Fundamentals Of Combustion (Part 1)

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Lecture – 32

Lennard-Jones potential model for diffusivity

Let us start this lecture with a thought process.

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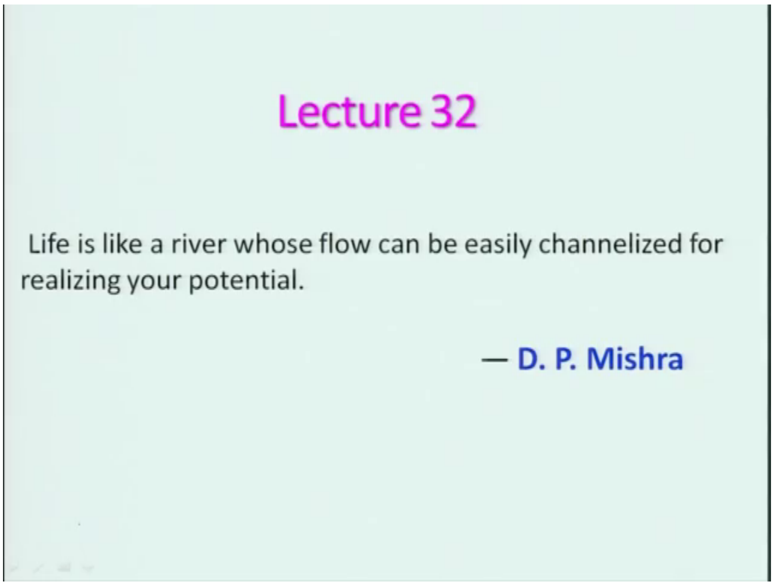

Lecture 32

Life is like a river whose flow can be easily channelized for realizing your potential.

— D. P. Mishra

Life is like a river whose flow can be easily channelized for realizing your potential; not stopping it putting it down. If you recall that in the last lecture, we basically looked that you know how to relate the properties, property means transport properties like viscosity, then conductivity, thermal conductivity and diffusivity to the molecular properties like diameter and other things right and what I am thinking now we will also look at little bit now and later on will have to modify it further because if you recall that we had arrived this relationship using a very simple kinetic theory of gases right.

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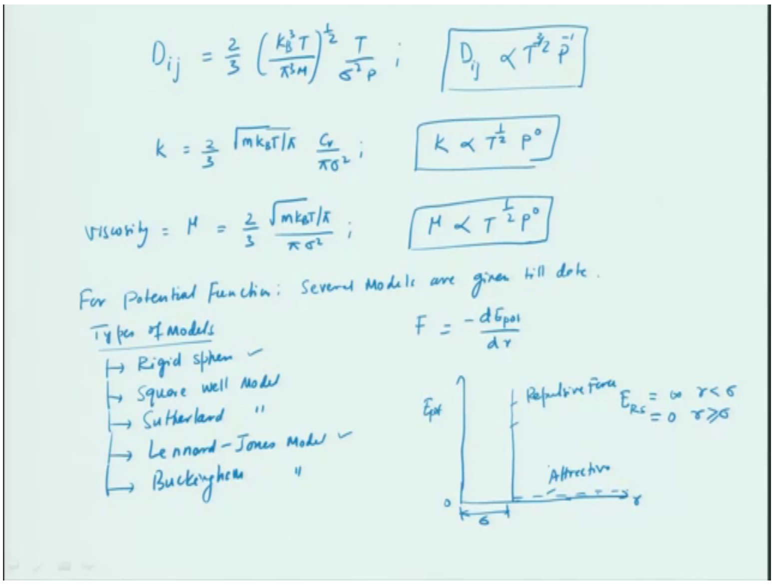

$$D_{ij} = \frac{2}{3}\left(\frac{k_B^3 T}{\pi^3 M}\right)^{\frac{1}{2}} \frac{T}{\sigma^2 P} \; ; \qquad \boxed{D_{ij} \propto T^{3/2} P^{-1}}$$

$$k = \frac{3}{3} \sqrt{m k_B T/\pi} \, \frac{C_v}{\pi \sigma^2} \; ; \qquad \boxed{k \propto T^{\frac{1}{2}} P^0}$$

$$\text{viscosity} = \mu = \frac{2}{3} \frac{\sqrt{m k_B T/\pi}}{\pi \sigma^2} \; ; \qquad \boxed{\mu \propto T^{\frac{1}{2}} P^0}$$

For Potential Function: Several Models are given till date.

