Experiments in Diffusion: Gases, Liquids, and Solids for Under Five Dollars

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Prerequisite Knowledge: The student should be familiar with the basics of materials science, metallography, and chemistry. Levels at which these experiments are performed are freshman, second semester junior year, and either semester senior year. The students are first given a lecture on diffusion. The juniors and seniors should have already had a laboratory experiment on metallography and sample preparation. Safe laboratory practice should be observed at all times (eg. Goggles, gloves, aprons, etc.).

Objectives:
The objectives of these experiments are to show that the subject of diffusion is not really so hard to understand and that it plays an important role in our daily lives. Diffusion of molecules through the air can be determined using our sense of smell. Liquid diffusion can be observed using a paper towel or ink in water. Solid diffusion can be observed by measuring the movement of the coloration of a dopant ion in a glass stirring rod or dyes in plastic glue sticks. The objectives, then , are to measure the diffusion rates for solids, liquids, and gases using simple techniques to yield sophisticated answers. Diffusion coefficients will be determined, and curve fitting the graphical results will be performed.

Equipment and supplies:
(1) Metallurgical preparation and polishing apparatus (Buehler Co.),
(2) Glass or quartz stirring rods (Fisher Scientific),
(3) Cupric chloride, Petri dishes, test tubes, tongs, bunsen burners, small beakers (Fisher Scientific),
(4) Food Coloring, vanilla or garlic extract, paper towels (grocery store),
(5) Metallurgical microscope (Olympus, Zeiss, etc.),
(6) Timers (split time preferred), and
(7) Hot melt clear and colored glue sticks.

Abstract:
Differences in velocities of diffusing species of solids, liquids, and gases can capture the imagination of students of all ages. Using common utensils, host materials, and diffusing media, along with some ingenuity and novelty in team efforts, students can measure the actual velocities of diffusing solids, liquids, and gases, and have fun in the process.

There is no need for high temperatures such as are needed to observe these processes in steels, oxides, and the like. By increasing temperature, pressure, and kinetic energy of the molecules, students may study these phenomena at whatever level of involvement they deem necessary in these three experiments. They can apply graded levels of mathematics for the analyses of these data. The comments and variations are encouraging to the professor, and the basic principles of diffusion are retained for longer periods of time than from "conventional wisdom" pedagogy. These experiments work very well with middle school as well as college students.[1] The comments are very positive to date.

Introduction:

Solid state diffusion plays many roles in the modern world. It make it possible to control impurites in semiconductors, sinter metallic and nonmetallic particles, oxidize various materials, control surface alloying of metals, color minerals and gemstones, and make solid state lasers work, to name a few. The process is dependant on high temperature of the solids, the higher the temperature, the more vibration occurs that allows the atoms to let the diffusant through. For instance, arsenic in silicon will not diffuse at room temperature and will diffuse only a few micrometers after 3 hours at $1000^{o}C$. Clearly, solid state diffusion plays a major role in many facets of our lives.

The odor of a skunk reaching our nose (sensor for smell), even when there is no wind coming from that direction immediately brings to mind the diffusion of gases. The time to detect the odor at room temperature over a 10 meter distance might be as long as ten seconds. If diffusion of gaseous molecular species is said to proceed at velocities of up to 10^{3} m/s, why do we not smell things almost instantaneously? As in the case of solids, the atoms or molecules of the "host" gas "get in the way" (the atoms are separated by approximately 100 nm, making the time of diffusion appreciably longer than if there were no gas present.

The diffusion of liquids in liquids is slower than in gases, due to the lower kinetic energy of the liquid itself. The atoms or molecules are closer together, providing for a path with many more collisions per unit length than the case of gaseous diffusion. For instance, the time necessary to diffuse a drop of food dye in water from the center to the edges of a 20 cm. container might be a few minutes at room temperature.

