

Molecules in Motion
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Lecture – 37
Molecular Motion in Liquids (Contd.)

Welcome to another lecture in Molecules in Motion.

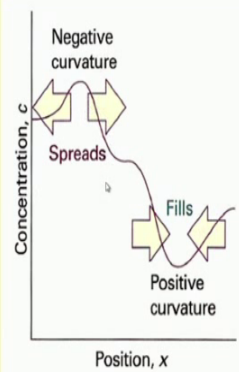
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Molecular Motion in Liquids: The Diffusion Equation:

- The **Diffusion Equation** shows that the rate of change of concentration is proportional to the curvature (more precisely, to the second derivative) of the concentration with respect to distance.

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

- If the **concentration changes sharply from point to point** then the **concentration changes rapidly with time**. We say the **distribution is highly wrinkled**



The graph illustrates the relationship between concentration and position. In the region of negative curvature, the concentration is spreading out. In the region of positive curvature, the concentration is filling in.

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What we were talking about in the last class, we will take it this up to begin with. We were now trying to establish the rate of change of concentration; that means, change of concentration with time. And we had derived this equation where we said the rate of change of concentration that is dc by dt is equal to the second derivative of the concentration at the various x y z direction.

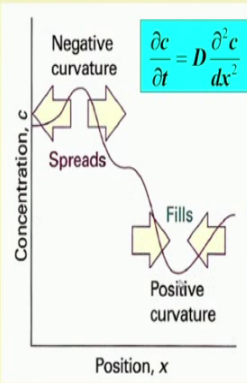
So, the diffusion equation which we had established in the last class was related the rate of change of concentration is was proportional to the curvature; that means the second derivative of concentration with respect to distance. We had taken this graph where we had x axis as the position for the particles at various concentration, and this is the concentration axis. So, what we were seeing if the concentration changes very sharply from one point to the other in the medium, then we say the concentration of the particles change rapidly with time.

So, if you have changed with of concentration, a drastic change in concentration from one point in x to another point in x plus x delta x , then we say the concentration changes rapidly with time. That means, at two points in the same axis along suppose x axis we are moving the particles along x axis; if a particle at x equal to 1 is different or drastically different from a distance say 1 cm from x initial x , then we say the concentration changes rapidly with time and the system is supposed to be highly wrinkled. Now what are these curvatures which we are looking into and what do they signify let us look at this in detail.

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Molecular Motion in Liquids: The Diffusion Equation:

- If the **curvature (or, the second derivation) of the concentration vs position plot is positive** (i.e., a dip), the **change in concentration is positive**; the **dip tends to fill**.
- If the **curvature or, the second derivation) of the concentration vs plot is negative** (i.e., a heap), the **change in concentration is negative**; the **heap tends to spread**
- If the **curvature is zero**, then the **concentration is constant in time**



The graph shows a plot of Concentration, c versus Position, x . It illustrates two types of curvature: 'Negative curvature' (a dip) labeled 'Spreads' and 'Positive curvature' (a heap) labeled 'Fills'. The diffusion equation is shown as $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$.

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The curvature or a second derivative of the concentration verses position plot is positive. If this is a positive, since it is a second derivative. So, which one should be positive? This will be a positive curve, second derivative this is the positive curve and this positive curve signifies a dip the curvature or the second derivative of the concentration versus position plot is positive the dip like here we have the concentration change is supposed to be positive and if the change is positive then what do you have? We have a dip in the concentration and there is going to be a tendency to fill this dip.

Now, what happens if the curvature or the second derivative of the plot of the concentration versus position is negative? If it is negative then you have a heap, what does heap mean? The change in concentration is negative; that means heap the change in the concentration is negative what does that mean? That means the heap tends to spread

out. And if the curvature is zero what happens if the curvature is zero? The curvature zero means the concentration is constant with time.

So, the three things we have taken here is, how the concentration is changing with position and we read the curvature from this plot; if the curvature is positive then we say that the change in concentration with time is positive. Change in time concentration with time is positive; that means, with time the dip will be filled more and more you get towards uniformity. When if the curvature of this the concentration versus position plot is negative then; that means, we get a heap like this means, the change in concentration is rate of change of concentration is negative; that means, you have a tendency, the heap to spread out.