Types of Models

- Rigid sphere ✓
- Square well Model
- Sutherland "
- Lennard-Jones Model ✓
- Buckingham "

$$F = -\frac{dE_{pot}}{dr}$$

$$E_{RS} = \infty \quad r < \sigma$$
$$= 0 \quad r \geq \sigma$$

So, if you recall that we had basically derive this formula for the mass diffusivity right, 2 by 3 and K B cube T divided by pi cube m half T by sigma square and P. So, this is for the mass diffusivity right and if you consider this diffusivity right is basically proportional to what T power to the 3 by 2 and P power to the minus 1; that means, inversely proportional to the pressure right.

And if you look at thermal conductivity right, we are derived as basically this relationship I am not derived I left it I guess that you might have derived by this time, if not please derive it which is very simple right and this is root over M K B T divided by pi into C v divided by pi sigma square ; keep in mind this K B is basically Boltzmann constant right and T is your temperature mass is the mass of the what you call molecules and in similar fashion, if look at K is basically proportional to what half and P power to the 0; that means, it is independent operation right.

Similar with viscosity this you know like viscosity is basically mu is nothing but again 3 root over M K B T divide by pi by pi sigma square and the similar way you can find out basically it is power to the half and P not. It is independent operation right for the gas, but if you recall that simple theory of kinetics sorry simple kinetic theory of gases that we had used earlier for deriving this relationship for the thermal conductivity viscosity and diffusivity right, in that case what are the assumption here we had made ?

Because their we assume there will be elastic collision and there is no interaction between the molecules except during the collision right and both will be spherical in nature which one the particles; particle means it can be atom, it can be what you call radical, it can be molecule that is the particle what we consider, but is it really possible that there would not be any what you call interactions or will it be spherical no na, need not to be and also the rigid ; the molecule only rigid because there will be of course, there are various kinds of you know this thing you can consider one is polar, another is nonpolar right. If you nonpolar considered there will be basically the dipole moment will be there, if it is a bimolecular and trimolecular, triatomic or diatomic molecules right, then there will be interaction with this.

Suppose one molecule will come over there will be dipole moment and that will be inducing the other molecules also. So, as a result, there will be there will be what you call a effect will be there; that means, whenever they are coming like, there will be some kind of interaction will be there because one molecule will be coming closer to another molecule, there will be dipole moment there will be some kind of a what you call attractive forces and when you come very near there will be repulsive forces right which we consider, but in a little different way right. That model what we use right is basically rigid sphere model right and that give something potential which will be right and that potential has to be taken care. This potentially if you look at there are several models right.

For potential functions right there are several models. To take care of you know potential between this molecule during interactions right, there will be potential function has to be taken. There will be some force field right in the molecules and there are several models are being given by the various people models are given right; till date and several more model will be also coming up in future, but what model we had considered earlier is this one that is what you call types of models right. There are several types we had considered Rigid sphere.

And there will be also what you call square well model and there will be what you call Sutherland model, Sutherland some people call Sutherland model; there will be Lennard Jones model and Buckingham, there are several of them. What we are considering till now is the rigid sphere model right and in that case what will be looking at basically force will be de, this is the potential right by d r, d r is the basically radial direction you are talking about right.

Now we will be among all this thing, we have already discuss about Rigid sphere model till now we have considered, we will be considering the Lennard Jones model because that is being used very much in the combustion problem and it is easier to handle and, but rest of the things is not only this what you call 5 of them I have jotted down, but there are several models you know like if you look at this molecular theory of gases by Curtis and the bird and then Hirschfelder, you will find that several model are there. So, if you look at the model, what we had considers is basically this is the potential rigid sphere model right which is consider as let us say this is your repulsive forces and this is here.