The diffusion of a species in a solid is the slowest of all. The spaces between molecules or atoms is small (of ther order of a few tenths of a nanometer) and, therefore, the temperature necessary to allow diffusion of impurities over some small distance in a reasonable time is high. The cases which involve the diffusion of liquids or gases in solids, or gases in liquids are governed by similar laws of kinetics and have distinct proportionality constants, called diffusion coefficients, for each separate case. In all cases, diffusion has a driving force or forces which govern how fast the diffusant will travel in the host substance. Some of the factors governing the delivery of the energy necessary to make this happen are: gradients in pressure, gradients in temperature, pressure, temperature, size of the molecule, kinetic energy of the molecules (both diffusant and host), spacing of the molecules of the host, defects in the host, electric fields (voltage gradients), and photonic effects.

A theoretical background describing diffusion and the equations which govern it may be found in the Appendix at the end of this paper. The diffusion coefficient, D, will be proportional to the distance by the following formula

$$x_{1/2} = \text{sqrt } (Dt) \qquad\qquad (1)$$

where $x_{1/2}$ is the distance at which the concentration is 1/2 of the initial concentration of the diffusant tracked, and t is the time at temperature or the time of diffusion.

Experiment:

1. Diffusion of two gases

In order to perform this experiment, five students will need to stand in line with an "interperson spacing" of one meter (shown in Figure 1) in a relatively draft-free room (Note: A draft is a form of force changing the diffusion velocity). Person #1 will drop a few drops of vanilla or garlic extract onto a paper towel or cotton cloth, at which time all will start their stopwatches.
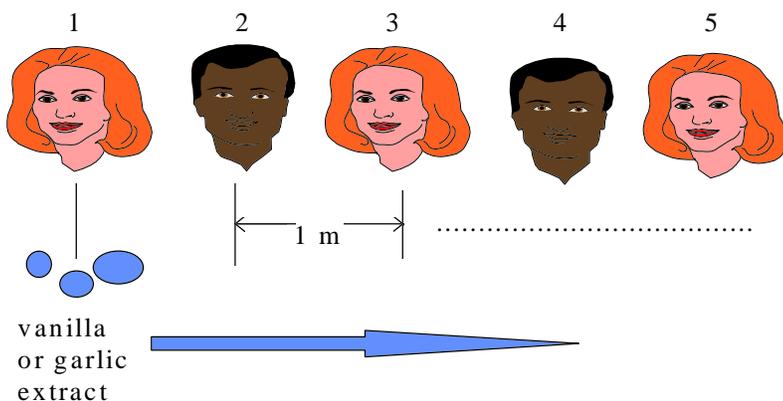

Figure 1
Schematic for diffusion of gases

As each person detects the odor of the vanilla or garlic, he/she should stop the stopwatch and record the time in Table 1 below. The paper towel should then be sealed in a plastic bag, brought out of the room, and disposed of properly. A second and third trial should be performed and recorded, disposing of the towel as before.

Table 1
Diffusion of gases data

Distance (m)	Trial 1 (sec.)	Trial 2 (sec.)	Trial 3 (sec.)
1			
2			
3			
4			

Average the sets of data and plot distance vs time. Calculate (estimate) a diffusion coefficient for this experiment. Curve fit the plot for a polynomial and an exponential. Calculate the velocity of the diffusant gas in the room air.

2. Diffusion of Two Liquids

Set a Petri dish or shallow Corning Ware dish on top of a bullseye (shown in Figure 2) in the center of an overhead projector platen.
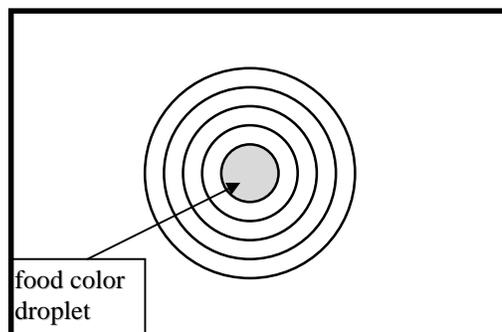
Figure 2
Water-filled dish on projector with bullseye

Pour to approximately 10 mm depth cold water in the dish and allow it to settle and stop all motion. Put a 20% (vol.) aqueous solution of food coloring or ink in propylene or ethylene glycol (anti-foaming and wetting agent) with this solution. Lower the dropper about 2mm below the surface of the water and squeeze a drop carefully into the water in the center of the bullseye. Start timing the color front movement as it passes each ring of the bullseye and record the time corresponding to the distance reached in a table like the one shown in Table 2. Using the overhead projector will enhance the student's ability to estimate the movement.

