101.3 - 7.895)}{101.3} = 0.035 \text{ Kmol/m}^3$$

$$C_{BM} = \frac{C_{B1} - C_{B2}}{\ln\left(\frac{C_{B1}}{C_{B2}}\right)} = \frac{0.038 - 0.035}{\ln\left(\frac{0.038}{0.035}\right)} = 0.0365 \text{ Kmol/m}^3$$

Now,

$$D_{AB} = \frac{\rho_1 C_{BM}}{2M_A S C_A C_T} = \frac{866.9 \times 0.0365}{2 \times 92 \times 2.96 \times 10^{-3} \times 0.038 \times 0.551 \times 10^8} = 8.15 \times 10^{-6} \text{ m}^2/\text{sec at } 40 \text{ }^\circ\text{C}$$

From Gilliland's correlation,

$$\text{For temperature} = 313.15 \text{ K, } D = \frac{0.0043 \sqrt{T^3 \left[\frac{1}{M_A} + \frac{1}{M_B} \right]}}{P \left(V_A^{1/3} + V_B^{1/3} \right)^2}$$

$$= \frac{0.0043 \sqrt{313.15^3 \left(\frac{1}{92} + \frac{1}{29} \right)}}{1 \times (118.3^{1/3} + 29.9^{1/3})^2} = 0.081 \text{ cm}^2/\text{sec} = 8.1 \times 10^{-6} \text{ m}^2/\text{sec}$$

6.8.3 Diffusing component Benzene(A) and Non-diffusing component is Air(B)

Operating temperature = 40°C = 313.15 K

Pressure = 101.3 KN/m²

Table 6.8: Experimental Data for diffusion of Benzene in air at 40°C

SL NO	Time(Θ) (sec $\times 10^3$)	X, mm	(X - X ₀), mm	$\Theta / (X - X_0)$, Sec $\times 10^3$ /mm
1	0	0	0	-
2	1.8	1.4	1.4	1.286
3	3.6	2.65	2.65	1.358
4	5.4	3.9	3.9	1.385
5	7.2	4.5	4.5	1.6

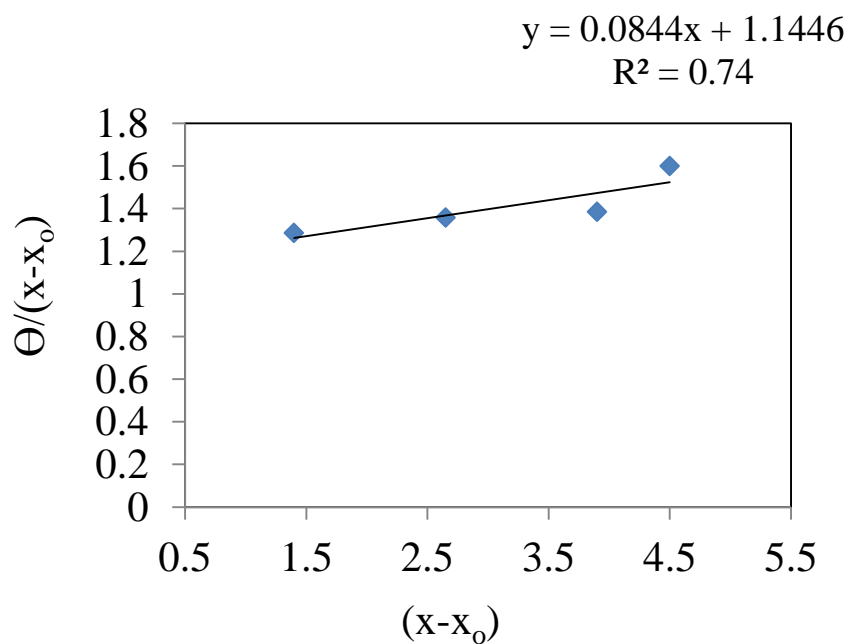


Fig 6.7 Plot of (X-X₀) vs. $\Theta / (X - X_0)$ at 313.15K for Benzene

Vapour pressure of Benzene can be obtained from the equation 6.23

$$VP = \exp \left[C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5} \right]$$

Where T is in K and VP in KPa.