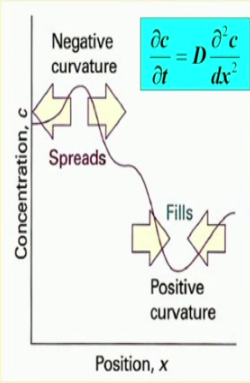
Dip means the solution nearby will try to make it uniform; heap means it is going to spread so, that the uniformity is it is tending towards uniform solution. If the curvature is zero; that means the, you will not have any change in concentration with time. So, the derivation what we are saying is we are seeing the special change in concentration, but what we are talking about is the change in concentration with time.

The change in concentration in time if it is positive, change in concentration of the whatever the particles is negative; that means, you have a heap which is supposed to be spreading out if it is a dip, then you have a positive change in concentration with time. And if there is no change in curvature, then we say there is no change in concentration with time.

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Molecular Motion in Liquids: The Diffusion Equation:

- If the **curvature is zero**, then the **concentration is constant in time**.
- If the **concentration decreases linearly with distance**, then the **concentration at any point is constant** because the **inflow of particles is exactly balanced by the outflow**.
- The diffusion equation can be regarded as a mathematical formulation of the **intuitive notion that there is a natural tendency for the wrinkles in a distribution to disappear**. More succinctly: **Nature abhors a wrinkle**.



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

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What happens if the concentration decreases linearly with distance? If you keep increasing the distance and the concentration linearly decreases, then the concentration at any point is constant because the inflow of particle is exactly balanced by the outflow. So, if diffusion equation is regarded as a mathematical formulation of any intuitive notion that a nature tendency for a wrinkle in a distribution to disappear. That means, that equation which we have derived gives us a mathematical formulation, which is intuitive to what nature has a tendency towards. Nature has a tendency towards having the wrinkles distributed and disappear that means nature abhors wrinkles.

So, what is if you are asked how do you prove that nature abhors wrinkles, you come up with these two plots here you have a change in concentration, positive change negative change in concentration, which is signified by a negative curvature in the concentration versus position plot. This means that there is a negative change in concentration with time; that means, what does it mean? It means that you have a heap and from there, you are trying to heap is the wrinkle which is generated, and you are trying to get it uniform by spreading. So, if there is a negative concentration rate of concentration; that means what we are talking about is a heap, where the system is going to be prone towards spreading it.

And if you are having a dip in the concentration; that means, if your concentration versus distance plot in the second derivative gives you a positive curvature; that means, that the

system is going to have a dip in concentration, and which will be tried to filled be uniform by filling up the dip.

So, these two conditions are supposed to be giving rise to a system, where you naturally have a tendency to have no wrinkles and this wrinkles are removed by redistribution of the particles either by filling in the dip or spreading of the heap. And when there is a linear decrease in concentration with distance if it is a uniform decrease; that means, the slope is constant; that means, at any point the concentration is constant and; that means, the inflow of particle is balances by the outflow.

So, if there is a linear decrease if the concentration decreases with linear linearly with the distance; that means, the slope is constant; that means, if the slope is constant; that means, the concentration at that point is constant and that means that the inflow of particle exactly balances out the outlaw of the particles from the system. Because the nature abhors wrinkle and it will all particles whether they form a heap or they form a dip will try to give rise to a distribution. So, that the distribution either the heap or the dip is spread out and made uniform.

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Molecular Motion in Liquids: The Diffusion Equation:


Diffusion with Convection:


- The transport of particles arising from the motion of a streaming fluid is called **Convection**.
- If for the moment we **ignore diffusion**, then the **flux of particles with molar concentration, c** , passing through an window of area, A , in an interval, Δt , when the fluid is flowing at a velocity, v , can be calculated in the way we have used several times before (by counting the particles within a distance $v \Delta t$) will be given as:

$$J(\text{flux of particles}) = \frac{cAv\Delta t}{A\Delta t} = cv$$

Let this J be called the **Convective Flux**



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So, we had talked about how we had derived the diffusion equation in the whatever we have taken up in the just the lecture now, we had talked about the Fick's diffusion. Fick's law of diffusion was how we had talked about the movement of the particles now; suppose the diffusion is not through Fick's law. Suppose the transport of the particles

arise from the motion of a streaming fluid and that streaming fluid we call as convection. So, if you are having a particle movement of the particles through a medium because of the streaming of the fluid and this streaming of the fluid is what we call as the convection current.