Table 2
Diffusion data for liquids

Distance (mm)	Trial 1 (sec.)	Trial 2 (sec.)	Trial 3 (sec.)
5			
10			
15			
20			

Average the three trials and estimate the diffusion coefficient for this experiment. You may do the same with "hot" water and see if the results are different. Calculate the velocity of the dye in the water.

3. Diffusion of a liquid into a solid

CAUTION: This experiment will produce HCl gas and should be performed under a fume hood for safety. Gently heat a Pyrex test tube, vertically clamped to a ring stand, which is approximately 1/3 filled with $CuCl_2 \cdot 2H_2O$, over a bunsen burner until the cupric chloride just melts ($435^{o}C$). This experiment can also be performed using a small beaker heated on a hot plate. Score and cut a quartz or glass rod to a length approximately 4 cm longer than the test tube or beaker. Carefully place the glass rod into the test tube or beaker and leave it at this temperature for 10 to 15 minutes. Remove the rod and allow it to cool on a flameproof laboratory fiber board. Score and cut the end of the rod to expose a "clean" cross section of the diffused couple. Wash the rod in running water until it is clean. Measure the "depth of diffusion" of the Cu^{++} ion into the glass. Estimate the diffusion coefficient for this experiment.

Do this experiment for multiple times at this temperature (example in Table 3) and record the data. Calculate the velocity of the diffusant into the glass rod material.

Table 3
Data for solid diffusion

Trial number	Depth of diff. (mm)	Time of diff. (min.)	Temp. of diff. (^{o}C)
1			
2			
3			

If you have a non-corrodable thermocouple, you may perform the experiment at various temperatures slightly below the melting point of the cupric chloride and estimate an activation energy of diffusion.

(Optional)

It is also interesting to put two glue gun sticks (polypropylene), one colored and one clear, in a test tube or aluminum foil boat which just fits them (approximately 1 cm.) and mark their interface on the tube or foil. Place the test tube on a small ring stand and put it into an oven for 10 minutes or so at a temperature above its melting point (approximately 140°C). Take the samples out and let them cool to room temperature. Have the students make their own observations. What is the same and what is different when the above experiments are compared with this one involving the glue sticks?

Reporting

The student should not only write his or her findings, but should suggest variations of these experiments for other substances and methodologies. Order of magnitude values for the diffusion coefficient (in m^2/s) for the three experiments are as follows:

(a) gaseous, $\sim 10^{-1}$, (b) liquid, $\sim 10^{-6}$, (c) solid, $\sim 10^{-11}$

Reports should be judged on the basis of not only data "correctness" but on the basis of suggestions for improvement, error sources and estimates, observations, etc.

Appendix: An Overview of Diffusion Mechanisms and Theory

A knowledge of mass transfer mechanisms is essential for the description of how atoms (molecules) move in solids, liquids and gases. The diffusing species make use of vacancies in order to move around in the host substance. In fact, when there are line vacancies, the atoms move at a much faster rate down the "pipe", as can be seen in the case of grain boundaries in solids. For point vacancies, an equilibrium number of vacancies, and hence the number of "atom jumps", can be calculated by determining the amount of energy, or **activation energy**, ΔE, necessary for an atom to leave a lattice site and create a vacancy. It can be shown by Boltzman statistics that, given a total or initial number of atoms, n_i, a fraction of these, n, at a given temperature, attain sufficient energy to escape from regular lattice points and create vacancies. The energy is related to this fraction by

