STUDY OF THE RELATIVE, FREE DIFFUSION VELOCITIES OF ELECTROLYTES IN AQUEOUS MEDIUM

A DISSERTATION SUBMITTED TO THE UNIVERSITY OF DHAKA FOR THE DEGREE OF MASTER OF PHILOSOPHY IN CHEMISTRY.

SUBMITTED BY

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CERTIFICATE

This is certify that the thesis entitled "study of the relative, free diffusion velocities of electrolytes in aqueous medium" has been prepared and submitted for the degree of master of philosophy of the department of chemistry, university of Dhaka by Md. Masud Hossain under our supervision.

It is farther to certify that the research work embodied in the thesis is authentic and suitable for awarding M Phil degree in chemistry.

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Dhaka Bangladesh	Dhaka Bangladesh

DEDICATED

TO

MY BELOVED PARENTS, BROTHERS & SISTERS

AND

FOR THOSE WHO DEDICATED THEIR LIVES ON THE WAY OF CREATOR

Acknowledgement

In recapitulating the name of the persons and authorities to whom I owe a great debt for carrying out this research. I would like to mention first of all, the name of Professor Dr. G M Golzar Hossain and Professor Dr. Abul Khair, Department of Chemistry, University of Dhaka; through their dynamic supervision and constant support have enabled me to carry out this research work.

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ABASTRACT

A novel liquid diffusion tube closed and cylindrical termed Diffusimeter was fabricated from glass tube and straight bore stopcocks to measure relative velocities of electrolytes in free diffusion. Solutions of two electrolytes known to give characteristic reaction were put one above each of two stopcocks and then released concurrently to diffuse head on through water in the diffusion path and finally to produce a precipitate or color as indicator at the encounter. Experimental objective required entry of time elapsed for the reaction mark to appear and the distances traveled by the electrolytes. The velocity ratio termed distance traveled ratio (DTR) was found to match with the Molar Mass Ratio Square Root (MMRSR) of the electrolyte pair taken in order. A direct proportionality between the velocity and the square root of molar mass was thus revalidated. The heavier electrolyte moved faster contrary to the gaseous diffusion. The results hinted hydration numbers of the diffusing electrolytes. Diffusion velocities of thirty salts were determined using this novel, innovative Diffusimetric Method named DTR model. Surprisingly NH_4Cl and NH_4SCN showed similar velocities. HCl and LiCl showed low diffusion rates due to their cation's high charge to size ratio. Apparently $MgCl_2$, $CaCl_2$, and $SrCl_2$ diffused with one H_2O each but $BaCl_2$, $AgNO_3$, and Fe^{III} alum with none. NaCl showed relatively high rate which traces its fitness as antibacterial agent and bio-salt in human. Na_2SO_4 and K_2SO_4 showed identical velocities which together with metatheses hypothesize sylvite mineral formation mechanism over geological periods. Close diffusion rates of $ZnCl_2$ and $CdCl_2$ traces reasons for cadmium's presence in zinc ores. Diffusion controlled effects are shown in Fe^{III} salt's reactions with NH_4SCN; the DTR reveals reactant pair's encounter nature at their conjunction. Manipulating electrolyte's concentrations crystalline precipitates were obtained.

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INTRODUCTION

Introduction

1.1 General

Staring back at the genesis of concepts and models that are already familiar, it always comes as a surprise to discover how prone we are to consider them as quite obvious. We realize how these "evidences" required - eras perhaps - centuries of approximations, errors, intuitions and recession through reading old publications. Diffusion is also heart of these evidences. Foregoing of the diffusion science with the evidence in enormous practical area of modern science, it seems surprising that scholars of the Enlightenment century apparently did not observe the mechanism of many technical process and confined in its scope which are controlled by diffusion phenomena.

Thus "study of relative free diffusion velocities of electrolytes in aqueous medium" with giving emphasis on the fundamental aspects of the experimental observation and theoretical description, where practical consideration and technical operation is encountered, will be milestones in the development of diffusion science and new door in its confined scope. The study brings wide interdisciplinary appeal which is ideal for professional researcher in interrelating principle concept of physics, biology, chemistry and mathematics of modern diffusion science. To clarify the basic feature of the experiment and its observation the universal theory of diffusion includes the followings:

Diffusion is one kind of transport phenomenon; it is a spontaneous mixing of one substance with another when in contact or separated by a semi permeable membrane or micro porous barrier. The rate of the diffusion is proportional to the concentration of the substance and increases with the temperature. Diffusion occurs most readily in gases, less in liquid and least in solid. The phenomenon readily observed when a drop of colored water added to clear water or when smoke from a chimney dissipates into the air. In these cases, diffusion is the result of turbulent fluid motion rather than chemical reactions or the application of external force. In cell biology, diffusion described as a form of "passive transport", by which substances cross membranes. It is a main form of transport for necessary materials such as amino acids within cells.[1]

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[1] Maton, Anthea; Jean Hopkins, Susan Johnson, David LaHart, MaryannaQuon Warner, Jill D. Wright (1997). Cells Building Blocks of Life. Upper Saddle River, New Jersey: Prentice Hall. pp. 66–67

1.2 Diffusion

Diffusion is the movement of particles (atoms, ions or molecules) from a region in which they are in higher concentration to regions of lower concentration. A good example of diffusion is food coloring. If we place a drop of red food coloring in a beaker of water eventually the entire beaker of water will have a red tint. The food coloring moved through the water until it was equally distributed throughout the beaker. Diffusion takes place along a concentration gradient. A concentration gradient exists until the diffused substance is evenly distributed.

Figure 1: diffusion through water, Yellow color diffusing through water

The glass on the left contains hot water, while the glass on the right contains cold water. The color was added to the cold water slightly before the color was added to the hot water, yet after a few seconds it has diffused more thoroughly through the hot water.

Everyday examples of diffusion are:

1. Sugar will diffuse through tea until the entire cup of tea is sweet. (Stirring the tea to speed up the diffusion.)
2. The odors of food cooking diffuse throughout the kitchen. Opening the kitchen door it will spread into the next room.

The movement of these molecules is said to be passive. No energy is needed to be provided. The natural kinetic energy of the particles supplies the energy.

Examples of diffusion in science are:

1. Carbon dioxide entering the stomata of leaves.
2. Oxygen diffusing out of the stomata and lenticels of leaves.

1.3 Rudimentary Concept of Diffusion

Diffusion is one of several transport phenomena that occur in nature. A distinguishing feature of diffusion is that it results in mixing or mass transport, without requiring bulk motion. Thus, diffusion should not be confused with convection, or advections, which are other transport mechanisms that utilize bulk motion to move particles from one place to another. In Latin, "diffundere" means "to spread out".

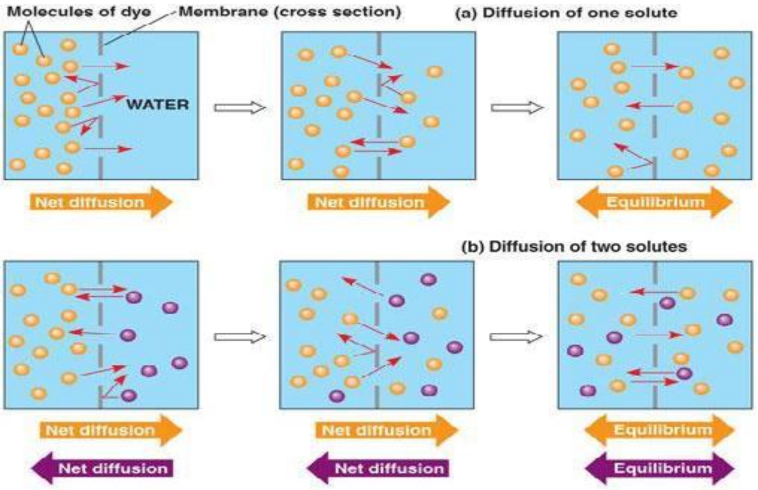

Figure 2: Mechanism of Diffusion

There are two ways to introduce the motion of diffusion: either a phenomenological approach starting with Fick's laws and their mathematical consequences, or a physical and atomistic one, by considering the random walk of the diffusing particles.[2]

In the phenomenological approach, according to Fick's laws, the diffusion flux is proportional to the minus gradient of concentrations. It goes from regions of higher concentration to regions of lower concentration. Sometime later, various generalizations of Fick's laws were developed in the frame of thermodynamics and non-equilibrium thermodynamics.[3]

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[2] *J. Phil Bert (2005). One and a half century of diffusion: Fick, Einstein, before and beyond. Diffusion Fundamentals, 2, 1.1--1.10.*

[3] *S.R. De Groot, P. Mazur (1962). Non-equilibrium Thermodynamics. North-Holland, Amsterdam.*

When some particles are dissolved in a glass of water initially, the particles are all near one corner of the glass. If the particles all randomly move around ("diffuse") in the water, then the particles will eventually become distributed randomly and uniformly and organized (but diffusion will still continue to occur, just that there will be no net flux). From the atomistic point of view, diffusion is considered as a result of the random walk of the diffusing particles. In molecular diffusion, the moving molecules are self-propelled by thermal energy. Random walk of small particles in suspension in a fluid was discovered in 1827 by Robert Brown. The theory of the Brownian motion and the atomistic backgrounds of diffusion were developed by Albert Einstein.

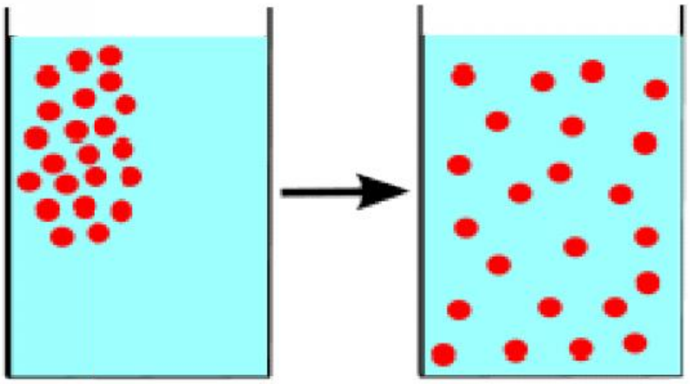

Figure 3: Concept of time-dependent process

Now, the concept of diffusion is widely used in: physics (particle diffusion), chemistry, biology, sociology, economics, and finance (diffusion of people, ideas and of price values). The concept of diffusion is typically applied to any subject matter involving random walk in ensembles of individuals.

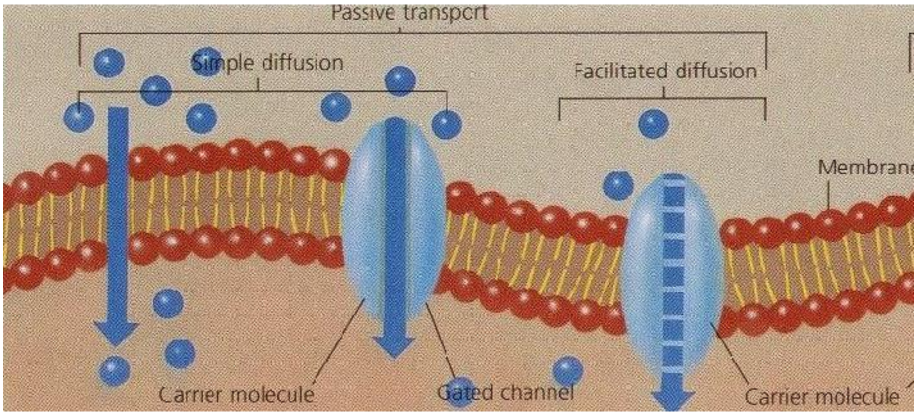

Figure 4: Simple diffusion through a plasma membrane

1.4 Principles of Diffusion

The theoretical principles of diffusion were outline by Adoloph Fick's in 1855. These were adopted mainly for gases and liquids as diffusion of solids was almost unknown that time. Fick inspired by Thomas Graham who presented his law of diffusion of gases to the royal society in 1831. Visible evidence of the universal importance of diffusion has been and is being furnished in mush details. The small size of the ultimate physiological units of organisms and by the universal presence in these units of differentially permeable membranes which limit also control the entrance and movement within the body of bio molecules and ions. The bodies of higher organism have diffusion oriented special structure adaptations.

The thin walls and enlarged surfaces of respiratory organs like lungs, fish gills or insect tracheae, the thin hair-like projections in plant leaves and roots that absorb water and dissolve minerals, the spacing in capillaries, the intestinal villi of mammals are few of the varied examples intimately connected to diffusion.

Diffusion is one of the chief means by which, in accordance with second law of thermodynamics, the distribution of matter and energy in the universe tends constantly to become less and less orderly and more and more of the sort that would result from the operation of the laws of chance.

Historically, there has always been a close relation between the study of diffusion and the biological sciences. However, the same early studies of diffusion across membranes or membrane diffusion undoubtedly stimulated the work on free diffusion of Graham and Fick.

1.5 Diffusion in Gases, Liquids and Solids

In gases, diffusion takes place counter to gravity, and the rate follows the Graham's law. Carbon dioxide diffuses in air until a uniform mixture results. In liquids molecules move in gravitational field although their masses make the effective forces infinitesimal. Diffusion is in liquid clearly demonstrated by pouring a layer of water over a layer of ink in a narrow glass tube. The boundary between the ink and water is distinct at first, but it slowly blurs as the ink diffuses upwards in to the clear water and the water diffuses downward into the ink.

Eventually the ink and water spread evenly along the tube without stirring. Such movement of molecules is response to the concentration gradient is diffusion; a solid diffuses into a liquid as it dissolves. One solid might diffuses slowly into another where are in contact.

1.6 Diffusion in Biological Species

Diffusion is a common phenomenon in all plants and animals. Cell membranes act as barriers to most, but not all, molecules. Development of a cell membrane that could allow some materials to pass while constraining the movement of other molecules was a major step in the evolution of the cell. Cell membranes are differentially (or semi-) permeable barriers separating the inner cellular environment from the outer cellular (or external) environment. Osmosis and dialysis are two natural processes that use of diffusion.

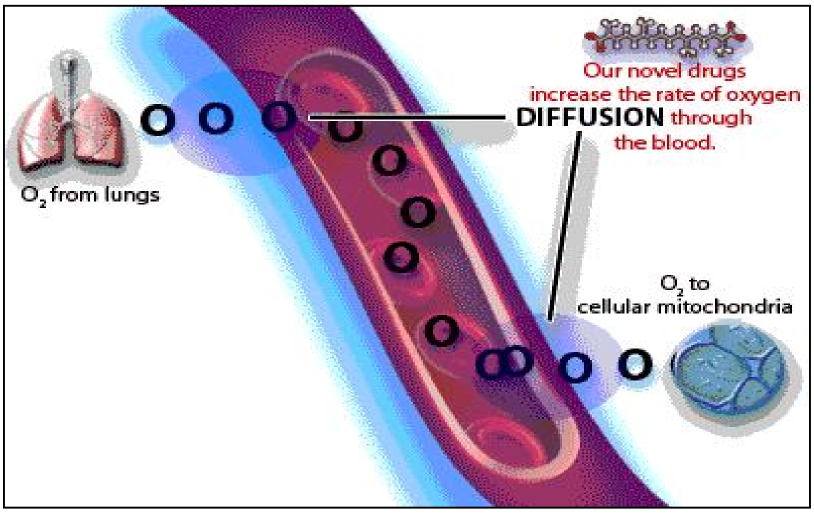

Figure 5: Diffusion of Oxygen through the Blood

All cells acquire the molecules and ions they need from their surrounding extra cellular fluid (ECF). There is an unceasing traffic of molecules and ions, in and out of the cell through its plasma membrane. Examples: glucose, Na^+, Ca^{2+} [15]. In eukaryotic cells, there is also transport in and out of membrane-bounded intracellular compartments such as the nucleus, endoplasmic reticulum, and mitochondria. Examples: proteins, mRNA, Ca^{2+}, ATP. The process of diffusion is one of great practical importance in biological sciences. Every cell, every organism, at every moment of its existence, is dependent upon this process for supplying nutrients into its body, for distributing nutrients within the body boundaries, and for removing injurious metabolic products to a safe distance. Particularly, in mammalian lungs, a process of diffusion takes place in the alveoli: due to differences in partial pressures across the alveolar-capillary membrane, oxygen diffuses into the blood and carbon dioxide diffuses out. In simple term, diffusion is the most widespread of all cellular activities.