This is basically E potential right energy. This E stand for energy for potential and this is the r direction and this the you know distance is sigma, sigma is a diameter of the sphere what you are considered and this is your repulsive forces and this is your attractive forces; that means, it will be 0. What is the meaning of that?

E, if I you can look at rigid sphere is equal to infinity when r is less than sigma; that means, repulsive forces will be very high right when it is r is less than sigma smaller than that and this will be 0 when r is greater than equal to sigma; that means, it will be I put it here, but actually it is 0 just to differentiate because if I say this is 0 right, this I am putting just to make a difference otherwise it is 0 ok; are you getting?

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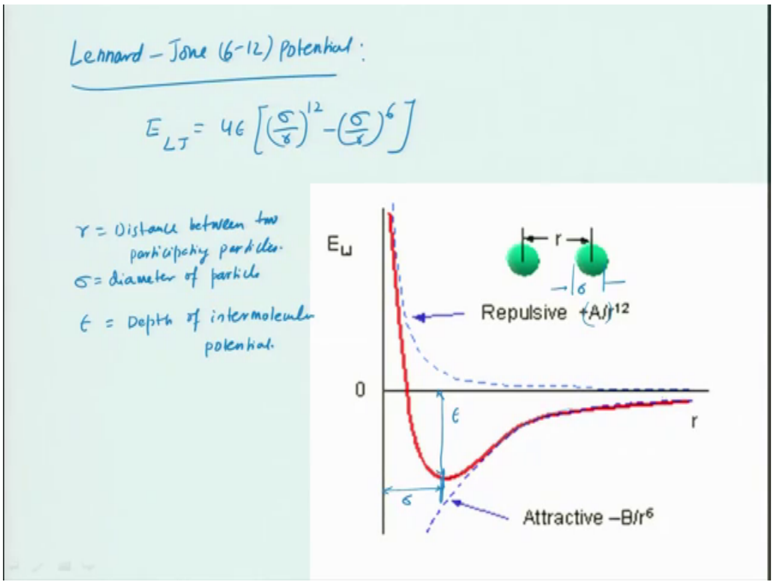

Lennard – Jone (6-12) Potential :

$$E_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

r = Distance between two participating particles.

σ = diameter of particle

ϵ = Depth of intermolecular potential.

But if you look at the real situation, this is ideal situation ideal gas you know, but in real gas what will consider is basically there will be repulsive forces A divided by r right. You can say this is power to the 12 right, B power to what you call r 6 this is that attractive forces keep in mind this 12 and 6 right, this will be and when is sum it of you will get this is the red line. This is the actual potential what will be coming the red line; the total together, it will be together. Now this is if you look at this diameter is basically sigma the distance between 2 particle is a r right is consider and keep in mind that this is basically if I consider, this is your sigma right.

And this is I can consider right r this may be here epsilon right, epsilon is sigma is what? Sigma is basically diameter of particle and sigma is the depth of intermolecular potential. So, and this is basically known as what Lennard Jones 6, 12 right potential.

Keep in mind that I can take this instead of 6, 12 or 6, I can take some other thing as well. I can take anything as a matter of fact E I J, L J right is equal to 4 epsilon sigma by r 12 minus sigma by r 6. This is the potential what is being considered right and as I told this 12 and 6, you might be thinking like is it the right model or wrong it is did not be because that depends on the kind of molecules you are handling ok, but why and large people found this is good and also it is you know convenient to handle mathematical that is why people put 12 and 16 that is the reason what you know I was given.

And I was surprised to know that is not it like; that means, there is a lot of scope for you people to improve on this model and we you are considering because we are happy with this and within the error what will be getting right. So, what will be discussing only this Lennard Jones 6, 12 potential right or you can say 12, 6 potential right. So, that is and we will be seeing that how it is for that, we need to look at basically this datas right you can either you know get that from the some data book or you can have some you know inversely you will find out the diameter of the molecules suppose some new molecules kind of thing and this r is the as I told it is the distance between r is the distance between two what you call participating particles right, between two participating particles.