$$n/n_i = C \exp(-\Delta E/kT) \qquad (A1)$$

or in semi-logarithmic plotting of n vs 1/T, a straight line with slope -ΔE/k, where C is a constant dependent on the material, k is Boltzman's constant (1.38 x 10^{-23} J/K), T is the absolute temperature in degrees Kelvin, ΔE is the activation energy in Joules. Stated simply, if a bar of material composed of two materials in solution along which there is a gradient in composition is heated to a temperature above room temperature (usually near its melting point), the solute atoms

will become redistributed, attempting to make the composition more uniform. Thermal energy supplies the the atom or molecule with sufficient vibrational energy to allow the solute atoms to move from a region of higher concentration to one of lower concentration.

In one dimension, considering a segment of solid Δx, shown in Figure A1(a), the concentration of solute at x_o is C_o and the concentration of solute at x_1 is C_1. The non-steady state condition is shown in Figure A1(b) for increasing times.

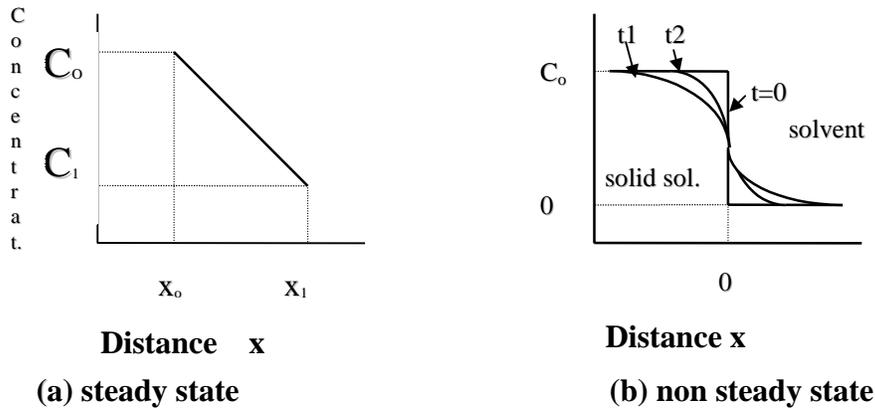
(a) steady state

(b) non steady state

Figure A1
Diffusion of Atoms

The diffusion flux J_{12} is the amount of material passing through a unit area in the x-direction per unit time and is proportional to the concentration gradient dC/dx by Fick's first law as
$$J_{12} = -D \, dC/dx , \qquad (A2)$$
where D is the proportionality constant called the **diffusivity** or **diffusion coefficient**. This is more generally stated as Fick's second law
$$dC/dt = d/dx(D \, dC/dx) \qquad (A3)$$
for the general case where D is concentration dependent under non-steady state conditions.
Solving these equations for the boundary conditions
(a) At t = 0, C = 0 for all x>0, (b) At t = 0, C = C_o for all x<0, and   (c) At x = 0, C not = C_o for all t>0, gives
$$C = C_o/2[1 - \text{erfc}(x/(2\sqrt{Dt}))], \qquad (A4)$$
where **erfc** refers to the **Gaussian error function**. The point at which the concentration of the diffusant is 1/2 of the initial concentration gives a simple relation most often used by scientists. This relationship is given in the body of this paper and may be used for the desired calculation of the diffusion coefficient. The diffusion coefficient, on the other hand, varies with temperature according to an Arrhenius-type of equation,
$$D = D_o \exp(-E_A/kT) = a^2 (E_A/Nh)\exp(-E_A/kT) \qquad (A5)$$
where a is the interatomic distance, N is Avogadro"s number, h is Planck's constant (6.6 x 10^{26} atoms per kilogram mole). The values of D_o for a number of solid materials are given in any number of reference books and papers on the subject.[2]

References:
1.   A. B. Ellis, et al., "Teaching General Chemistry: A Materials Science Companion", A.C.S. Books, 1993. pp.463-472.
2.   W. Jost, *Diffusion in Solids, Liquids, and Gases*, New York, Academic Press, Inc., 1952.