For Benzene

$$C_1 = 71.10718, C_2 = -6281.04, C_3 = -8.433613, C_4 = 6.1984 \times 10^{-6}, C_5 = 2$$

With these values of constants the vapour pressure of Toluene at 313.15 K is

$$\begin{aligned} VP &= \exp \left[71.10718 - \frac{6281.04}{313.15} - 8.433613 \times \ln(313.15) + 6.1984 \times 10^{-6} \times 313.15^2 \right] \\ &= 24.34 \text{ KPa} \end{aligned}$$

Fig 6.5 yields a slope 0.0844

Least square equation of this line is

$$y = mx + C$$

$$\text{i.e. } y = 0.0844x + 1.1446 \text{ and } R^2 = 0.74$$

From the graph, slope, $s = 0.0844 \text{ sec} \times 10^3 / \text{mm}^2 = 0.844 \times 10^8 \text{ sec/m}^2$

Total pressure = 101.3 KN/m²

Kilogram molecular volume of a gas = 22.4 m³ at 273.15 K

$$\text{Total concentration} = C_T = \frac{1 \times 273.15}{22.4 \times T} = \frac{12.19}{T} = \frac{12.19}{313.15} = 0.038 \text{ Kmol/m}^3$$

Molecular weight of Toluene = $M_A = 78 \text{ Kg/mol}$

$$C_A = \text{concentration of Benzene} = C_A = \frac{(V.P)_A}{(P)_{\text{total pressure in KN/m}^2}} \cdot C_T = 6.13 \times 10^{-3}$$

Kmol/m³

Density of Benzene = $\rho_1 = 876.5 \text{ Kg/m}^3$

$$C_{B1} = \frac{273.15}{22.4 \times 313.15} = 0.038 \text{ Kmol/m}^3$$

$$C_{B2} = \frac{C_{B1} \times (P - (V.P)_A)}{P} = \frac{0.038 \times (101.3 - 24.34)}{101.3} = 0.0288 \text{ Kmol/m}^3$$

$$C_{BM} = \frac{C_{B1} - C_{B2}}{\ln\left(\frac{C_{B1}}{C_{B2}}\right)} = \frac{0.038 - 0.0288}{\ln\left(\frac{0.038}{0.0288}\right)} = 0.033 \text{ Kmol/m}^3$$

Now,

$$\begin{aligned} D_{AB} &= \frac{\rho_1 C_{BM}}{2M_A S C_A C_T} = \frac{876.5 \times 0.033}{2 \times 78 \times 6.13 \times 10^{-3} \times 0.038 \times 0.844 \times 10^8} \\ &= 8.53 \times 10^{-6} \text{ m}^2/\text{sec at } 40^\circ \text{C} \end{aligned}$$

From Gilliland's correlation,

$$\begin{aligned}
 \text{For temperature} = 313.15 \text{ K, } D &= \frac{0.0043 \sqrt{T^3 \left[\frac{1}{M_A} + \frac{1}{M_B} \right]}}{P \left(V_A^{1/3} + V_B^{1/3} \right)^2} \\
 &= \frac{0.0043 \sqrt{313.15^3 \left(\frac{1}{78} + \frac{1}{29} \right)}}{1 \times (99.82^{1/3} + 29.9^{1/3})^2} \\
 &= 0.084 \text{ cm}^2/\text{sec} \\
 &= 8.4 \times 10^{-6} \text{ m}^2/\text{sec}
 \end{aligned}$$

6.9 Result

The binary diffusion coefficients of different solvents acetone, carbon tetrachloride, benzene and toluene were determined and listed below.

