Chapter 7

An Experiment to Study
Molecular Diffusion in Liquids

7.1 Introduction

Diffusion is a phenomenon of theoretical and practical importance (Bouchet & Mevrel (2002); Crooks (1989); Digenov & Reiner (2005); Fate & Lynn (1990); King et al. (1989); Kohler et al. (2010); Lhuillier (1986); Mankidy et al. (2010); Rehfeldt & Stichlmair (2007); Whitmire & Blaylock (2004)). It is included in the curriculum in Biology, Chemistry, Physics and Engineering courses right from elementary level to advanced ones and there are demonstrations at the elementary level and advanced experiments at the research level. However, most undergraduate physics laboratories do not have an experiment that allows students to visualize diffusion as a phenomenon. A long time interval is required for diffusion to produce measurable concentration changes in a solution and it is hence difficult to devise a suitable experiment that can be completed in one lab session (Burden et al. (2004); Clifford & Ochiai (1980); Gover (1967); Irina (1980); Linder et al. (1976); Meir et al. (2005); Paz (1969); Ray et al. (2007); Watts (1962); Wongwilai et al. (2010)).

Diffusion as a phenomenon is the mechanism underlying many technical processes known to mankind for ages, examples being “cementation” a process used for gold or silver refining, carbon diffusion to produce steel from iron, diffusion soldering of gold artefacts, and the colors of stained glasses, earthenware and
7. An Experiment to Study Molecular Diffusion in Liquids

china. The Scottish chemist, Thomas Graham conducted the first quantitative study of diffusion. Graham was the inventor of dialysis, which he defined as a method of separation, by diffusion through a membrane. Diffusion occurs when molecules move from an area of higher chemical potential to one of lower chemical potential. For many systems, we can replace the chemical potential by the concentration. When two or more substances diffuse into one another, they move from two distinct substances toward a single solution of uniform concentration.

If two liquids are miscible, which means they can dissolve in each other, a binary diffusion coefficient can be defined for the inter-diffusion of two initially pure liquids.

In this chapter we describe an experimental setup to study molecules diffusing in a solvent. A glass tube filled with water is placed horizontally and KMnO$_4$ solution of a certain concentration is added at one end. As the KMnO$_4$ diffuses through water, the optical density changes because of the color change. We setup an LED and LDR arrangement at different points along the glass tube to measure the optical density. The detectors are calibrated with known KMnO$_4$ concentrations. The data allows one to understand the basic physics of diffusion. The square root $t$ dependence is clearly seen and the experiment is also set up to measure the diffusion coefficient. Due to the color change, the student is able to visually observe the diffusion process.

7.2 Theory

Each substance diffuses at a different rate due to the interactions at the molecular level. The rate of diffusion depends on several factors such as molecular size, viscosity and the temperature (Crank (1980); Cussler (1997)). Fick's laws of diffusion empirically describe the relation between the diffusion coefficient and diffusion. Fick's first law relates the flux $J$ (the amount of material passing through a unit area), to the concentration gradient. The diffusion coefficient is the proportionality coefficient between the flux and the concentration gradient. In one dimension, it is written as

$$ J = D \frac{\partial \rho}{\partial x} \quad (7.1) $$

106
We will use Fick’s second law in one dimension, which is derived from Fick’s first law,

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$  \hspace{1cm} (7.2)

where \( \rho(x, t) \) is the concentration as a function of the position \( x \) and time \( t \), and \( D \) is the diffusion coefficient. The form of Fick’s law in equation (7.2) is linear because of the assumption of a constant diffusion coefficient.

The cross section of the pipe is very small compared to its length. Therefore, the diffusion of ions inside the pipe is essentially one-dimensional with the diffusion equation given by

$$\frac{\partial^2 \rho(x, t)}{\partial x^2} = \frac{1}{D} \frac{\partial \rho(x, t)}{\partial t}$$  \hspace{1cm} (7.3)

where \( \rho(x, t) \) is the concentration of diffusing particles integrated over the cross section of the pipe and \( D \) is the diffusion constant. We define the Fourier transformation \( \tilde{\rho}(k, t) \) of the concentration \( \rho(x, t) \), and they related to each other via the following equations.