1.7 Gaseous Diffusion and Uranium Enrichment

Graham's law of diffusion is also can be applied in uranium enrichment. It is a technique used for separating the light isotope of ^{235}U from the heavy isotope of ^{238}U from a mixture of two. Inter halogens ClF_3 or BrF_3 are used as oxidizing agents in the purification of uranium from its fission products.

$$U\ (s) + 3ClF_3\ (g) = UF_6 + 3ClF\ (g)$$

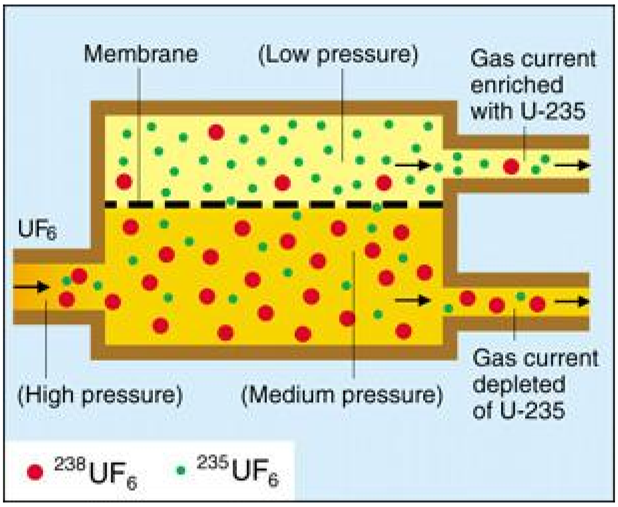

Figure 6: Gaseous diffusion and uranium enrichment

The uranium hexafluoride is a mixture of $^{235}UF_6$ and $^{238}UF_6$ are allowed to diffuse through a micro porous barrier, whose apertures are of molecular dimensions. the isotope ^{238}U and ^{235}U are in a ratio of 140 :1 because of the vastly greater number of heavier isotope and extremely small difference in their masses, the mixture must pass through a barrier a great many times to obtain a high concentration of the ^{235}U isotope. The diffusion rates being inversely proportional to the square root of their molar masses, the ideal separation factor is $\sqrt{}M1\ M2$, where M1 is the molar mass of $^{235}UF_6$ and M2 is of UF_6. This method is still use for uranium enrichment for nuclear reactors.

1.8 Brownian movement and mechanism of diffusion

The kinetic theory presupposes the existence of molecules. We have just seen that the behavior of gases can explained in more or less satisfactory manner with the help of the kinetic theory. The question arises as to whether this agreement of experiment with theory is the only basis of the acceptance of the kinetic theory of matter or is there any direct evidence of the existence of molecules and their erratic movement. The molecules are too small to seen under the most powerful microscope. An attempt at direct observation of molecules and their movement would therefore, be futile. It is important, however to consider other evidences which will justify the assumptions of kinetic theory. One such evidence provided by the experiment of botanist Robert brown. Brown while experimenting with pollen grains, observed that when suspended in a liquid this extremely small particles were in continuous irregular zigzag motion. This motion of suspended particles, which were the later, observed for emulsions of mastic and gamboges and of minute colloidal particles also known as the Brownian movement. The cause of the movement has been the subject of much investigation. It established that the motion was not due to the thermal or mechanical agitation, for it persists when placed in underground callers for years. It is also not due to light used in observing the particles under microscope, as the same movement observed even when the intensity of light was decreased thousand fold. The nature of the particles has very little influence upon their movement, but their size has considerable effect, the smaller the particles, the more violent the movement. In all cases, the movement found to go on indefinitely.

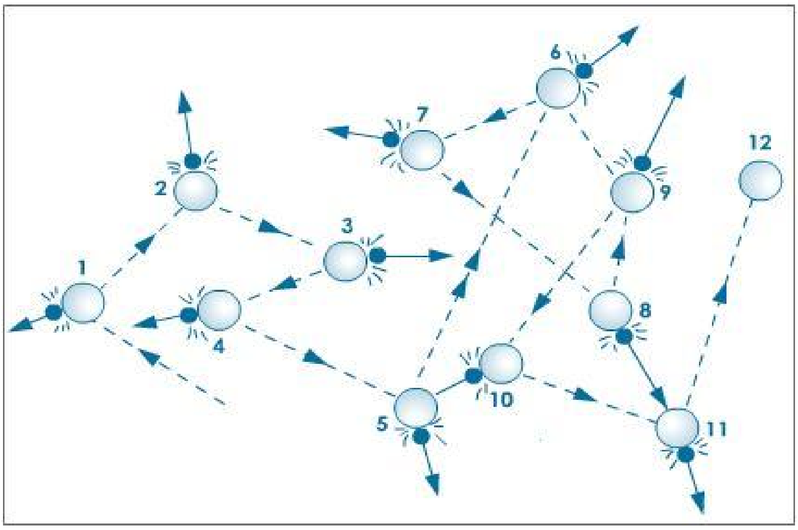

Figure 7: Brownian movement and mechanism of diffusion

The explanation of the phenomenon of Brownian movement is that the violent zigzag motion of the particles caused by the collision of the suspended particles by the molecules of medium, which they are in continuous irregular motion. The movement of particles is therefore, a reflection of the movements of the molecules. (14) After a long investigation

Brownian movement was shown by Einstein in 1905 and later by the others to be a visible demonstration of the mechanism of diffusion.

1.9 Specific Gaseous Diffusion

Gaseous diffusion often demonstrated [4] (Figure 8) by the reaction between gaseous NH_3 and HCl. Two cotton plugs soaked with aqueous NH_3 and HCl are placed simultaneously at the ends of a long glass tube the evaporating molecules travel in opposite directions. After a few minutes the NH_3 and HCl meet at a point forming a ring of white fume of NH_4Cl. This is the reaction point.

The distance travelled by NH_3 and HCl molecules as well as the time required for the reaction to occur were recorded. The relative velocities of NH_3 and HCl in cms^{-1} were calculated.

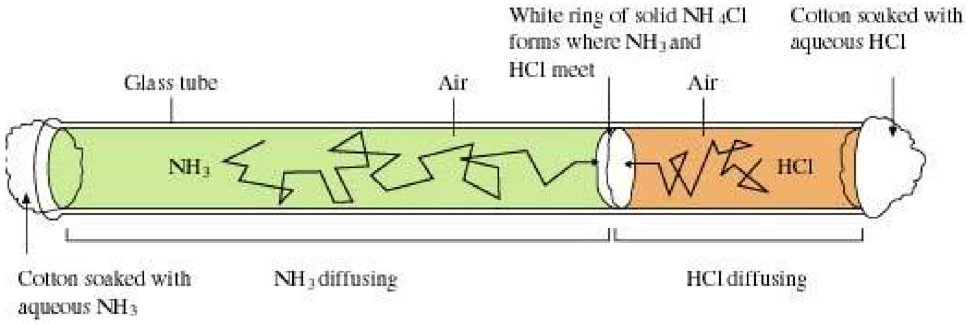

Figure 8: A Gas-Diffusion Tube

The lighter gas moves faster than the heavier as is evident in figure-8, where the white fume forms closer to the HCl plug and further from the NH_3 plug.

Molecules of gases move with very high speeds. They collide as they move. The numbers of such collisions is also very high. Collisions make the molecules slow. The velocities of NH_3 and HCl molecules at 25° C are 450 and 660 ms^{-1} respectively, whereas it takes quite a time for the NH_3 and HCl to meet inside the diffusion tube.

Effusion is also a well elucidated and extensively applied gaseous property, being defined as the licking of a gas through a small aperture. The grahams law of diffusion states; the diffusion rate of a gas is inversely proportional to the square root of molar its mass; mathematically it is represented in equation as:

$$V_d \infty \frac{1}{m}$$

The Grahams law of effusion[4] states that the effusion rate of a gas through a given orifice is inversely proportional to the square root of its molar mass.

1.10.1 Fick's law and the basis of diffusion

In 1855, physiologist Adolf Fick first reported[5] his now-well-known laws governing the transport of mass through diffusive means. He published on liquid diffusion mathematically treating salt movement in liquids as a diffusion process, analogous to heat diffusion. Less recognized is the fact that Fick also provided a detailed account of the implications of salt diffusion to transport through membranes. A careful look at Fick [1855] shows that his conceptualization of molecular diffusion was more comprehensive than could be captured with the mathematical methods available to him, and therefore his expression referred to as Fick's law dealt only with salt flux. He viewed salt diffusion in liquids as a binary process, with salt moving in one way and water moving in the other.

Fick's analysis of the consequences of such a binary process operating in a hydrophilic pore in a membrane offers insights that are relevant to earth system. [6] It is no Table that Fick's work primarily concerned diffusion in fluids, because at the time, diffusion in solids was not considered generally possible. In this theoretical framework, diffusion is due to fluctuations whose dimensions range from the molecular scale to the macroscopic scale**.** [7]

1.10.2 Fick's first law

It 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 (spatial derivative). In one (spatial) dimension, this is

$$J = -D\frac{\partial \phi}{\partial x}$$

Where, J is the diffusion flux in dimensions of [(amount of substance) $L^{-2}t^{-1}$]. J measures the amount of substance that will flow through a small area during a small time interval. D

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[4]. *J. B. Russel , General Chemistry, 2nd Ed., McGraw Hill, 1992, pp 137-139.*

[5]. *Fick,A. (1855), On liquid diffusion, Philos.Mag.J. Sci.,10, 31–39.*

[6]. *D. Brogioli and A. Vailati, Diffusive mass transfer by nonequilibrium fluctuations: Fick's law revisited, Phys. Rev. E 63, 012105/1-4 (2001)*

[7]. *Bird, R.B. (1956),Theory of diffusion,Adv.Chem. Eng.,1, 156–239.*

is the diffusion coefficient or diffusivity in dimensions of [$L^{-2}t^{-1}$], ϕ (for ideal mixtures) is the concentration in dimensions of [(amount of substance) L^{-3}], x is the position [L].

D is proportional to the squared velocity of the diffusing particles, which depends on the temperature, viscosity of the fluid and the size of the particles according to the Stokes-Einstein relation. In dilute aqueous solutions the diffusion coefficients of most ions are similar and have values at room temperature in the range of 0.6×10^{-9} to 2×10^{-9} m^2/s. For biological molecules the diffusion coefficients normally range from 10^{-11} to 10^{-10} m^2/s.

In two or more dimensions we must use ∇, the Del or gradient operator, which generalizes the first derivative, obtaining

$$J = -D\nabla$$

The driving force for the one-dimensional diffusion is the quantity $\frac{\partial \phi}{\partial x}$ which for ideal mixtures is the concentration gradient. In chemical systems other than ideal solutions or mixtures, the driving force for diffusion of each species is the gradient of chemical potential of this species. Then Fick's first law (one-dimensional case) can be written as

$$J_i = -\frac{Dc_i}{RT}\frac{\partial \mu_i}{\partial x}$$

Where the index i denotes the ith species, c is the concentration (mol/m^3), R is the universal gas constant (J/(K mol)), T is the absolute temperature (K), and μ is the chemical potential (J/mol).

1.10.3 Fick’s second law

Fick's second law predicts how diffusion causes the concentration field to change with time:

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2}$$

Where, ϕ is the concentration in dimensions of [(amount of substance) $length^{-3}$], t is time (s), D is the diffusion coefficient in dimensions of [$length^2 time^{-1}$], x is the position [length].

It can be derived from Fick's First law and the mass balance:

$$\frac{\partial \phi}{\partial t} = -\frac{\partial}{\partial x}J = \frac{\partial}{\partial x}(D\frac{\partial}{\partial x}\phi)$$

Assuming the diffusion coefficient D to be a constant we can exchange the orders of the differentiating and multiplying by the constant:

$$\frac{\partial}{\partial x}(D\frac{\partial}{\partial x}\phi) = D\frac{\partial}{\partial x}\frac{\partial}{\partial x}\phi = D\frac{\partial^2\phi}{\partial x^2}$$

And, thus, receive the form of the Fick's equations as was stated above.

For the case of diffusion in two or more dimensions Fick's Second Law becomes

$$\frac{\partial\phi}{\partial t} = D\nabla^2\phi,$$

which is analogous to the heat equation.

If the diffusion coefficient is not a constant, but depends upon the coordinate and/or concentration, Fick's Second Law yields

$$\frac{\partial\phi}{\partial t} = \nabla.(D\nabla\phi)$$

An important example is the case where φ is at a steady state, i.e. the concentration does not change by time, so that the left part of the above equation is identically zero. In one dimension with constant D, the solution for the concentration will be a linear change of concentrations along x. In two or more dimensions we obtain which is Laplace's equation $\nabla^2\phi = 0$. Solutions which are called harmonic functions by mathematicians [8] [9] [10]

1.11 The characteristic and the extent of diffusion coefficient or Diffusivity- D

Treating Brownian motion as a three dimensional random walk, the mean Brownian displacement x of a particle from its original position along a given axis after a time t is given by Einstein's equation

$$D = \frac{t}{2}(\frac{x^2}{t^2}) \text{ Or } D \ \infty \ V^2 \qquad (3)$$

D, is the diffusion coefficient. The diffusion coefficient of a suspended material is related to the frictional coefficient f, of the particles by Stoke Einstein,

$$D\,\mathrm{f} = \mathrm{Kt} \qquad (4)$$

Where, f=6Πηa, η the viscosity of medium and 'a' is the radius of the particle.

D, is proportional to the squared velocity, v, of the diffusing particles according to Stoke Einstein equation and depends on the temperature, viscosity of the fluid and the size of the particles. in dilute aqueous solutions the diffusion coefficients of most ions are similar and

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[8]. *Cussler,E. L (1984), Diffusion, Mass Transfer in FluidSystems, 525 pp.,Cambridge Univ. Press,N.Y.*

[9]. Atkins, Peter (1998), Physical Chemistry (6th ed.), New York: Freeman, pp. 180

[10]. *W.F. Smith, Foundations of Materials Science and Engineering 3rd ed., McGraw-Hill (2004)*

have values that at room temperatures are in the range of 0.6×10^{-9} to2×10^{-9} For a system containing a spherical particles, $D \ \infty \ \frac{1}{\sqrt[3]{m}}$, where m is the particle mass. For systems containing asymmetric particles, D is correspondingly smaller. Since $D = \frac{kt}{f}$, the ratio D/D_o, D being the experimental diffusion coefficient and D_o the coefficient of system containing the equivalent un-solvated spheres, is equal to the reciprocal of frictional ratio f/f_o.

1.12 An experiment to demonstrate diffusion

Diffusion is not easy to observe, because other transport phenomena, especially convocation, are more efficient on length scales above millimeters. Diffusion is most important on microscopic scales. Diffusion can demonstrated with a wide glass tube, paper, two corks, some cotton wool soaked in ammonia solution and some red litmus paper. By corking, the two ends of a wide glass-tube and plugging the wet cotton wool with one of the corks, and litmus paper can hang with a thread within the tube. It will observe that the red litmus papers turn blue. This is because the ammonia molecules travel by diffusion from the higher concentration in the cotton wool to the lower concentration in the rest of the glass tube. As ammonia solution is alkaline, the red litmus papers turn blue. By changing the concentration of ammonia, the rate of color change of the litmus papers can changed.