Table 6.9 Experimental values of diffusional coefficients of some organic solvents

System	Temperature(°C)	Diffusivity(m ² /sec)
Air-Acetone	40	10.3×10 ⁻⁶
	50	10.68×10 ⁻⁶
	60	12.54 ×10 ⁻⁶
Air-CCl ₄	35	8.87×10 ⁻⁶
	45	8.986×10 ⁻⁶
	55	9.16×10 ⁻⁶
Air-Benzene	40	8.53×10 ⁻⁶
Air-Toluene	40	8.15×10 ⁻⁶

7.1 Conclusion

This project work highlights the following facts:

(a) Binary diffusion coefficients of some industrially important organic solvents in air (*a case of diffusion of A through stagnant non-diffusing B*) are effectively measured at widely different temperatures and at atmospheric pressure in a Stefan tube set up. The data shows that diffusivity varies considerably with temperature (directly proportional) and inversely varies with pressure consistently for all the cases.

(b) Similarly, in case of spherical geometry (naphthalene balls) the average diffusivity is found to be 3.43×10^{-7} m²/sec whereas for cylindrical geometry (camphor pellets) the diffusivity value stands at 3.8×10^{-7} m²/sec. This indicates that it takes longer to diffuse from a cylindrical shaped particle as compared to that in a spherical particle.

7.2 Future works

The present work can be extended to carry out further research in the following area:

(a) Systematic investigation on hydrocarbon systems to carry out binary diffusion studies followed by multi-component assessment to calculate overall mass transfer coefficients which would eventually be helpful in designing mass transfer equipments like distillation (equimolar counter-current diffusion) and absorption columns/strippers (diffusion of A through stagnant non-diffusing B).

(b) Liquid-liquid diffusion and/or gas-gas diffusion can also be extensively studied fundamental to important unit operations.

(c) This study can particularly be useful in processed food packaging industries for controlled assessment of diffusion of nutrients, aroma etc. for maintaining global standards (aesthetics as well as nutrition wise).

(d) Diffusion studies (Knudsen and Surface diffusion) can be extended to heterogeneous gas-solid catalytic reactions (particularly for catalysts with varying geometries) to understand the mechanism further

REFERENCES

- [1] Warren L. McCabe, Julian C. Smith, Peter Harriott, "Unit operations of chemical engineering", McGraw-Hill 7th edition, 17, p.527-564 (2010)
- [2] Robert E. Treybal, "Mass-Transfer operations-Diffusion", ed-2nd ch2, p21-93
- [3] Binay K. Dutta, "Principle of Mass-Transfer and separation process-molecular diffusion", edition-5th, 2013, p-11-42.
- [4] F. Curtiss and R. B. Bird, "Multicomponent diffusion," Ind. Eng. Chem. Res. 38, 2515 (1999)
- [5] Bird, R. B., W. E. Stewart, and E. N. Lightfoot: "Transport phenomena," Wiley, New York, 1960.
- [6] Arnold, J. H., "Studies in Diffusion: III Unsteady-State Vaporization and Adsorption." Trans. AIChE. 1944, 40, p 361.
- [7] Slattery C. John, Bird Byron R., "Calculation of the diffusion coefficient of dilute gases" AIChE. J., 1985, 4, p 140-145.
- [8] Hayduck, W., and H. Laudie: AIChE. J., 20, 611, 1974
- [9] Hiss, T. G., and E. L. Cussler: AIChE J., 19, 698, 1973
- [10] Jost, W., "Diffusion in solids, liquids and gases," Academic, New York, 1960
- [11] Newman, A. B.: Trans. AIChE j., 27, 203, 310, 1931
- [12] R. Van der Vaart, C. Huiskes, H. Bosch, T. Reith, Principle of diffusion (2000) 214.
- [13] Hines, A.L., and R.N. Maddox, Mass transfer –Fundamentals and applications, Prentice Hall, 1985.
- [14] Perry's Chemical Engineers' Handbook, 7th edition, McGraw-Hill, New York, 1997
- [15] Skelland, A.H.P., diffusional mass transfer, John Wiley, New York, 1974

[16] Benitez, J., Principle and Modern applications of mass transfer, Wiley Interscience, New York, 2002.

[17] Sherwood, T.K., R.L. Pigford, and C.R. Reid, Mass Transfer, McGraw Hill, New York, 1975.