So, if the transport is not due to the diffusion of particles and is not guided by the Fick's first law of diffusion we say let us consider the transport of particles moving through a stream of moving through a medium, which is a streaming fluid; that means, it is having a convection current associated. So, if we do that, for that movement we ignore the diffusion. Now the flux of particle with molar concentration c passing through a window A in time interval Δt , when the fluid is moving with a velocity v can be calculated as we have done in several times before the flux being the total number of particles the number density passing through the window A of area v into Δt divided by area into Δt .

We if you had called talked about number density, then we would have multiplied by number density and we would have come made to amount of particle by divided by Avogadro number.

So, here what we have? We have just taken c and not multiplied by Avogadro number, because we have actually multiplied by Avogadro number and divided by the Avogadro number to get you the number of the flux of particle in terms of the amount. So, the flux of particle in terms of the amount can be the molar concentration into Avogadro number divided by Avogadro number.

So, Avogadro number is cancelled of into the volume element which we have area of interest A into v is the velocity d is the Δt . So, the length of the volume and element will be equal to v into Δt . We have done this number of times and the flux will be the number of particles divided by area into Δt .

So, if you see what you get is the molar concentration c , it is the amount of the flux which is moving through the window of area A into the velocity of the particles which are moving. So, we call this J as the convection flux.

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Molecular Motion in Liquids: The Diffusion Equation:

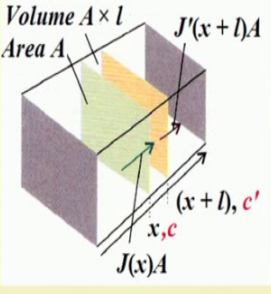
Diffusion with Convection:

• The **rate of change of concentration in a slab** of thickness l and area A is, by the same argument as before and **assuming that the velocity of the particles does not depend on the position**

• The **NET flux of particles** in a region is the difference between the **flux of particles** entering from the region on the left and the **flux of particles** leaving to the region on the right, will be =

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

$J(\text{flux of particles}) = \frac{cAv\Delta t}{A\Delta t} = cv$



The diagram shows a 3D rectangular slab. The left face is at position x with concentration c and flux $J(x)cA$ entering. The right face is at position $x+l$ with concentration c' and flux $J'(x+l)c'A$ leaving. The volume of the slab is $A \times l$ and the area of the faces is A .

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If this is the convection flux, then what happens; if you remember in the last one which we had talked about the diffusion we had talked about the ions moving from this side to this side under the concentration gradient. Now here what we want to find out? We want to find out the rate of change of concentration of the particles in the in terms of amount in the slab of thickness l this is the thickness l and area A .

By the same argument as we had talked about in the while we were deriving the Fick's second law the second differential equation, which we had taken with rate of change in concentration proportional to the concentration a second derivative of the concentration and with respect to distance. So, if we are looking at this, then what happens? If you are having some particles moving into this area and some particles moving out, then the total flux of particle inside this will be what you have at j at the position J equal to x and minus that of the particles coming out at J equal to j plus x plus l .

So, the net flux of particles in this region is the difference between flux of particles amount of particles entering the region on from left hand side and the flux of particle leaving the region of interest like this is A into l from this we are leaving and going to the right hand side. So, the change in concentration the rate of change in concentration in this area of interest l into A will be nothing, but the change in flux which we see at x and the and to that of the flux, which is going out at x plus l divided by l .