1.13 Types of Diffusion

Fundamentally, two types of diffusion are distinguished:

Tracer diffusion is a spontaneous mixing of molecules which taking place in the absence of concentration (or chemical potential) gradient. This type of diffusion can be followed using isotopic tracers, hence the name. The tracer diffusion usually assumed to be identical to self-diffusion (assuming no significant isotopic effect). This diffusion can take place under equilibrium.

Chemical diffusion occurs in the presence of concentration (or chemical potential) gradient and it results in net transport of mass. This is the process described by the diffusion equation. This diffusion is always a non-equilibrium process, increases the system entropy, and brings the system closer to equilibrium.

The diffusion coefficients for these two types of diffusion are generally different because the diffusion coefficient for chemical diffusion is binary and it includes the effects due to the correlation of the movement of the different diffusing species.

1.14 Other types of diffusion

The spreading of any quantity that can be described by the diffusion equation or a random walk model e.g. concentration, heat, momentum, ideas, price can be called diffusion. Some of the most important examples are been listed below:

- Atomic diffusion
- Brownian motion, for example of a single particle in a solvent
- Collective diffusion, the diffusion of a large number of possibly interacting, particles
- Eddy diffusion
- Diffusion of gas through small holes
- Electronic diffusion, resulting in an electric current called the diffusion current
- Facilitated diffusion, present in some organisms
- Gaseous diffusion, used for isotope separation
- Heat equation
- Ito diffusion
- Knudsen diffusion
- Momentum diffusion, ex. the diffusion of the hydrodynamic velocity field
- Osmosis is the diffusion of water through a cell membrane
- Photon diffusion
- Reverse diffusion
- Surface diffusion

1.15 Osmosis

The phenomenon of osmosis (from the Greek word for push) is the spontaneous passage of a pure solvent into a solution separated from it by a semi permeable membrane, a membrane permeable to the solvent but not to the solute[11]. It is the diffusion of water (solvent) through a semi permeable membrane[12] from a region of low solute concentration to a region of high solute concentration. The semi permeable membrane is permeable to the solvent, but not to

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[11] *. A. Fick, Phil. Mag. (1855), 10, 30. (in English)*

[12] *Haynie, Donald T. (2001), Biological Thermodynamics, Cambridge: Cambridge University Press, pp. 130–136*

the solute, resulting in a chemical potential difference across the membrane which drives the diffusion. That is, the solvent flows from the side of the membrane where the solution is weakest to the side where it is strongest, until the solution on both sides of the membrane is the same strength (that is, until the chemical potential is equal on both sides).

As mentioned before, osmosis can be opposed by increasing the pressure in the region of high solute concentration with respect to that in the low solute concentration region. The force per unit area required to prevent the passage of water through a semi-permeable membrane and into a solution of greater concentration is equivalent to the osmotic pressure of the solution or turgor. Osmotic pressure is a colligate property, meaning that the property depends on the concentration of the solute but not on its identity.

Diffusion through a Semi permeable Membrane

Some major examples of osmosis:

* Absorption of water by plant roots.
* Re absorption of water by the proximal and distal convoluted tubules of the nephron.
* Re absorption of tissue fluid into the venule ends of the blood capillaries.
* Absorption of water by the alimentary canal - stomach, small intestine and the colon.

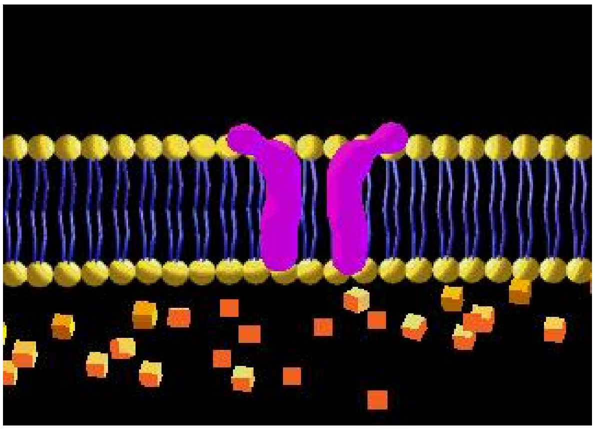

Figure 9: particles moving through a plasma membrane

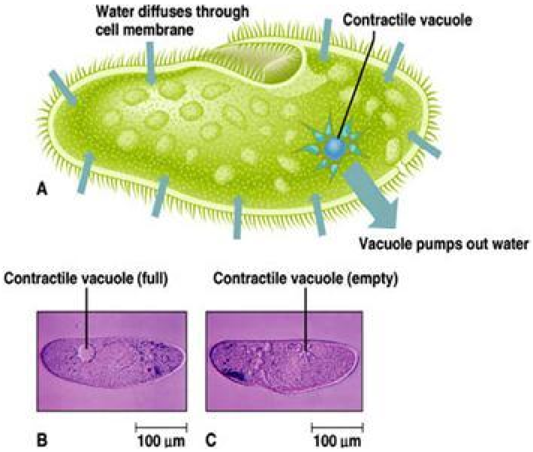

Figure 10: The kidneys maintain the blood at the correct concentration

This figure shows osmosis of particles. Note that when the particles are distributed equally on both sides of the membrane the osmosis stops.

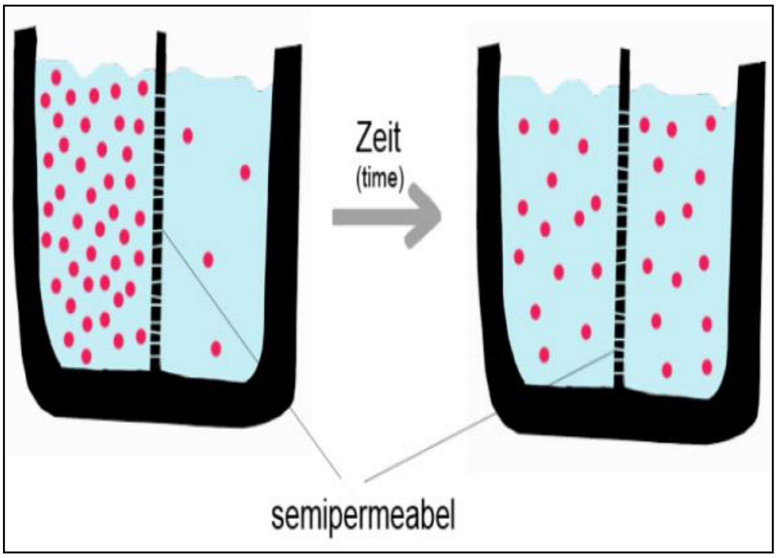

Figure 11: A Mechanism of Osmosis.

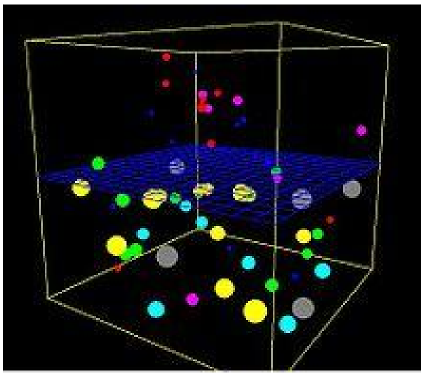

Figure 12: One frame of a computer simulation of osmosis

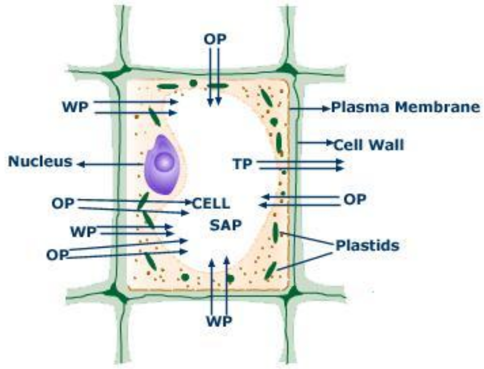

Figure 13: The actual pressure exerted by the protoplasm of turgid cell against cell wall is the turgor pressure

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The diagrams are showing relationship of Osmotic Pressure (OP), Turgor Pressure (TP) and Wall Pressure (WP). The actual pressure exerted by the protoplasm of turgid cell against cell wall is the turgor pressure.

Osmosis is an important topic in biology because it provides the primary means by which water is transported into and out of cells. Osmosis may occur when there is a partially permeable membrane, such as a cell membrane. When a cell is submerged in water, the water molecules pass through the cell membrane from an area of low solute concentration (outside the cell) to one of high solute concentration (inside the cell), this is called osmosis. The cell membrane is selectively permeable, so only necessary materials are let into the cell and waste left out. Pure water is more ordered than water in a solution; thus, from an entropic standpoint it takes some net energy to move water molecule from a disordered solution and "pack it in" with pure water. This is the same explanation as to why the disordered air does not spontaneously separate and order into oxygen and nitrogen; it would take energy for this to happen. Additionally, particle size has nonbearing on osmotic pressure, as this is the fundamental postulate of colligative properties.[13]

1.16 Light diffusion

The propagation of light through complex media is often diffusive. Take, for example, the scattering of sunlight through fog or dust in air, where it can be difficult to determine from where the light originates. This is a phenomenon that very often escapes our understanding but not our perception: light scatters by fat in a glass of milk or sunlight is dispersed through dust in air, the white of teeth or of chalk. Contrast this with photonic crystals, which transport light in a coherent manner. Disordered scattering elements may scramble an incident light beam, but we have found that substantial control of light transport can be, achieved even in presence of strong disorder. Disorder – which is normally regarded as a weakening factor in photonic devices plays a central role, and may make it possible to engineer the flow of diffuse light.

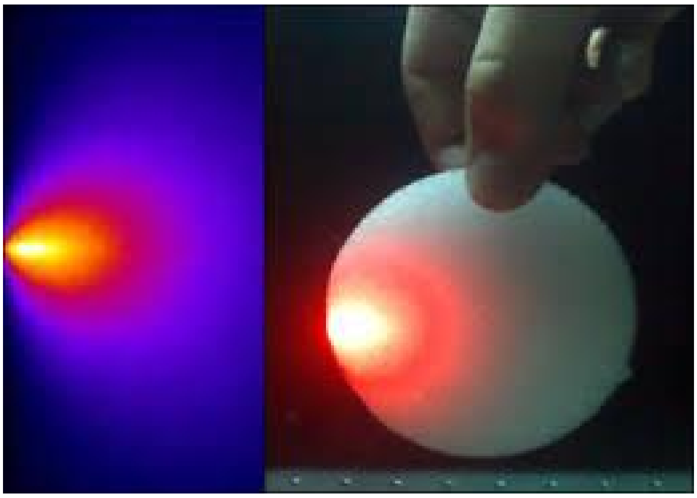

Figure 14: Light diffusion

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[13] *Borg, Frank (2003). "What is osmosis? Explanation and understanding of a physical phenomenon". Jyväskylä University, Chydenius Institute, Karleby, Finland. pp. 1-39.*

Diffusion is the net movement of molecules from a region of high concentration to a region of lower concentration due to random motion of molecules. In a solution with equal concentration at all places, some molecules will be moving out of a region at the same time other molecules are moving into that region. Molecules move in all directions and are in continual motion.

1.17 Atomic diffusion

Atomic diffusion is a diffusion process whereby the random thermally-activated movement of atoms in a solid results in the net transport of atoms. For example, helium atoms inside a balloon can diffuse through the wall of the balloon and escape, resulting in the balloon slowly deflating. Other air molecules (e.g. oxygen, nitrogen) have lower mobility and thus diffuse more slowly through the balloon wall. There is a concentration gradient in the balloon wall, because the balloon was initially filled with helium, and thus there is plenty of helium on the inside, but there is relatively little helium on the outside (helium is not a major component of air). The rate of transport is governed by the diffusivity and the concentration gradient.

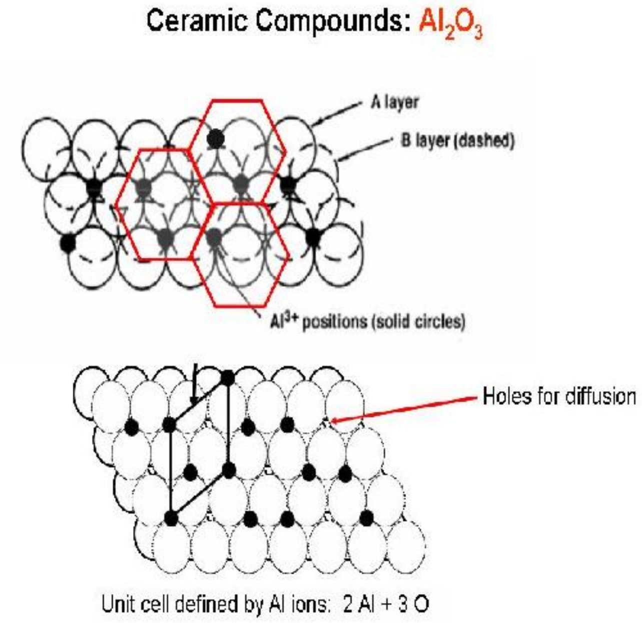

Figure 15: Atomic diffusion in crystal

1.18 Surface diffusion:

The figure is the model of single adatom diffusing across a square surface lattice. The frequency of vibration of the adatom is greater than the jump rate to nearby sites. Also, the model displays examples of both nearest-neighbor jumps (straight) and next-nearest-neighbor jumps (diagonal). Not to scale on a spatial or temporal basis.

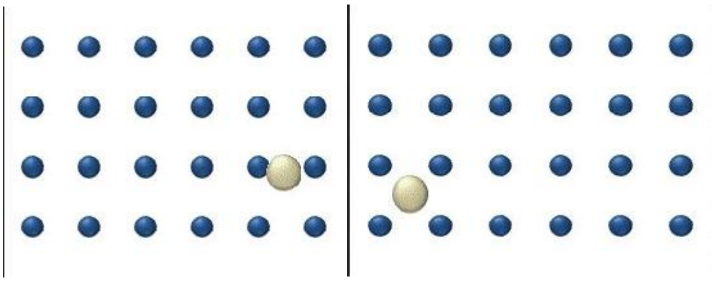

Figure 16: Surface diffusion

Surface diffusion is a general process involving the motion of adatoms, molecules, and atomic clusters (adparticles) at solid material surfaces.[14] The process can generally be thought of in terms of particles jumping between adjacent adsorption sites on a surface, as in figure.

1.19 Chemical diffusion

The adatoms block each other from moving to adjacent sites. As per Fick's law, flux is in the opposite direction of the concentration gradient, a purely statistical effect. The model is not intended to show repulsion or attraction and is not to scale on a spatial or temporal basis.

1.20 Intrinsic diffusion

It's occurs on a uniform surface (e.g. lacking steps or vacancies) such as a single terrace, where no adatom traps or sources are present. This regime is often studied using field ion microscopy, where in the terrace is a sharp sample tip on which an adparticle diffuses. Even in the case of a clean terrace the process may be influenced by non-uniformity near the edges of the terrace.