$$\tilde{\rho}(k, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \rho(x, t) e^{-ikx} \, dk$$

$$\rho(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{\rho}(k, t) e^{ikx} \, dk$$  \hspace{1cm} (7.4)

Starting with equation (7.3) and taking a Fourier transform of both sides we obtain

$$\int_{-\infty}^{\infty} \frac{\partial^2}{\partial x^2} \rho(x, t) e^{-ikx} \, dk = \frac{1}{D} \int_{-\infty}^{\infty} \frac{\partial}{\partial t} \rho(x, t) e^{-ikx} \, dk$$  \hspace{1cm} (7.5)

Using the derivative theorem of Fourier transform on the left hand side and bringing out the time derivative outside the integral on the right hand side we obtain

$$-k^2 \tilde{\rho}(k, t) = \frac{1}{D} \frac{\partial \tilde{\rho}(k, t)}{\partial t}.$$  \hspace{1cm} (7.6)

After rearrangement the above first-order differential equation can be written as

$$\frac{\partial \tilde{\rho}(k, t)}{\partial t} = -Dk^2 \tilde{\rho}(k, t)$$  \hspace{1cm} (7.7)

A direct integration gives the solution of this equation as

$$\tilde{\rho}(k, t) = \tilde{\rho}(k, 0) \exp(-Dk^2 t)$$  \hspace{1cm} (7.8)
Here $\tilde{\rho}(k,0)$ is the Fourier transform of the initial concentration profile $\rho(x,0)$ at time $t = 0$ (the initial condition for our problem). If we begin with a delta function concentration at $x = 0$ given by

$$\rho(x,0) = 2\pi \rho_0 \delta(x)$$  \hspace{1cm} (7.9)

we then readily obtain its Fourier transform as

$$\tilde{\rho}(k,0) = \rho_0$$  \hspace{1cm} (7.10)

Substituting this in equation (7.8) and carrying out the inverse Fourier transform we we obtain the desired solution of the diffusion equation

$$\rho(x,t) = \rho_0 \sqrt{\frac{1}{2Dt}} \exp\frac{-x^2}{4Dt}$$  \hspace{1cm} (7.11)

This is the solution of the diffusion equation which should describe the diffusion process inside the pipe. We make the following assumptions: the molecules diffuse in one dimension, the substances have an infinite space in which to diffuse, no chemical reactions occur, and there is no change in the volume of the system.

Note that we have presented above the one-dimensional solution of the diffusion equation, wherein diffusion of ions can take place in both directions. The idealized condition assumed is that we have an infinitely long thin pipe and the ions are injected in the center from where they diffuse symmetrically on both sides. In the actual experiment the situation is different. We add the concentrated solution of KMnO₄ at one closed end of the tube and the diffusion takes place only in one direction. The initial delta function approximation for concentration is also not strictly valid in reality. We are aware of these differences between theory and experiment, however the above simple solution of the diffusion equation qualitatively describes the diffusion process in the real experiment as well. Further, we have taken initial conditions as delta function concentration which too is not strictly valid, particularly near the source the differences from the delta function profile are expected to contribute significantly.

### 7.3 Experimental Setup

The measurements are proposed in this experiment include the concentration as a function of time at a given position, and the distance moved by the ions as a
7.3 Experimental Setup

function of $\sqrt{t}$. The main components of the experimental setup are illustrated in Figure 7.1 and consist of the following blocks: a diffusion channel, a light source and a detector.

![Diagram of experimental setup]

Figure 7.1: Schematic diagram of the various blocks of the experimental setup to measure diffusion.

7.3.1 Diffusion channel

It consists of a glass tube of length $\approx 100$ cm, inner diameter = 0.386 cm and outer diameter = 0.594 cm fitted on card board as shown in Figure 7.2. Two elbows are fixed at two ends of this tube. The tube is filled with water and $KMnO_4$ solution is used as the ion source. Since $KMnO_4$ is violet in color, the process of diffusion of $KMnO_4$ in water is visible to the eye.

7.3.2 Light source

White LED is used as the light source. The power to the LED is provided by a constant current source. Figure 7.3 shows the schematic diagram of the current source. IC LM334 is a 3-Terminal Adjustable Current source. With the
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.2: Photograph of the actual experimental setup to measure diffusion.

present values, a current of 31 mA flows through each diode, providing a constant light output. The LED is housed in an enclosure in order to limit the area of illumination.