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Molecular Motion in Liquids: The Diffusion Equation:

Diffusion with Convection:

$$J(\text{flux of particles}) = \frac{cAv\Delta t}{A\Delta t} = cv$$

- The **rate of change of concentration of particles in a slab** of thickness l and area A is, by the same argument as before and **assuming that the velocity of the particles does not depend on the position**, will therefore be:

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l} = \left\{ c - \left[c + \left(\frac{\partial c}{\partial x} \right) l \right] \right\} \frac{v}{l} = -v \left(\frac{\partial c}{\partial x} \right)$$

where, $c' = \left\{ c + \left(\frac{\partial c}{\partial x} \right) l \right\}$

$$\frac{\partial c}{\partial t} = -v \left(\frac{\partial c}{\partial x} \right) \rightarrow \text{The rate of change of concentration of particles due to CONVECTION}$$

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So, let us see what we get? The rate of change of concentrations in this slab of thickness l and area A is, by the same argument as that of done before assuming the velocity of particles do not depend on position, we remember this is in this particular thing we are assuming the velocity of particle is independent on the position of the particle. So, we do not need to take into account of the position as such.

So, what we are and what is the flux we have defined? Flux we have defined as c into v . And this flux in terms of the amount of the particles that is why we do not have the Avogadro number. Avogadro number was supposed to be multiplied and supposed to be here c into Avogadro number in number density, but we when we are converting that into the amount of particles, then we divided by Avogadro number. So, we are only left with c right.

So, the change in concentration the rate of change in concentration is going to be nothing, but the J at x minus the J at x minus l x plus l . So, if we have the J prime concentration as c plus the change of concentration of c with x into l is the new c which we have. Now we want to substitute that in terms of the J , c j is here in terms of concentration here, you apply this value J v as the condition for finding out the change in concentration with time.

So, if you are finding out the change in concentration with time, you substitute the value for J minus J and J prime and divided by l . So, what we have? We have taken see c is

already there and v will be always there; c is what is changing velocity for all particles are remaining same. So, I can take v and l as common. So, I have written v and l as separate.

Now, after that what you have? You have at point J equal to x and z at x J as j as x is something here right J x minus the J at x plus l at this point. So, the J at x minus the J at x plus l divided by l that we take v is the J is nothing, but c into v . So, we take v common and l common they are not changing with the concentration. So, they can be taken out what we have? C is the concentration at x and what is the concentration at the x plus l ? It is going to c plus c prime you can write c plus the change in concentration with distance into l right.

Now, if you simplify this you simplify this, what you have? You have, you just see you have c minus c . So, c gets cancelled, only thing which you are having is $d c$ by dx l this two gets cancelled right. So, what you have? We have dc by dx with a negative sign.

You can open up this. So, this becomes minus c and this becomes minus dc by dx into l , if you open up d and d minus will cancel off you have minus dc by dx into l , and the whole thing you have taken common is v by l . So, this l and this l is going to get cancelled. So, what you are left with? Minus velocity into the change in concentration with x right so, now, we have generated a new equation the diffusion equation with convection as the only contribution. The rate of change of concentration due to convection can be given by this equation. So, we have established the new equation diffusion equation, where we have diffusion only through the convection current in this medium.

So, the change in concentration where it is equal to minus the velocity of the particles in that medium into the gradient in velocity with special direction x y z and this rate of change of concentration is due to the convective flow.

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Molecular Motion in Liquids: The Diffusion Equation:

When Both Diffusion and Convection Occur:

- When Diffusion and Convection both occur then the total change of concentration of the particles in a region is the SUM of the TWO EFFECTS, and the **generalized diffusion equation is given as:**

$$\frac{\partial c}{\partial t} = \left[D \left(\frac{\partial^2 c}{\partial x^2} \right) \right] - v \left(\frac{\partial c}{\partial x} \right)$$

- A further refinement, which is important in chemistry, is the possibility that the concentrations of particles may change **as a result of reaction**. When reactions are included, we get a powerful differential equation for discussing the properties of reacting, diffusing, convecting systems and which is the basis of reactor design in chemical industry and of the utilization of resources in living cells.

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So, suppose we have both diffusion and convection occurring together in a system, we have diffusion as well as convection occurring.

So, what happens? Diffusion is going to be guided by the laws which is the first law of Fick's diffusion we substitute that and what do we get? If you remember we had derived this expression when we are talking about the diffusion being guided by Fick's first law of motion diffusion. So, this is the equation which we get in change in concentration or of the rate of change of concentration or change of concentration with time was equal to the second derivative of concentration, with respect to the position or d^2c/dx^2 . This was because of the diffusion of the ions due to concentration gradient and was guided by the Fick's first law of diffusion.