1.21 Atomic exchange

Atomic exchange involves exchange between an adatom and an adjacent atom within the surface lattice. After an atomic exchange event the adatom has taken the place of a surface atom and the surface atom has been displaced and has now become an adatom. This process may take place in both hetero diffusion (e.g. Pt adatoms on Ni) and self-diffusion (e.g. Pt adatoms on Pt). It is still unclear from a theoretical point of view why the atomic exchange

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[14] . *Oura, Lifshits, Saranin, Zotov, and Katayama 2003, p. 325*

mechanism is more predominant in some systems than in others. Current theory points towards multiple possibilities, including tensile surface stresses, surface relaxation about the adatom, and increased stability of the intermediate due to the fact that both atoms involved maintain high levels of coordination throughout the process. [15]

1.22 Tunneling diffusion

Tunneling diffusion is a physical manifestation of the quantum tunneling effect involving particles tunneling across diffusion barriers. It can occur in the case of low diffusing particle mass and low Ediff, and has been observed in the case of hydrogen diffusion on tungsten and copper surfaces.[16] The phenomenon is unique in that in the regime where the tunneling mechanism dominates, the diffusion rate is nearly temperature-independent.[17]

1.23 Vacancy diffusion

Vacancy diffusion can occur as the predominant method of surface diffusion at high coverage levels approaching complete coverage. This process is akin to the manner in which pieces slide around in a "sliding puzzle". It is very difficult to directly observe vacancy diffusion due to the typically high diffusion rates and low vacancy concentration.[18]

1.24 Cluster diffusion

Cluster diffusion involves motion of atomic clusters ranging in size from dimers to islands containing hundreds of atoms. Motion of the cluster may occur via the displacement of individual atoms, sections of the cluster, or the entire cluster moving at once. All of these processes involve a change in the cluster’s center of mass.

1.25 Turbulent diffusion

Turbulent diffusion is the transport of mass, heat, or momentum within a system due to random and chaotic time dependent motions.[19] It occurs when turbulent fluid systems reach critical conditions in response to shear flow, which results from a combination of steep concentration gradients, density gradients, and high velocities. It occurs much more rapidly than molecular diffusion and is therefore extremely important for problems concerning mixing and transport in systems dealing with combustion, contaminants, dissolved oxygen,

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[15] *Antczak, Ehrlich 2007, p. 48*

[16] *Oura, Lifshits, Saranin, Zotov, and Katayama 2003, p. 338-340*

[17] *Shustorovich 1991, p. 115*

[18] *Oura, Lifshits, Saranin, Zotov, and Katayama 2003, p. 340-341*

[19] *Hideto Yoshida; Masuda, Hiroaki; Higashitani, Kō (2006). Powder Technology Handbook (3rd ed.). Boca Raton*

and solutions in industry. In these fields, turbulent diffusion acts as an excellent process for quickly reducing the concentrations of a species in a fluid or environment, in cases where this is needed for rapid mixing during processing, or rapid pollutant or contaminant reduction for safety.

However, it has been extremely difficult to develop a concrete and fully functional model that can be applied to the diffusion of a species in all turbulent systems due to the inability to characterize both an instantaneous and predicted fluid velocity simultaneously. In turbulent flow, this is a result of several characteristics such as unpredictability, rapid diffusivity, high levels of fluctuating vorticity, and dissipation of kinetic energy.[20]

1.26 Convection diffusion

The convection–diffusion is a combination of the diffusion and convection (advection) process, and describes physical phenomena where particles, energy, or other physical quantities are transferred inside a physical system due to two processes: diffusion and convection.

Theory of mechanism of convective diffusion in our experiment:
Convection may happen in fluids at all scales larger than a few atoms. There are a variety of circumstances in which the forces required for natural and forced convection arise, leading to different types of convection. In broad terms, convection arises because of body forces acting within the fluid, such as gravity (buoyancy), or surface forces acting at a boundary of the fluid.

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[20]. *Roberts, P.J.W., & Webster, D.R. (2002). "Turbulent Diffusion". In Shen, Hayley H.. Environmental fluid mechanics: theories and applications. New York: American Society of Civil Engineers.*

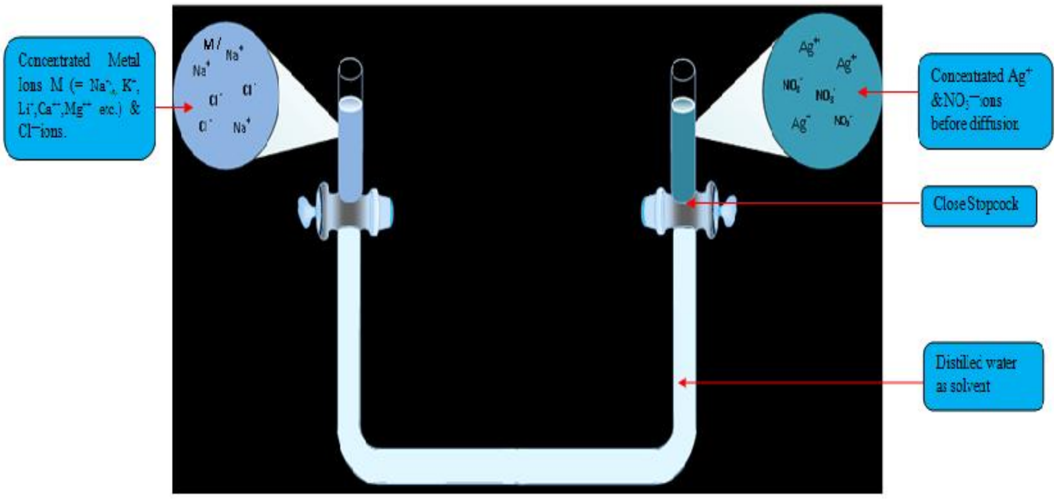


Figure 17: Instrument before diffusion

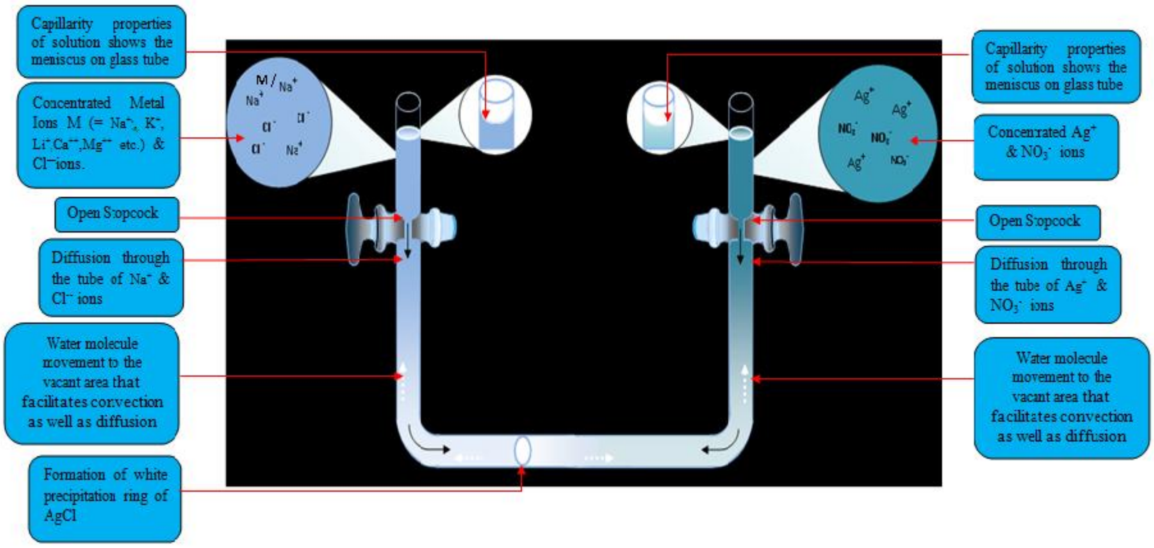


Figure 18: During Diffusion

1.27 Natural convection:

Natural convection, or free convection, occurs due to temperature differences which affect the density, and thus relative buoyancy, of the fluid. Heavier (more dense) components will fall, while lighter (less dense) components rise, leading to bulk fluid movement. Natural convection can only occur, therefore, in a gravitational field. A common example of natural convection is the rise of smoke from a fire. it can be seen in a pot of boiling water in which the hot and less-dense water on the bottom layer moves upwards in plumes, and the cool and more dense water near the top of the pot likewise sinks.

1.28 Forced convection:

In forced convection, also called heat advection, fluid movement results from external surface forces such as a fan or pump. Forced convection is typically used to increase the rate of heat exchange. Many types of mixing also utilize forced convection to distribute one substance within another. Forced convection also occurs as a by-product to other processes, such as the action of a propeller in a fluid or aerodynamic heating. Fluid radiator systems, and also heating and cooling of parts of the body by blood circulation, are other familiar examples of forced convection.

Forced convection may happen by natural means, such as when the heat of a fire causes expansion of air and bulk airflow by this means. In microgravity, such flow (which happens in all directions) along with diffusion is the only means by which fires are able to draw in fresh oxygen to maintain themselves. The shock wave that transfers heat and mass out of explosions is also a type of forced convection.

1.29 Gravitational or buoyant convection:

Gravitational convection is a type of natural convection induced by buoyancy variations resulting from material properties other than temperature. Typically this is caused by a variable composition of the fluid. If the varying property is a concentration gradient, it is known as solutal convection. For example, gravitational convection can be seen in the diffusion of a source of dry salt downward into wet soil due to the buoyancy of fresh water in saline.

1.30 Granular convection:

Vibration-induced convection occurs in powders and granulated materials in containers subject to vibration where an axis of vibration is parallel to the force of gravity. When the container accelerates upward, the bottom of the container pushes the entire contents upward. In contrast, when the container accelerates downward, the sides of the container push the adjacent material downward by friction, but the material more remote from the sides is less affected. The net result is a slow circulation of particles downward at the sides and upward in the middle.

If the container contains particles of different sizes, the downward-moving region at the sides is often narrower than the largest particles. Thus, larger particles tend to become sorted to the top of such a mixture. This is one possible explanation of the Brazil nut effect.

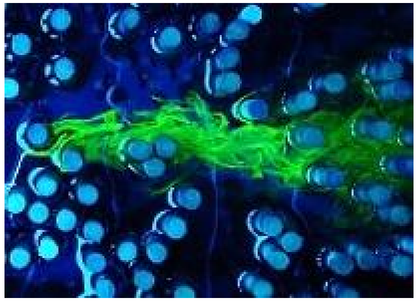
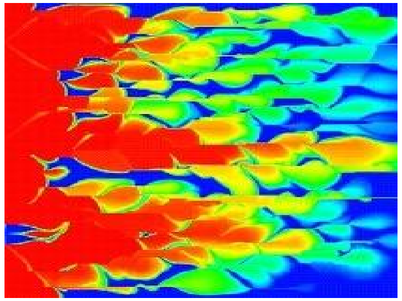
1.31 Thermo magnetic convection:

Thermo magnetic convection can occur when an external magnetic field is imposed on a Ferro-fluid magnetic field with varying magnetic susceptibility. In the presence of a temperature gradient this results in a non uniform magnetic body force, which leads to fluid movement. A Ferro-fluid is a liquid which becomes strongly magnetized in the presence of a magnetic field.

This form of heat transfer can be useful for cases where conventional convection fails to provide adequate heat transfer, e.g., in miniature micro scale devices or under reduced gravity conditions.

Table1.32: Difference between Convection Diffusion and Turbulent Diffusion

No	Subject matter	Turbulent diffusion	Convection diffusion
01	Definition	It is the transport of mass, heat or momentum within a system due to random and chaotic time dependent motions	It is the physical phenomena where particles, energy or other physical quantities are transferred inside a physical system due to convection and diffusion simultaneously.
02	Process rate	Vigorous process	Slower process
03	Occurrence	Occurs when turbulence system reach against – • Concentration gradient • Density gradient in critical condition of high velocity	Occurs when collective movement of molecules within fluids ensembles by the transfer of mass and energy.
04	Occurrence phase	Occurs in – liquid, gases, plasmas and solids	Occurs in liquids and gases, not in solids.
05	Double diffusive possibility	As it is random and chaotic process there is no chance of double diffusivity	Double diffusion may occur such as double diffusion convection
06	Fluid concentration	Acts as an excellent process for quickly reducing the concentration of species in a fluid or environment	Do not deal with the concentration gradient of molecules with in a system.
07	Dealings	Deals with the molecular- • concentration and • density • shear flow	Deals with molecular – • Energy and • enthalpy
08	Equation Derivation	Turbulent flow equation is derived from – • Elurean approach and • Lagrangian approach model is used	Convective diffusion derived from – • Continuity equation
09	Application of equation	For analyzing the statistics of species in turbulent flow	For describing the flow of ions dissolved in a liquid, with an electric field pulling the ions in some direction (as in gel electrophoresis)
10	Similarity	Turbulent flow equation is unique equation that	It is formally identical with the –

	with other equation	follows Elurean and Lagrangian model	• Fokker – Planck equation • Black – Scholes equation • Navier – Stokes equation
11	Explanation of other formula	Integrate Fickian diffusion theory	Einstein relation of kinetic theory may explain through convective-diffusion equation
12	Difficulties of application of formula	Applying mathematical equations to turbulent flow and diffusion is so difficult	Much easier compared to turbulent diffusion
13	Application	Concerns with mixing and transport system dealing with – • Combustion • Contaminants • Dissolved oxygen • Contaminants • Atmospheric diffusion and pollutants	It is mainly applied in - semiconductor physics
14	Figure	 Turbulent diffusion of molecule due to spatial heterogeneity in the velocity field	 Fluid convection, diffusion and dissolution reaction inside a finite space.

1.33 Hydrates

Hydrates are inorganic salts "containing water molecules combined in a definite ratio as an integral part of the crystal"[21] either that are bound to a metal center or that have crystallized with the metal complex. Such hydrates are also said to contain water of crystallization or water of hydration. If the water is heavy water, where the hydrogen involved is the isotope deuterium, then the term deuterate may be used in place of hydrate. Cobalt(II) chloride hexa hydrate

$Co(H_2O)_6Cl_2$A colorful example is cobalt(II) chloride, which turns from blue to magenta (red) upon hydration, and can therefore be used as a water indicator. The notation of hydrous compound · nH_2O, where n is the number of water molecules per molecule of salt, is commonly used to show that a salt is hydrated. The n is usually a low integer, though it is possible for fractional values to exist. In a monohydrate n is one, in a hexa hydrate n is 6 etc. Such water is also referred to as water of crystallization. Examples include borax deca hydrate and chalcanthite. Gas hydrates are clathrate hydrates (a class of solid hydrates of gases): water ice with gas molecules trapped within. When the gas is methane, it is called a methane hydrate. Many of this hydrates contain approximately 6-8 H_2O or 17 H_2O for every molecule (or atom) of solute. A hydrate which has lost water is referred to as an anhydride, and can normally lose further water only upon strong heating, if at all. A substance that does not contain any water is referred to as anhydrous.