7.3.3 Detector

An LDR (light dependent resistor) is used as a light detector. The resistance of the LDR decreases with the increase in the intensity of light falling on it. The schematic of the detector circuit is shown in Figure 7.4. LDR is connected in series to a 10 kΩ preset and a 1 kΩ potentiometer. The preset allows the setting of initial conditions for individual sensors and potentiometer is used to zero set individual sensors. The 4.7 kΩ resistor and 10 kΩ preset form a voltage divider to provide a reference voltage to the meters for zero setting. The LDR is housed in an enclosure to avoid ambient light interference.

The choice of material depends upon what technique we want to follow for the concentration measurement. One way is to use current as a function of the concentration in the liquid. This has few disadvantages (1) for measuring current, potential has to be applied which can have some local effects near the electrodes (2) the setup is not easily replicable. Therefore we decided to use optical measurement which has the advantage that the measurement is non-invasive and the setup is easily replicable and tune-able. The liquid selected as medium is water and $\text{K}_2\text{O}_4$ is used as the species which will diffuse into water. Diffusion of
Figure 7.3: Schematic diagram of the circuit to provide constant current to the LED. It is wired around a three terminal adjustable current source IC LM 334.
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.4: Schematic diagram of the detector circuit based upon light dependent resistance (LDR). LDR is a part of the potential divider circuit and changes in potential difference across the LDR represents changes in light intensity.
7.4 Measurement technique

$KMnO_4$ will change the optical density of water and which in turn will change the intensity of light passing through it. This forms the basis of the measurement.

![Schematic of the physical placement of the detector containing LED and LDR around the tube containing liquid](image)

**Figure 7.5:** Schematic of the physical placement of the detector containing LED and LDR around the tube containing liquid

### 7.4 Measurement technique

The measurement in this experiment is based on light intensity measurements. Figure 7.5 illustrates the schematic of the physical placement of the detector containing LED and LDR around the tube containing liquid. Light from LED passes through the tube containing liquid and is detected by the LDR. The LDR is a part of the potential divider. Due to the applied potential, potential difference develops across LDR. The resistance of LDR decreases with the increase in the intensity if light falling on it and vice-versa. The LDR has been connected in such a manner that the potential difference across it increases with the decrease in the intensity of light falling on it. The reading of the multimeter connected across the LDR increases as the transparency of the liquid in the tube decrease due to the presence of $KMnO_4$. The reading on the meter connected to a sensor is a function of the concentration of the $KMnO_4$ in the solution in the domain of that sensor.

#### 7.4.1 Calibration

The quantities involved in the measurement are concentration of $KmnO_4$ in water, and the position of sensor $x$ and time $t$. Position and time are separately
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.6: Calibration curve for sensor 1. Plot of the sensor 1 output in mV at different concentrations of the solution.
Results and Discussion

measurable. For finding out the concentration of $KMnO_4$ at a given time at a given position calibration is required with some standard solution. For calibration, solutions of following concentrations were prepared: 0.00125, 0.00166, 0.0025, 0.005, 0.01, 0.0125, 0.0166, 0.025, 0.05, 0.1, 0.125, 0.166, 0.25, 0.5, 1.0. All the values are in g/100ml. Output of all the sensors was measured with solutions of the above concentrations. The output of the sensor1 is shown in Figure 7.6, sensor2 in Figure 7.7, sensor3 in Figure 7.8 and sensor4 in Figure 7.9. In all these figures concentration is in (g/100ml) and output corresponding sensor is in (mV). This data is used to convert the output of sensors in (mV) to corresponding concentration values.

![Figure 7.7: Calibration curve for sensor 2. Plot of the sensor 2 output in mV at different concentrations of the solution.](image-url)
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.8: Calibration curve for sensor 3. Plot of the sensor 3 output in mV at different concentrations of the solution.
7.5 Results and Discussion

Figures 7.11, 7.12 and 7.13 show plots of the change in concentration of the solution in the domain of sensor 2, sensor 3 and sensor 4 respectively as a function of time. Figure 7.14 shows a plot of the distance moved by ions as function of \( \sqrt{t} \) at three different initial concentrations. The curve clearly shows the \( \sqrt{t} \) dependence of distance covered by the diffusing particles.