Then what we have evaluated? We have evaluated the Fick's; we have evaluated the diffusion through convection currents, and this convection current we have found out the change rate of change of concentration of the particles is going to be equal to minus v ; v is velocity of the particles in the medium into the change of concentration with x . So, now, we have two dx which is both going to be existing, you have diffusion plus you have convection occurring. When you have diffusion and convection both occurring then the total change of concentration of the particles in the region any particular region is going to be the sum of the two effects, which is existing it is because of the diffusion as well as the convection.

So, if because of the diffusion so, the change of concentration with time so, the change in concentration with time; that means, the rate of change of concentration is going to be the contribution because of the diffusion, that is because that is going to be the concentration gradient in concentration with position in the second derivative of change in concentration with position into the diffusion coefficient minus the velocity of the particles into the concentration change in concentration with position along anyone, any of the x or y or z axis.

So, the total sum, the total change in any process for any process when you have the concentration changing with time, where you both when it the process is not only guided by diffusion process, that mean the particles are moving through the medium not only guided by concentration gradient. But also because of the convectional currents existing in the system, and convectional current can be generated by if you have a temperature difference, you can have generate convectional current in the system.

So, the change in concentration with time will be the contribution of the two effects which you have; one is because of the diffusion of the particles through the system and the other one is because of the convection current generated in the system. So, this is if you have a equation like this. That means, you have to understand that the process which is occurring here is the change in concentration with time of the particles through a medium is not only guided by the diffusion process, but also guided by the convectional process. Convectional process will always be having a negative sign in between in front of the equation.

So, these equation what you have? These are actually quite important in chemistry and it is possible that the concentration of the particle may change with result of reaction as well. So, the concentration of the particles may when you are having a reaction, you any reaction is going to be having a change in concentration with time, then you can further modify this equation. It though it gets a slightly complicated. But these are types of particles the differential equations that you use to find out the information about the change of concentration of particles, when moving through a medium.

Suppose when the reactions are included if you are a system is undergoing a reaction, that the reactions are included we have a powerful differential equation, for discussing the property of reacting diffusing convecting systems; these are very important in the

chemical industry for designing reactors for many other purposes how the flow is going to be what sort of a system you are going to use, these equations become very important when you are trying to do applications in the chemical industry.

And it is also quite important in resources in living cells as well, because in I have which I have not discussed living cells and how the ions or the minerals are transported in our body. These are also most of the processes which we which are occurring in our body, where you have a diffusion where you have movement of various nutrients or cations, anions like sodium potassium moving through your body system in the blood system is actually dependent on or guided by diffusion processes.

And if they are guided by diffusion processes, we need to know what are the two conditions which we need to know is whether it is only diffusion control or you have diffusion and convection control or if you have other reactions which are taking place.

So, this is our fundamental equation, which gets modified according to systems which we are studying. We are not going to take up the solutions and further details of this equation, if we have understood till now, if we have understood what how we can justify that nature abhors wrinkles in a system if you have understood that convection contribute differently towards the migration of ions. And hence the concentration rate of concentration with time differs when you have only convection and to that of the rate of concentration change of concentration with time when it is only diffusion control.

And if the both the system both in nature actually you have both of them existing together like diffusion and convection existing together for the propagation of the particles through the medium. If such a system is arising then we have to just take the summation of the two effects which we have already studied separately; this is for the diffusion process control process and this is for the convection control process.

So, this concludes our discussion on the diffusion equation and motion of molecules in liquid. I will take up, we have talked about the what do you call the kinetic theory of gases; from that we had simplified and generalized and found out the various fundamental phenomenological equations. We have not derived the expressions for the diffusion coefficient, thermal coefficients in the next class; since we are almost and towards the end of the molecular motions in liquid, we will take up the fundamental parameters which we had discussed in the kinetic theory of gases, as to how they can be

used to find out the values of the α the diffusion coefficient, thermal coefficient and viscosity coefficient in the next class.

Thank you so much.