1.34.1 Atmospheric diffusion and pollutants

Atmospheric dispersion, [22] or diffusion, studies how pollutants are mixed in the environment. There are many factors included in this modeling process, such as which level of atmosphere(s) the mixing is taking place, the stability of the environment and what type of contaminant and source is being mixed. The Eulerian and Lagrangian (discussed below) models have both been used to simulate atmospheric diffusion, and are important for a proper understanding of how pollutants react and mix in different

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[21] *Hydrate". Farlex, Inc (TheFreeDictionary.com. http://www.thefreedictionary.com/hydrate. Retrieved 2009-07-08*

[22]. *Beychok, M.R. (2005). Fundamentals Of Stack Gas Dispersion (4th Edition ed.).*

environments. Both of these models take into account both vertical and horizontal wind, but additionally integrate Fickian diffusion theory to account for turbulence. While these methods have to use ideal conditions and make numerous assumptions, at this point in time, it is difficult to better calculate the effects of turbulent diffusion on pollutants. Fickian diffusion theory and further advancements in research on atmospheric diffusion can be applied to model the effects that current emission rates of pollutants from various sources have on the atmosphere.[23]

1.34.2 Turbulent diffusion flames

Using planar laser-induced fluorescence (PLIF) and particle image velocimetry (PIV) processes, there has been on-going research on the effects of turbulent diffusion in flames. Main areas of study include combustion systems in gas burners used for power generation and chemical reactions in jet diffusion flames involving methane (CH_4), hydrogen (H_2) and nitrogen (N_2). [24] Additionally, double-pulse Rayleigh temperature imaging has been used to correlate extinction and ignition sites with changes in temperature and the mixing of chemicals in flames.[25]

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[23]. *Walcek, C. J. (2002). "Effects of wind shear on pollution dispersion". Atmospheric Environment36 (3): 511–7.*

[24]. *Su, L. K., Sun, O. S., & Mungal, M. G. (2006). "Experimental investigation of stabilization mechanisms in turbulent, lifted jet diffusion flames". Combustion and Flame144 (3): 494–512.*

[25]. *Hult, J., Meier, U., Meier, W., Harvey, A., & Kaminski, C. F. (2005). "Experimental analysis of local flame extinction in a turbulent jet diffusion flame by high repetition 2-D laser techniques and multi-scalar measurements". Proceedings of the Combustion Institute30 (1): 701–9*

1.34.3 Application to Thermodynamics

[26] Thomas Graham (1805-1869), a Scottish chemist, found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. In other words, the relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles. The equation is

$$\frac{\text{Rate of effusion of gas}_1}{\text{Rate of effusion of gas}_2} = \sqrt{\frac{M_2}{M_1}}$$

WhereM_1 and M_2represent the molar masses of the gases. This equation is known as Graham's Law of Effusion.

The effusion rate for a gas depends directly on the average velocity of its particles. Thus, the faster the gas particles are moving, the more likely they are to pass through the effusion orifice. A figure of Graham's law of effusion linked below shows the rate of effusion (the rate at which the gas is transferred across the barrier through the pin hole) is inversely proportional to the square root of the mass of the gas molecules.

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[26]. *Zumdahl, Steven S. (2008). Chemical Principles. Boston: Houghton Mifflin Harcourt Publishing Company.*

Chapter Two

EXPERIMENTAL

Experimental

2.1 Experimental

This dissertation describes the process of manufacturing a newly invented glass diffusion tube being used to carry out a whole variety of chemical experiments in order to determine the relative diffusion velocities of solutes in water and thus to discover the 'Law of Electrolytic Diffusion' in one direction in a close system.

The law is a universal law and in the course of time the Reaction Diffuser [27] will be used in chemistry, chemistry related sciences, geology, biomedical engineering and environmental studies.

Chemistry is best known by its reactions in water as solvent. The glass diffusion tube termed as the Reaction Diffuser, Figure-5, can conveniently be used to carry out diffusion controlled reactions in water. Twenty two experiments were accomplished in water with interesting results.

The invention and discovery will find wide application in Chemistry, Chemical Engineering, Hydrogeology, Biomedical Engineering, Environment and a host of other fields.

Table 2.2: Abbreviations and definitions of new terminologies extensively used in write up that follows

Vd	Relative Velocity of Diffusion		T	Temperature in Kelvin
DPL	Diffusion Path Length		MMX	Molar Mass of compound MX. E.g., MNaCl = 58.45
SBD	Stopcock Bore Diameter		[MX]	Molarity of MX solution
VRS	Volume of Reactant Solution		MM	Atomic Weight of Element M. E.g., MNa = 23.00
DT	Distance Traveled		ZM	Atomic Number of Element M. E.g., ZNa = 11
DTR	Distance Traveled Ratio			

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[27] *Khair A, Golzar Hossain GM, Saiful Alam M, and Zakir Hossain Shaheen M (2010) Bangladesh Patent, Int. Cl^5 G01 N 13/00, 1004924.*

Table 2.3: Key Words

Reaction Diffuser	The newly invented glass diffusion tube having two vertical arms as one-way stopcocks, joined unidirectional and perpendicular to a long glass base tube.
Congenus Reactants and Syngenus Reactant	A series of reactants group wise or period wise or mixed, capable of yielding a common product with a single reactant is newly named as the Congenus Reactants, and the single reactant as the Syngenus Reactant. E.g. 1. In the reaction of Period-4 halides, KCl-$ZnCl_2$, with $AgNO_3$, the Period-4 halides are the Congenus Reactants and $AgNO_3$ is the Syngenus Reactant. 2. In the Group-1 sulfates reaction with $BaCl_2$, the sulfates are termed as the Congenus and the $BaCl_2$ as the Syngenus reactants. 3. The compound $FeNH_4(SO_4)_2.12H_2O$, $FeCl_3$ and $Fe(NO_3)_3$ reacts with NH_4SCN to give red $Fe(SCN)_3$ in solution. Here the formers are the Syngenus and the latter is the Syngenus Reactants.
Diffusimetric Method	The method of doing chemical experiments using a Reaction Diffuser.

2.4 Manufacturing Process of the Reaction Diffuser

The Reaction Diffuser is manufactured according to the following steps:

Step1. Two one-way stopcocks of identical stem and stopcock bore are taken. Also taken is a glass tube of suitable length and of bore closely similar to the stem of the stopcocks.

Step2. The ends of the long glass tube as base are joined to the two stopcocks parallel to each other and at 90o to the base with the stopcock keys outward. The Reaction Diffuser looks like a flat bottomed U-tube as in Figure-20.

Step 3: The upper stems of the stopcocks are cut off such that the lengths, AB and HG, are sufficient to contain 2-10 mL of the reactant solution.

Step 4: The Diffusion Path Length, CF, is measured using a narrow strip of paper holding it tight at D and E making sure that one end of the strip coincided with the point, C and the other reached the point F. A pencil mark spotted the point F and any extra length of paper above F is cut off. The strip length being the diffusion path length is measured in centimeter scale. Similarly DC, EF, AB and HG lengths are measured. Horizontal clamping of the Reaction Diffuser in each experiment was ensured using surveyor's level.

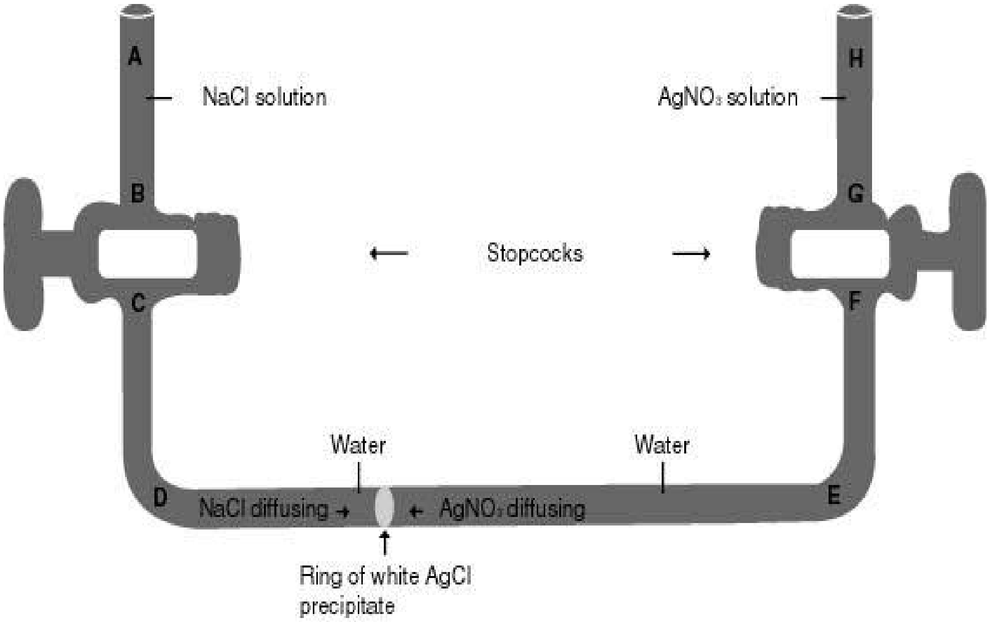

Figure 19: **The Reaction Diffuser**

Replicating the Reaction Diffuser with the same parameters using manual glass blowing is impossible. Identical parameters would only be ensured through controlled and regulated manufacturing process. Indeed Reaction Diffusers of different parameters can be adopted to satisfy different needs. It's like having pipettes of different volumes. Important to note is that stopcock bore of any diameter satisfies the newly discovered law. Higher diameter ensures higher velocity.

Referring back to Figure-20 the DC and EF as also AB and HG lengths should be optimum and equal. Indeed the stopcocks are the arms of the U-tube. The reaction diffuser is represented by the ABCDEFGH or AH line. The points D and E are the inward-surface mid points of the bents at the two joints. The CDEF or CF distance is taken as the diffusion path length, DPL. The BC and GF are the lengths of the two stopcock holes not included in the DPL.

Step 5: The reaction diffuser can be filled with water above B and G, holding the tube slanting initially and then horizontal, making sure that no bubble sticks in the diffusion path. On closing the stopcocks and turning the tube upside down, the liquid above B and G can be drained off. Any residual water is removed using dropper. This exercise will leave the diffusion tube and the stopcock holes water filled.

Table-2.5: Dimensions of the Reaction Diffusers Used in this Study

Sl No.	Diffusion Path Length, DPL, i.e., CDEF = CF cm	CD and EF, cm	Stopcock bore diameter, SBD, cm	Water volume contained in DPL, mL	Volume of the Reactant Solution, VRS, taken in AB and HG, mL	Outside diameter of stopcock stem, cm	Observation
	1	2	3	4	5	6	7
1	28.2	3.5 and 4.0	0.45	25.0	2.0	0.9	A Reaction Diffuser once damaged could not be replicated by manual glass blowing.
2	16.9	2.5 and 2.7	0.45	14.0	2 and 1.2	0.9	
3	33	4.2	0.45	28.5	2.0	0.9	
4	24.3	5.0 and 5.4	0.9	32.7	2.0	1.4	

Step 6: The reaction diffuser requires frequent cleaning to avoid sticking of air bubbles and solid precipitate along the diffusion path. For instance if solid AgCl sticks, it can be removed using dilute ammonia solution. Sticking air bubbles can be removed by soft tapping.

Using the reaction diffuser we performed the following eleven experiments and consequently discovered some characteristic diffusion properties of salts in water including the Law of Diffusion of Electrolytes Water.

2.6 General Objectives of the Experiments

1. Measuring the relative velocities of diffusion, Vd, of salts in water.
2. Observing any periodicity in diffusion velocities of salts.
3. Observing any characteristic difference between electrolytic diffusion and gaseous diffusion.
4. To observe if the diffusion velocities of electrolytes obey Fick's law.
5. Establishing any relation between the rates of diffusion of salts and their molar masses.
6. Observing the effects of dissociation of salts and hydrolysis of ions upon the diffusion rates.
7. Observe any change in Vd with change in Diffusion Path Length, DPL.
8. Observing any change in Vd with change in Stopcock Bore Diameter, SBD.
9. Working out any mathematical relation from Vd vs [Salt] or –ln Vd vs [Salt] plots.

2.7 General Procedure

Measure the diffusion path length of the reaction diffuser as also the DC and EF lengths using narrow paper strips and a centimeter scale. Open the two stopcocks and fill it with distilled water above B and G points making sure to remove any air bubble sticking inside by soft tapping of the tube. Close the stopcocks and turn the tube upside down to drain off the water above B and G. Use dropper to remove any water residue.

Reactant solutions, 2.0 ml each, were taken in AB and HG using separate graduated pipettes. These experiments were carried out by two partners. Only AR grade chemicals were used.

The concentrations used for the congenus and syngenus reactants were 0.1M, 0.2M, 0.3M and 0.4M in most cases, higher concentrations were also used. In every reaction corresponding concentration was used for the reactant pair. The bath temperature or room temperature was recorded; thermostat was used in most cases. The two stopcocks were opened simultaneously making sure that their bores and the diffusion tube bores are aligned.

A stopwatch was used to record the time. The two reactant solutions diffused towards each other and eventually meet and do the reaction showing up a mark of precipitate or color.

The time elapsed and the distance traveled by any one of the reacting solutes were recorded. Narrow paper strips and centimeter scale were used to record the distance traveled by one of the reacting solutes. That of the other was obtained by subtracting this distance from the diffusion path length.

The reaction diffuser was then rotated by 180^{o} and the experiment redone to minimize the instrumental errors. The average of the time elapsed and the distance traveled were calculated. This is one experimental run. Such runs were repeated 3 or 4 times to obtain values close to the real.

Although manufacturing of the reaction diffuser and the method of data collection were crude, yet in each experiment meaningful results were obtained through taking repeated runs. Digital recording of time elapsed and distance traveled will bring about sophistication in the Diffusimetric Method and initiate an innovative era in chemical experimentation.

The distance traveled ratio for a set of congenus compounds were calculated and presented in Tabular form. The computed values of the square root of molar mass ratio of the two solutes, with most probable value of their hydration numbers, were shown for comparison. For example

$$\mathrm{KCl(aq)} + \mathrm{AgNO_3(aq)} = \mathrm{AgCl(s)}\downarrow + \mathrm{KNO_3(aq)}$$

$$\frac{\text{Diffusion Velocity of KCl}}{\text{Diffusion Velocity of AgNO}_3} = \frac{\text{Distance travelled by KCl}}{\text{Distance travelled by AgNO}_3} = \sqrt{\frac{M_{KCl}}{M_{AgNO_3}}}$$

The ratio of the relative velocities at corresponding concentrations of the two salts were the same as the ratio of the distances travelled by them; the time being the same as shown by the above equation. Here M_{KCl} and M_{AgNO3} are the molar mass of KCl and $AgNO_3$ respectively. The Vd values were presented graphically

Table 2.8: Reactions Taking Place in the Reaction Diffuser

Group of period	Congenus Reactant in Aqueous Solution	Syngenous Reactant in Aqueous Solution	Remarkable reaction product
1	2	3	4
G1	MCl : M = H, Li, Na, K, Rb, Cs	$AgNO_3$	AgCl↓
G2	MCl_2 : M = Mg,Ca,Sr,Ba	$AgNO_3$	AgCl↓
G12	MCl_2 : M = Mg,Ca,Sr,Ba	$AgNO_3$	AgCl↓
G1	M_2SO_4 : M = Li, Na, K	$BaCl_2$	$BaSO_4$↓
G13	$AlCl_3$	$AgNO_3$	AgCl↓
	NH_4Cl	$AgNO_3$	AgCl↓
G8	Fe^{III}-salts: Fe^{III}-alum, $Fe(NO_3)_3$, $FeCl_3$	NH_4SCN	$Fe(SCN)_3$ Red coloration
P4	Period-4 chlorides: K, Ca, Cr, Mn, Co, Ni, Cu, Zn	$AgNO_3$	AgCl↓
G8	Fe^{III}-alum	$BaCl_2$	$BaSO_4$↓
G8	$FeCl_3$	$AgNO_3$	AgCl↓

Chapter Three

GENERAL ENUNCIATIONS

3.1 Reactions carried out to determine diffusion velocities and some general enunciations

Reactions of congenus chlorides of Group 1, 2, and 12 including NH_4Cl, $AlCl_3$, and $FeCl_3$ with syngenus $AgNO_3$, Group1 sulfates and Fe^{III} alum with $BaCl_2$, and $FeCl_3$, $Fe(NO_3)_3$, and Fe^{III} alum with NH_4SCN at corresponding concentrations were carried out. Reactions of NaCl and $AgNO_3$ at constant $AgNO_3$ concentration but different NaCl concentrations are also reported.