Four sensors (sensor 1, sensor 2, sensor 3, sensor 4) are positioned at 7cm, 11.3cm, 15.4cm and 19cm respectively relative to the position 'A' where concentrated \( KMnO_4 \) solution is to be added as shown in the Figure 7.2. A solution of concentration 5g/100ml is used as the source of diffusing ions. The major challenge in this experiment is to avoid flow due to gravity and turbulence due
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.10: Concentration vs time plot for sensor 1. The values of sensor 1 (converted to g/100ml) using the calibration curve are plotted as a function of time. The sensor has been kept at the distance of 7cm from the source. The solid line is the fitted curve. Since the actual source is not a delta function the fitted curve differs from the actual curve for this detector significantly.
7.5 Results and Discussion

Figure 7.11: Concentration vs time plot for sensor 2. The values of sensor 2 (converted to g/100ml) using the calibration curve plotted as a function of time. The detector distance in this case is 11.3cm. The solid line again is the plot from the solution of the diffusion equation. Here the fitted curve is closer to the experimental data compared to the first detector.
7. An Experiment to Study Molecular Diffusion in Liquids

Figure 7.12: Concentration vs time plot for sensor 3. The values of sensor 3 (converted to g/100ml) using the calibration curve plotted as a function of time. In this case the detector is at a distance 15.4cm and the solid curve is again is the solution of the diffusion equation. In this case the agreement is better.

to addition of $KMnO_4$ in the tube. To avoid contribution due to gravity, end ‘B’ (Figure 7.2) of the tube should be raised slightly and to avoid turbulence the first sensor is placed at distance from the end ‘A’. At point ‘A’, where the $KMnO_4$ is added, there is a small vertical column. The initial turbulence due to the addition of the solution fizzes out by the time the ions reach first sensor. Time $t$ is set to zero when the ions reach the sensor1. Since very high concentration is used rate of diffusion is expected to be high. This is evident from the data for the first sensor. Figure 7.10 shows a plot of the change in concentration of the solution in the domain of sensor1 as a function of time. The time of arrival of the first molecule is 64 second. After this time the concentration increases rapidly and
saturates at 384 second. Further increase is expected but the time required for that is very large. The fitting is done keeping all the graphs detectors in mind and giving more weight-age to detectors at larger distances. This is needed since the theoretical solution uses a delta function source instead of a concentration step function used in the experiment. Therefore, the agreement of theoretical curves and the experimental data is expected to be only qualitative. With this in mind the average diffusion coefficient $D$ comes out to be 0.035 cm$^2$/s.

7.6 Conclusions

An apparatus has been designed and fabricated to study diffusion in an undergraduate physics laboratory. The ions are inserted in a pipe full of water and their diffusion is studied by measuring their concentration at different spatial positions as a function of time. The concentration is inferred from a measurement of the resistance of water at different spatial locations. The concentration dynamics matches the solution of the one-dimensional diffusion equation with appropriate boundary conditions. When two species of ions are inserted which have different diffusion constants two different solutions of the diffusion equation are required. In this case we will assume that they diffuse independently with two different diffusion constants. The diffusion constants can be estimated quantitatively by appropriate fitting and interpolation. This setup allows the student to explore the concept of diffusion in detail and in an open-ended fashion. Work is still in progress on this experiment and the details of the theory and the experimental setup are being refined. As is clear from the celebration curves the sensitivity of the measurement is reduced as one moves to larger values of the concentration. This too needs to be refined to get better quantitative results. At this stage the setup is good for demonstrating qualitative features of diffusion. In fact for modeling the actual experiment we need to solve diffusion equation with the experimentally correct boundary conditions and in that case exact analytical solutions are not available.
Figure 7.13: Concentration vs time plot for sensor 4. The values of sensor 1 (converted to g/100ml) using the calibration curve are plotted as a function of time. The detector distance in this case is 19cm and the solid curve is again the solution of the diffusion equation.
Figure 7.14: Plot of distance covered by the ions and the square root of time at three different initial concentrations.
7. An Experiment to Study Molecular Diffusion in Liquids