The hydration number of a salt in the solid form and in diffusion may differ and for separate identity they, say Group1 halides, were represented as $MCl.YH_2O$ and $MCl.yH_2O$ respectively. Y and y are either zero or small whole numbers and if zero were often omitted. Each Table shows the DTR and MMRSR values for a reacting salt pair and at the right the composition and molar mass of $MCl.yH_2O$. The plots are mostly the relative diffusion velocity $V_d$versus[salt] and in some cases V_d versus M_{salt}or V_d versus Z_M. Each reaction gave two relative velocities which were given abbreviated representation in the plot area. For Group1 MCl and $AgNO_3$ reactions the relative velocities of $AgNO_3$ were represented by $V_{dAg+ -MCl}$; few other abbreviations were also used. The x-axis in many cases shows both syngenus and congenus reactant concentrations which are equal.

The work employed AR or R&D grade chemicals, 2.0 mL reactant solutions, corresponding concentrations unless otherwise mentioned, 0.40 cm stopcock bore diameter, and 33 cm DPL if not otherwise, and room temperatures ranging from 302-306K. Narrow temperature gap was observed to have minor affect on the diffusion rates. The DTR for an electrolyte pair shows good agreement with their MMRSR which occasionally fitted well if y H_2O molecules were put in place with the diffusing electrolyte. Number y for the syngenus $AgNO_3$, $BaCl_2$, and NH_4SCN was found to be zero. Essential to note that salts $MCl_2.YH_2O$ transform to $MCl_2.yH_2O$ unit for unit in solution and so $[MCl_2.YH_2O]$ and $[MCl_2.yH_2O]$ are the same but $MCl_2.YH_2O$ and $MCl_2.yH_2O$ are not.

In aqueous medium the primary sphere of some cations contains definite number of water molecules strongly held to them in the primary sphere thus increasing the molar mass of the salts and their velocities. Associated water molecules on the other hand in unspecified numbers are weakly held to the ions in the secondary sphere thus adding to the volume of the salts and reducing the velocities. Hypothetically the velocity of a salt could be around hundred cms^{-1} or more, but in reality it is only a fraction of a centimeter. The high hydration radius of the ion associates and their collisions with the countless millions of surrounding water molecules make the electrolytes’ movement incredibly slow.

Cleaning the diffusion tube was done using dilute ammonia to get rid of sticking AgCl, concentrated sulfuric acid to get rid of $BaSO_4$, and dipping the diffusimeter in acid bath taking care of the safety of the stopcock and its plastic cap if any.

Chapter Four

RESULTS AND DISCUSSION

Result and Discussion

4.1 Reactions of Group 1 chlorides and $AgNO_3$

$MCl(aq) + AgNO_3(aq) = AgCl(s) + MNO_3\ (aq)$ M = H, Li, Na, K, Rb …………… 1

The average distance traveled ratio for each MCl-$AgNO_3$ pair is close to its molar mass ratio square root (Table 4.2) which ensures direct proportionality between electrolyte's diffusion velocity and square root of its molar mass. The new diffusimetric method or diffusimetry elegantly revalidates the law of electrolytic diffusion.

The V_{dHCl} show sudden fall (Fig. 21 from those of V_{dLiCl} firstly for the high hydration of H^+ ion caused by its smallest ion radius (10^{-5} pm) [28] and secondly for the high percent atomic number drop from Li to H. Plots of V_{dMCl} versus [MCl] (Fig. 20) is in agreement with the Fick's first law and as such these observations are all Fickian. The plots of five MCl appear in order of their molar masses with the most massive one, RbCl, occupying the uppermost position and the least massive, HCl, the lowermost. The velocities converge at lower concentrations as though they are heading towards zero at zero concentration and diverge at higher for momentum. The NaCl plot rises up a little and comes closer to that of KCl leaving a noticeable gap between NaCl and LiCl lines. The comparative higher velocities of NaCl may be one of the reasons for its fitness as a biosalt in many living organisms including human and an antibacterial agent. The closer velocities of Na^+ and K^+ make the ion pumping across the cell membrane essential[29]**.** The narrowly differing $V_{dAg+\ -MCl}$ appeared twined at some points because of experimental flaw arising out of bare data collection process (Fig. 22).

Salt NaCl at 0.1M and 0.7M shows diffusion velocities of 0.11 and 0.45 cms^{-1} respectively. Calculations show the diffusing chlorides MCl hold no H_2O in the primary sphere though solid LiCl holds one in the sample used (Table 4.2). Cotton et al.

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[28]**.** *Emsley J (1991) The Elements, 2nd Ed., Oxford University Press, p88,106.*

[29]**.** *Shriver DF, Atkins PW, and Langford CH (1991) Inorganic Chemistry, Oxford University Press, Oxford, p608.*

speculated Na^+ and K^+ to have tetrahedrally arranged four H_2O in solution[30] but this is not evident in this study. At constant [$AgNO_3$] but different [NaCl] the quotient DTR (Table 4.7) increases with increasing [NaCl] and maximizes at the corresponding concentration of 0.9M. The DTR plot as a function of [NaCl] gives a smooth, convex curve (not shown). The wide gap between NaCl and $AgNO_3$ plots (Fig. 23) is in keeping with their high molar mass difference.

Table 4.2: DTR and MMRSR for diffusing MCl-$AgNO_3$ pairs; MCl is Group 1 chlorides

Congenus MCl.YH$_2$O	FW, gmol^{-1}	DTR = $\frac{DT_{MCl}}{DT_{AgNO3}}$							Average DTR	MMRSR = $\sqrt{\frac{MCl}{AgNO_3}}$
		0.1 M	0.2 M	0.3M	0.4M	0.5 M	0.6 M	0.7 M		
1	2	3	4	5	6	7	8	9	10	11
HCl	36.5	0.38	0.40	0.40	0.42	0.41	0.41	0.41	0.40	0.46
LiCl.H$_2$O	60.41	0.47	0..45	0.47	0.49	0.48	0.49	0.53	0.48	0.50
NaCl	58.44	0.62	0.60	0.62	0.59	0.63	0.64	0.63	0.62	0.59
KCl	74.55	0.66	0.63	0.63	0.62	0.61	0.62	0.66	0.63	0.66
RbCl	120.92	0.86	0.82	0.82	0.84	0.86	0.84	0.82	0.84	0.84

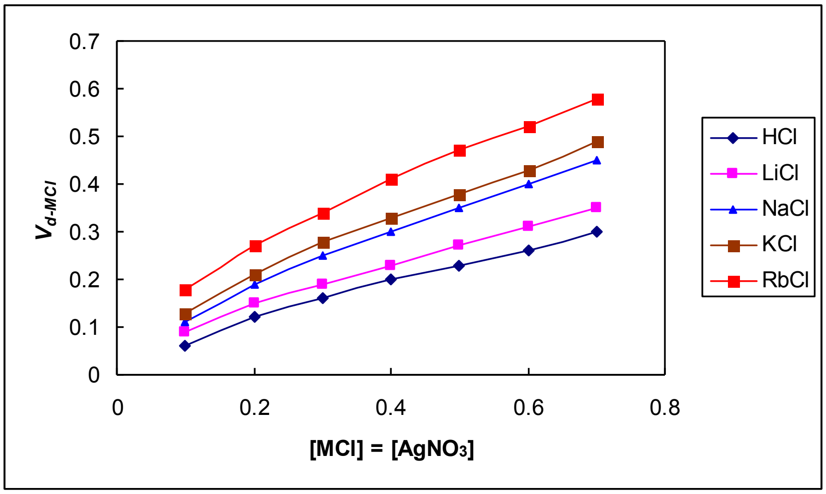

Figure 20: Plots of $V_{d_{MCl}}$ versus [MCl], MCl are Group 1 chlorides, for MCl-$AgNO_3$ reactions.

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[30] *Cotton FA, Wilkinson G, and Gaus L (1987) Basic Inorganic Chemistry, 2nd Ed., John Wiley and Sons, New York, p271.*

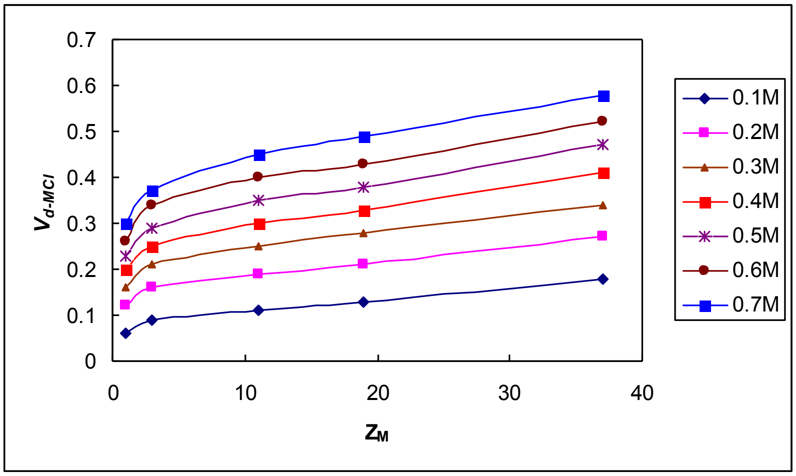

Figure 21: Plots of $V_{d_{\text{MCl}}}$ versus Z_M for MCl-$AgNO_3$ reactions. M is Group1 elements.

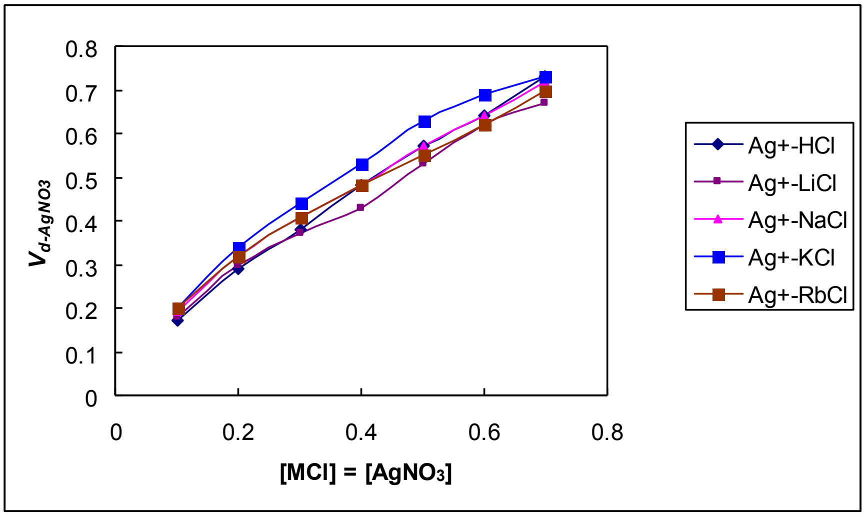

Fig. 22: Plots of V_{dAgNO3} versus [MCl] for MCl-$AgNO_3$ reactions

Table 4.3: DTR at different [NaCl] but constant [$AgNO_3$] = 0.9M and MMRSR for NaCl-$AgNO_3$ pair

Congenus NaCl	FW, gmol^{-1}	DTR									MMRSR= $\sqrt{\frac{NaCl}{AgNO_3}}$, y=0
		0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M	0.9M	
1	2	3	4	5	6	7	8	9	10	11	12
NaCl	58.44	0.29	0.36	0.42	0.47	0.52	0.56	0.59	0.61	0.64	0.59

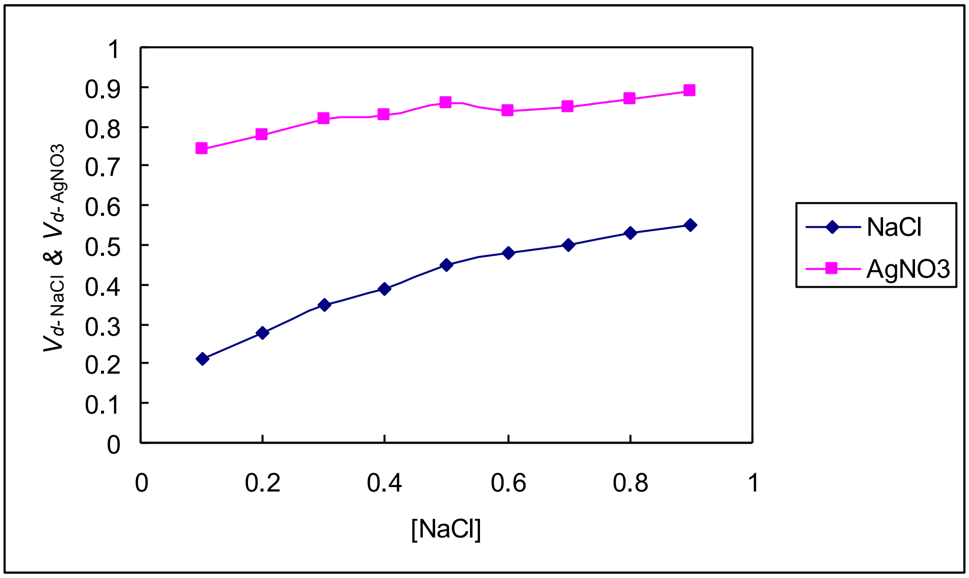

Figure 23: Plots of $V_{d_{\mathrm{NaCl}}}$ and $V_{d_{\mathrm{AgNO_3}}}$ versus [NaCl] for NaCl-$AgNO_3$ reaction at different [NaCl] but constant [$AgNO_3$] = 0.9M

4.4 Reactions of Group 2 chlorides and $AgNO_3$

MCl_2(aq) + 2$AgNO_3$(aq) = 2AgCl(s) + $M(NO_3)_2$ (aq) M = Mg, Ca, Sr, Ba ………… 2

Aqueous solutions of $MgCl_2$, $CaCl_2$, and $SrCl_2$ diffuse with one H_2O each but $BaCl_2$ with none (Table 4.5). Such observations are remarkable for Mg^{2+} is known to hold 6 water molecules though loosely in aqueous solution[31,32,33,34]. The lowermost position for magnesium chloride in Fig. 24 and 25 suggests that the diffusing species is not $MgCl_2.6H_2O$ but $MgCl_2.H_2O$ the lowest molar mass electrolyte. The Mg^{2+}-OH_2 bond in solution being weak, some H_2O molecules break away in the rushing diffusion process making room for $[Mg\text{-}H_2O]^{2+}$ unit to spearhead less hindered. The diffusimetric method

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[31]. *Cotton FA and Wilkinson G (1972) Advanced Inorganic Chemistry, 3rd Ed., Interscience Publishers, New York, p217.*

[32]. *Matwiyoff NA and Taube H (1968) Journal of the American Chemical Society 90:2796.*

[33]. *Nakamura S and Meiboom S (1967) Journal of the American Chemical Society 89:1765.*

[34]. *Hatashi H, Sarkari M, Zeinali M and ZareAliabadi H (2010) Australian. Journal of Basic and Applied Sciences 4:4766-4771.*

with digital recording system for time and length may be more rigorous in determining the hydration numbers of ions in solution.

Table 4.5: DTR and MMRSR for diffusing MCl_2-$AgNO_3$ pairs. M is Group 2 metals

Congenus $MCl_2.YH_2O$	FW, $gmol^{-1}$	DTR				Average DTR	MMRSR= $\sqrt{\frac{MCl_2.yH_2O}{AgNO_3}}$	FW, diffusing salt, $gmol^{-1}$
		0.1M	0.2M	0.3M	0.4M			
1	2	3	4	5	6	7	8	9
$MgCl_2.6H_2O$	203.31	0.80	0.80	0.79	0.81	0.80	0.82 y=1	$MgCl_2.H_2O$ 113.24
$CaCl_2$	110.99	0.89	0.85	0.84	0.86	0.86	0.87 y=1	$CaCl_2.H_2O$ 129.01
$SrCl_2.6H_2O$	266.62	1.1	1.0	0.99	1.0	1.0	1.0 y=1	$SrCl_2.H_2O$ 176.55
$BaCl_2.2H_2O$	244.28	1.1	1.1	1.1	1.1	1.1	1.1 y=0	$BaCl_2$ 208.25

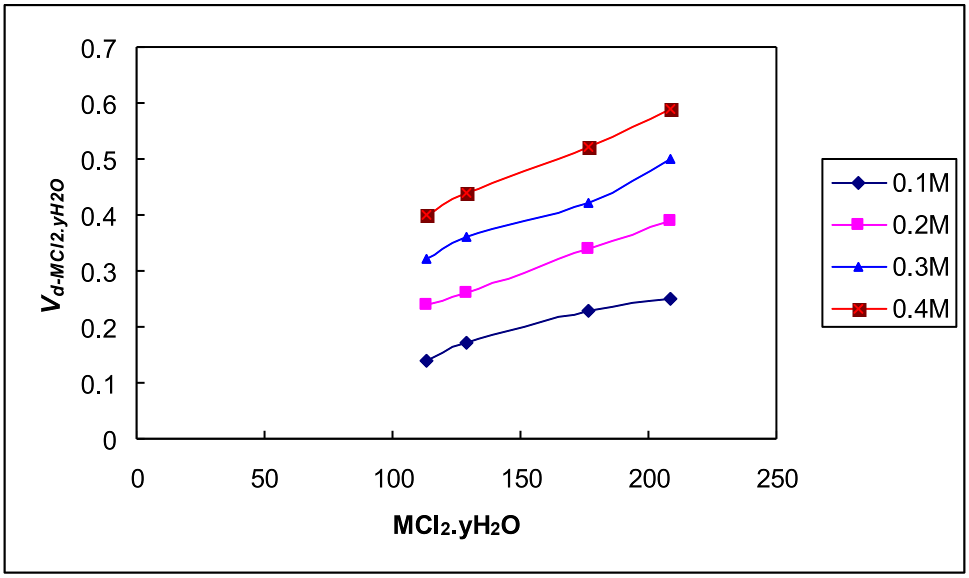

Figure 24: Plots of $V_{dMCl2.yH2O}$, M are Group 2 metals, versus $MCl_2.yH_2O$ molar masses for MCl_2-$AgNO_3$ reactions

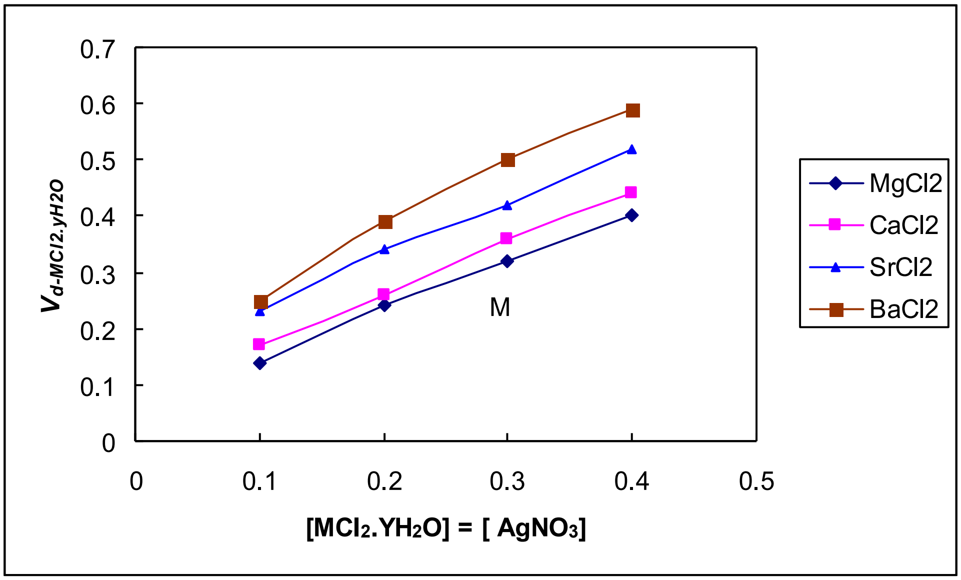

Figure 25: Plots of $V_{dMCl2.yH2O}$, M are Group 2 metals, versus [$MCl_2.YH_2O$] for MCl_2-$AgNO_3$ reactions

4.6 Reactions of Group 1 sulfates and $BaCl_2$; [M_2SO_4] = [$BaCl_2$] = 0.2M, 0.3M, 0.4M, and 0.5M

$M_2SO_4(aq) + 2BaCl_2(aq) = 2BaSO_4(s) + 2MCl\ (aq)$ M = H, Li, Na, K ……………… 3

Salts Li_2SO_4 and Na_2SO_4 travel with one H_2O each (Table 4.7). Significantly it is noted that the sulfates of sodium and magnesium have the same velocities (Fig. 26). This is due partly to the extra mass contributed by the strong binding of one H_2O molecule to sodium sulfate and partly to the inherent higher Na^+ mobility (Fig. 20). Almost a linear progression of each of the plots in Fig. 26 justifies y value assignments to $M_2SO_4.yH_2O$ (Table 4.7). Equal rates of $Na_2SO_4.H_2O$ and K_2SO_4 along with their metatheses with surrounding chlorides hypothesize the formation of mineral sylvite (consisting of 57 percent NaCl and 43 percent KCl) over geological periods[35].

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[35]. *Lewis RJ Sr (1993) Hawley's Condensed Chemical Dictionary, 12th Ed., New York, p1110.*

Table 4.7: DTR and MMRSR for diffusing M_2SO_4-$BaCl_2$ pairs; M being Group 1 metals.

Congenus $M_2SO_4.YH_2O$	FW, $gmol^{-1}$	DTR				Average DTR	MMRSR = $\sqrt{\frac{M_2SO_4.yH_2O}{BaCl_2}}$	FW, diffusing congenus, $gmol^{-1}$
		0.2M	0.3M	0.4M	0.5M			
1	2	3	4	5	6	7	8	9
H_2SO_4	98.08	0.68	0.68	0.68	0.66	0.68	0.69 y=0	H_2SO_4 98.08
$Li_2SO_4.H_2O$	127.96	0.78	0. 75	0.79	0.80	0.78	0.78 y=1	$Li_2SO_4.H_2O$ 127.95
Na_2SO_4	142.04	0.84	0.91	0.89	0.84	0.87	0.88 y=1	$Na_2SO_4.H_2O$ 160.06
K_2SO_4	174.27	0.90	0.90	0.92	0.92	0.91	0.91 y=0	K_2SO_4 174.27

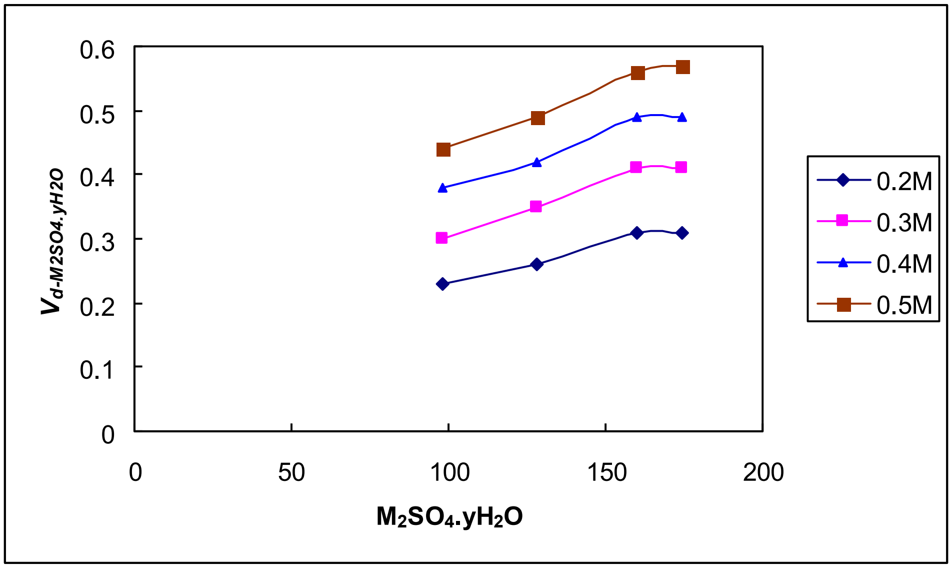

Figure 26: Plots of $V_{dM2SO4.yH2O}$ versus $M_2SO_4.yH_2O$ molar masses; M is Group 1 metals

4.8 Reactions of Group 12 chlorides and $AgNO_3$

MCl_2 (aq) + $2AgNO_3$(aq) = 2AgCl(s) + $M(NO_3)_2$ (aq), M = Zn and Cd ………… 4

Zinc is an important bio element; more than 100 zinc enzymes are performing crucial metabolic functions in the humans alone. In concentrated solution $ZnCl_2$ exists as 6 coordinate $[Zn(H_2O)_6]^{2+}$ and $ZnCl_2.4H_2O$ [36]. Zn^{2+} ion as a d^{10} system can hold two H_2O

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[36] *Cotton FA, Wilkinson G, Murillo CA and Bochmann M (1999) Advanced Inorganic Chemistry, 6th Ed., Wiley Interscience, p605.*

molecules with a linear geometry convenient to spearheading a nearby hole in the liquid structure during diffusion[37]. In fact $ZnCl_2$ in these observations appears to travel as dihydrate (Table 4.9). A close difference (Fig. 27) between the velocities of the two chlorides traces the reason for cadmium's presence in most zinc ores[38]. The persistent narrow difference in diffusion rates for an 11.0 $gmol^{-1}$ molar mass difference between $ZnCl_2.H_2O$ and $CdCl_2$ demonstrates good precision record of the new diffusimetric method. Coincidence in some of the average DTR values of the two chlorides (Table 4.9) is attributed to the value recording in two significant figures.

Table 4.9: DTR and MMRSR for MCl_2-$AgNO_3$ pairs. M is Group 12 metals

Congenus $MCl_2.YH_2O$	FW, $gmol^{-1}$	DTR				Average DTR	MMRSR = $\sqrt{\frac{MCl_2.yH_2O}{AgNO_3}}$	FW, diffusing salt, $gmol^{-1}$
		0.1M	0.2M	0.3M	0.4M			
1	2	3	4	5	6	7	8	9
$ZnCl_2$	136.39	0.96	1.0	0.93	1.0	1.0	1.0 y = 2	$ZnCl_2.2H_2O$ 172.4
$CdCl_2$	183.4	0.96	1.0	1.0	1.0	1.0	1.0 y = 0	$CdCl_2$ 183.4

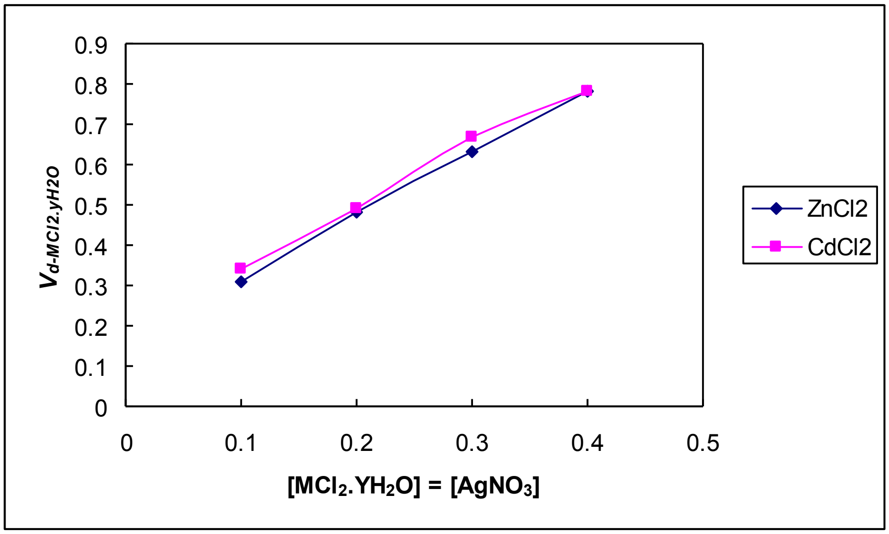

Figure 27: Plots of $V_{dMCl2.yH2O}$ versus $[MCl_2.YH_2O]$ for MCl_2-$AgNO_3$ reactions, M being Group 12 metals

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[37]. *King EL (1964) How Chemical Reactions Occur, W. A. Benjamin, p65.*

[38]. *Partington JR (1965) A Textbook of Inorganic Chemistry, 6th Ed., ELBS and Macmillan & Co Ltd., London, p784.*

4.10 Reactions of NH_4Cl and NH_4SCN with $AgNO_3$:

Experiments carried out at 297K

$NH_4X(aq) + AgNO_3(aq) = AgX(s) + NH_4NO_3(aq)$, X = Cl^- or SCN^- …………… 5

The dissociation constants of NH_4Cl, NH_4^+, and HSCN in water are infinity, $5.5x10^{-10}$, and 0.014 respectively. Evidently hydration of NH_4Cl and NH_4^+ is complete and also that Cl^- is a weak base but SCN^- is strong which in turn suggests as having some covalence in NH_4SCN. Movement of a covalent compound in a polar solvent is sluggish. Hydration of the dissociated NH_4^+ and the covalence in NH_4SCN are both diffusion retarding. Indeed the relative velocities of NH_4SCN in NH_4SCN-$AgNO_3$ pair are significantly low and incidentally equal to those of the low molar mass NH_4Cl in NH_4Cl-$AgNO_3$ pair. Another noTable point is that the rates of $AgNO_3$ in NH_4SCN-$AgNO_3$ pair are slightly higher than those in NH_4Cl-$AgNO_3$ pair (Fig. 28). It is apparent thus that a slow syngenus can make its congenus rates higher. Moreover this diffusion controlled reactions the closest approach distance between $AgNO_3$ and NH_4SCN is less than that between $AgNO_3$ and NH_4Cl because $AgNO_3$ comes closer to the low outer electron density SCN^- group than it does to high electron density Cl^- ion. Indeed AgSCN is more insoluble than AgCl. As such both kinetic and thermodynamic grounds suggest higher velocity to $AgNO_3$ in NH_4SCN-$AgNO_3$ pair than in the other pair.

Table 4.11: DTR, MMRSR and %DTR decrease from MMRSR for NH_4X-$AgNO_3$ reactions

Congenus NH_4X	FW, $gmol^{-1}$	DTR				Average DTR	MMRSR = $\sqrt{\frac{NH_4X}{AgNO_3}}$	Per cent DTR decrease
		0.1M	0.2M	0.3M	0.4M			
1	2	3	4	5	6	7	8	9
NH_4Cl	53.49	0.44	0.44	0.45	0.45	0.45	0.56	20
NH_4SCN	76.12	0.43	0.44	0.42	0.43	0.43	0.67	36

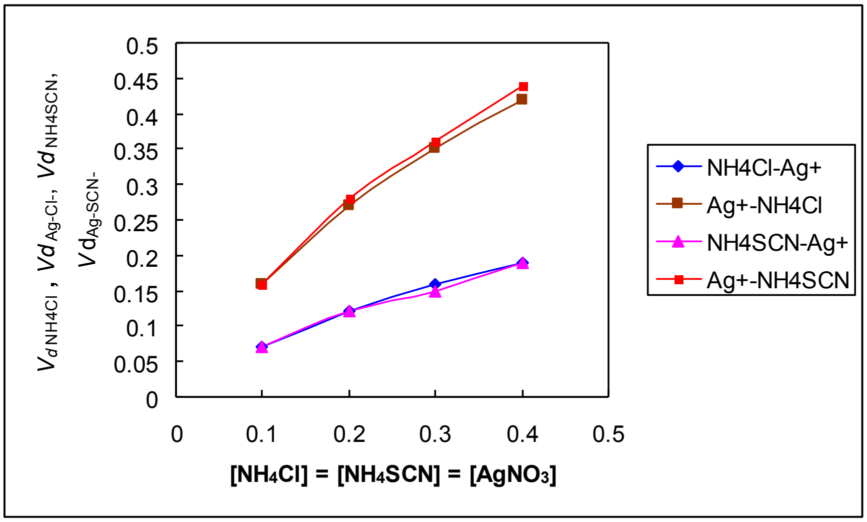

Figure 28: Plots of V_{dNH4Cl} and V_{dAgNO3} in NH_4Cl-$AgNO_3$ pair and of $V_{dNH4SCN}$ and V_{dAgNO3} in NH_4SCN-$AgNO_3$ pair versus corresponding concentrations of reactants. The expressions for example NH_4Cl-Ag^+ and NH_4SCN-Ag^+ on the right of the plot area refer to the relative velocities of NH_4Cl and NH_4SCN respectively with respect to syngenus $AgNO_3$.

4.12 Reactions of Fe^{III} salts with $BaCl_2$, $AgNO_3$, and NH_4SCN

Reaction pair: **a** Fe^{III} alum(aq) + $BaCl_2$(aq) = $BaSO_4$(s) + Product, and **b** Fe^{III} alum(aq) + NH_4SCN(aq) = $Fe(SCN)_3$(aq) + Product 6,7

Reaction pair: **c** $FeCl_3$(aq) + $3AgNO_3$(aq) = 3AgCl(s) + Product, and **d** $FeCl_3$(aq) + $3NH_4SCN$(aq) = $Fe(SCN)_3$(aq) + Product 8,9

In Table 4.13, Rows 1, 2 show that the Fe^{III} alum and $FeCl_3$ diffuse with no H_2O in keeping with which $Fe(NO_3)_3$ is also assigned as having no H_2O molecule (Row 4). For the reactions with syngenus NH_4SCN (Rows 3, 4, and 5) the DTR values are unusually high whereas with the other syngenus reactant NH_4Cl (Rows 1, 2) the values are closely normal. Higher DTR values are due to the lower rates of NH_4SCN (Fig. 28) the denominator reactant.

As is known the diffusion controlled reactions show almost similar reaction constants within the range of 10^9 to10^{10} $M^{-1}s^{-1}$ and depend little on the nature of the reactants[39]**.**The

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[39]. *Katakis D and Gordorn G (1987) Mechanisms of Inorganic Reactions, John Wiley & Sons, New York, p72.*

percent DTR rise over MMRSR in reactions of $Fe(NH_4)(SO_4)_2$-NH_4SCN, $FeCl_3$-NH_4SCN, and $Fe(NO_3)_3$-NH_4SCN pairs (Table 4.13) are 52, 53, and 54 respectively.

Almost similar values reflect the diffusion controlled nature of these reactions and the extent to which the closest approach distances differ. Visibly the closest approach distance is least in $Fe(NH_4)(SO_4)_2$-NH_4SCN and most in $Fe(NO_3)_3$-NH_4SCN with $FeCl_3$-NH_4SCN pair in between. The closest approach distance is governed by factors like steric hindrance and charges on the approaching ions including their peripheral lone pairs in both attractive (Reactions **a** and **c**) and repulsive (Reactions **b** and **d**) encounters as in Fig. 30 and Fig. 31. In the plots (Fig. 29) the heavy weight Fe^{III} alum occupies the two upper positions and the comparative light weight $FeCl_3$ the two lower ones. Incidentally again the velocities of Fe^{III} alum with respect to NH_4SCN and of $FeCl_3$ with respect to $AgNO_3$ almost overlap. It may be mentioned that $FeCl_3$ has a planar structure[40].

Table-4.13: DTR and the molar mass ratio square root of Fe^{III} salt- $BaCl_2$, Fe^{III} salt- NH_4SCN, and Fe $(NO_3)_3$- NH_4SCN pairs

Sl	Reactions	FW, congenus	DTR				Average DTR	MMRSR = $\sqrt{\frac{Fe^{III} salt.yH_2O}{AgNO_3, BaCl_2, NH_4SCN}}$ y = 0	FW, diffusing congenus
			0.1M	0.2M	0.3M	0.4M			
	1	2	3	4	5	6	7	8	9
1	$Fe(NH_4)(SO_4)_2.12H_2O$ + $BaCl_2$	482.25	1.02	1.04	1.05	1.04	1.04	1.13 y=0	$Fe(NH_4)$ $(SO_4)_2$ M= 265..95
2	$FeCl_3.6H_2O + AgNO_3$	270.30	0.94	0.95	0.92	0.93	0.94	0.98 y=0	$FeCl_3$ M = 162.21
3	$Fe(NH_4)(SO_4)_2.12H_2O$ + NH_4SCN	482.25	2.98	2.88	2.84	2.84	2.89	1.90 y=0	$Fe(NH_4)$ $(SO_4)_2$ M= 265..95
4	$Fe(NO_3)_3.9H_2O + NH_4SCN$	404.00	2.84	2.79	2.79	2.71	2.78	1.80 y=0	$Fe(NO_3)_3$ M = 241..83
5	$FeCl_3.6H_2O$ + NH_4SCN	270.30	2.37	2.40	2.24	2.14	2.29	1.50 y=0	$FeCl_3$ M = 162..21

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[40]. *Wells AF (1993) Structural Inorganic Chemistry, 5th Ed., Oxford Science Publications, New York, p444.*

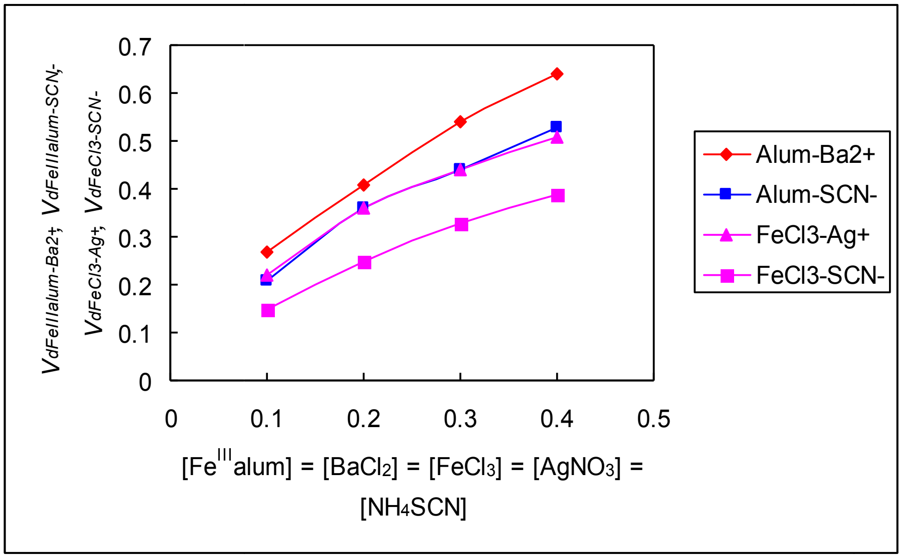

Figure 29: Plots of $V_{dFeIII\ alum}$ and V_{dFeCl3} versus [Fe (NH_4) $(SO_4)_2$] and [$FeCl_3$] respectively. Velocities of Fe $(NO_3)_3$ with respect to NH_4SCN are excluded in the plot area for clarity.

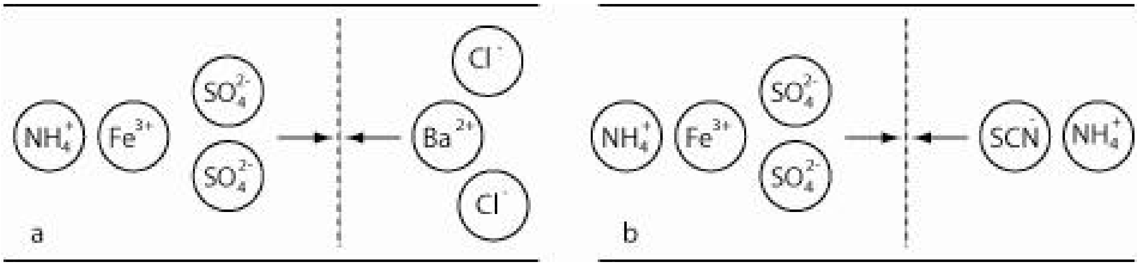

Figure 30: Schematic encounters in diffusion controlled reactions: ***a*** for attractive encounter between Fe^{III} alum and $BaCl_2$ and ***b*** for repulsive encounter between Fe^{III} alum and NH_4SCN

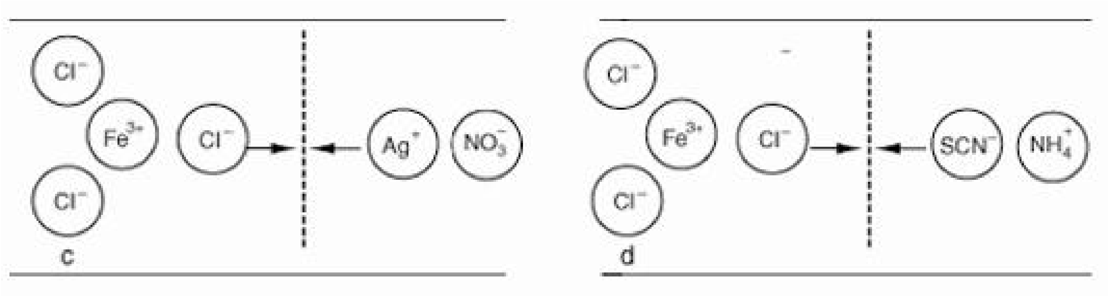

Figure 31: Schematic encounters in diffusion controlled reactions: ***c*** for attractive encounter between $FeCl_3$ and $AgNO_3$ and ***d*** for repulsive encounter between $FeCl_3$ and NH_4SCN

4.14 Capillary action:

Capillary action is a phenomenon where liquid spontaneously rises in a narrow space such as a thin tube, or in porous materials. This effect can cause liquids to flow against the force of gravity. It occurs because of inter-molecular attractive forces between the liquid and solid surrounding surfaces; if the diameter of the tube is sufficiently small, then the combination of surface tension and forces of adhesion between the liquid and container act to lift the liquid.

4.15 Marangoni effect:

The Marangoni effect is the convection of fluid along an interface between dissimilar substances because of variations in surface tension. Surface tension can vary because of inhomogeneous composition of the substances, and/or the temperature-dependence of surface tension forces. In the latter case the effect is known as thermo-capillary convection. A well-known phenomenon exhibiting this type of convection is the "tears of wine"

4.16 Combustion

In a zero-gravity environment, there can be no buoyancy forces, and thus no natural (free) convection possible, so flames in many circumstances without gravity smother in their own waste gases. However, flames may be maintained with any type of forced convection (breeze); or (in high oxygen environments in "still" gas environments) entirely from the minimal forced convection that occurs as heat-induced expansion (not buoyancy) of gases allows for ventilation of the flame, as waste gases move outward and cool, and fresh high-oxygen gas moves in to take up the low pressure zones created when flame-exhaust water condenses.

From the above concept of convection mechanism our experiment is similar to -

- Gravitational or buoyant convection
- Capillary action, as the experiment involves

- Gravity of solute and solvent
- Buoyant action of the solvent

- Capillary action of the medium (water)
- No thermal difference activity (as the transfer of molecules occurs at room temperature)

The convection and diffusion process may describe as:

i. The $AgNO_3$ solution and NaCl solution undergo to the solution through the tube due to 3 reason –

    a. Gravitational force due to higher density of solute
    b. Low buoyant force of the solvent
    c. Higher concentration than solvent i.e. diffusion into medium

Buoyancy-induced convection not due to heat is known as gravitational convection. Gravitational heat convection is the same as free convection. However, differential buoyancy forces that cause convection in gravity fields may result from sources of density variations in fluids other than those produced by heat, such as variable composition.

ii. Capillary action of the solvent that lifted the solvent upper void of the tube produced by movement of the solutes into the lower positions. Capillary action, capillarity, capillary motion, or wicking is the ability of a substance to draw another substance into it. It occurs when the adhesive intermolecular forces between the liquid and a substance are stronger than the cohesive intermolecular forces inside the liquid. The effect causes a concave meniscus to form where the substance is touching a vertical surface.

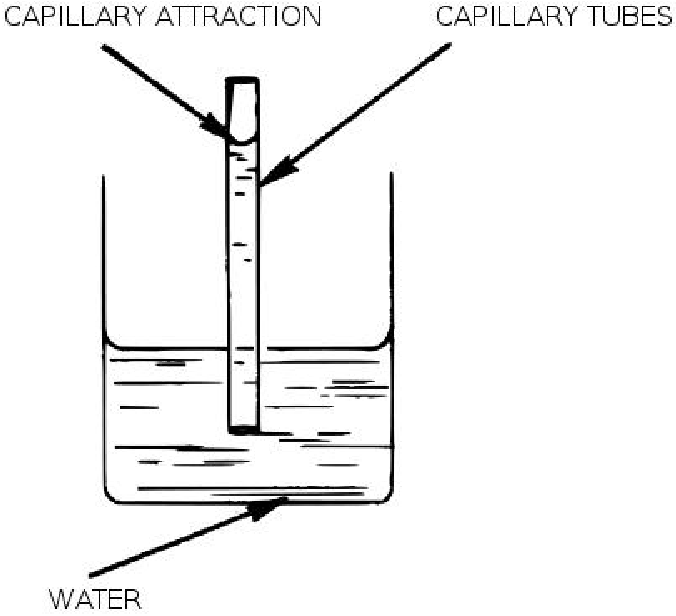

Figure 32: Demonstration of capillary attraction of water

In these circumstances the solutes $AgNO_3$ and NaCl are also moving to their low concentration area that is defined as diffusion. Thus according to the basic concept of the convection and diffusion the process of the experiment may also defined as convective diffusion as both are occurring simultaneously.

CONCLUSION

Conclusion

The novel diffusimeter is straightforward glassware efficient in determining electrolytes' relative, free diffusion velocities and discloses thus a host of their other properties and characteristics. This study observes inter alia that the velocity of a solute decreases with increasing diffusion path length and increases with its stopcock bore diameter and temperature. These measurements elegantly reconfirm the law of electrolytic diffusion which contrary to gaseous diffusion manifests direct proportionality between electrolyte's diffusion velocity and square root of its molar mass. It is apparent that a diffusing electrolyte may assume an altogether different hydration number and the orientation of the floating ions. The diffusimetric method termed DTR Model has the prospect of determining among other things the electrolyte concentration, molar mass of a salt, its purity, solvent polarity and diffusion rate, complex composition by continuous variation method, percent covalent character in an ionic compound and accomplishing precipitate crystallization and isotope separation. Diffusimetry is a powerful tool in qualitatively assessing the closest approach distance between pairs of reacting electrolytes and throwing light on the nature of their electrostatic interactions. The instrument can be used to design interesting and thought inciting chemistry experiments of both qualitative and quantitative nature befitting all levels of chemistry education and making chemistry more computational. Finally the electrolytic diffusion law is not new but its exposition to a whole variety of chemical investigations is certainly novel.

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