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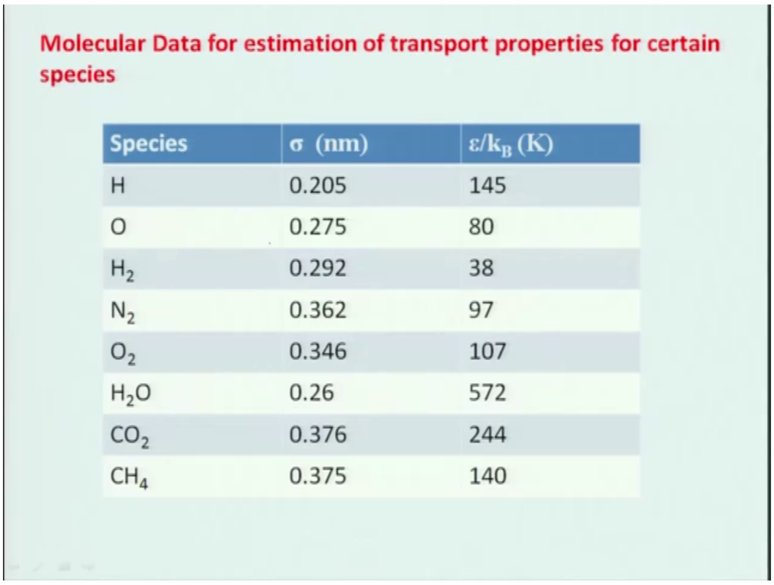

Molecular Data for estimation of transport properties for certain species

Species	σ (nm)	ε/k_B (K)
H	0.205	145
O	0.275	80
H_2	0.292	38
N_2	0.362	97
O_2	0.346	107
H_2O	0.26	572
CO_2	0.376	244
CH_4	0.375	140

So, let us look at this you know if I want to get this thing, then actually I will gets molecular data sigma right and that will be you know it is given some of the species H, O, H 2 kind of things and these are the diameter of the particle which is ordered of nanometres right and this epsilon is the depth of intermolecular potential and this k B is your Boltzmann constant right.

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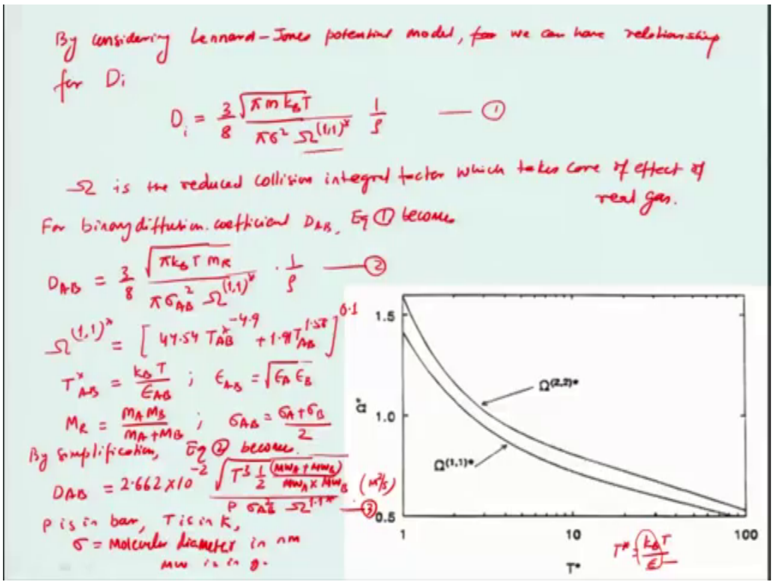

By considering Lennard-Jones potential model, for we can have relationship for D_i

$$D_i = \frac{3}{8}\frac{\sqrt{\pi m k_B T}}{\pi\sigma^2 \underline{\Omega^{(1,1)*}}}\frac{1}{\rho} \quad \text{—①}$$

Ω is the reduced collision integral factor which takes care of effect of real gas.

For binary diffusion coefficient D_{AB}, Eq ① become

$$D_{AB} = \frac{3}{8}\frac{\sqrt{\pi k_B T m_R}}{\pi\sigma_{AB}^2\,\Omega^{(1,1)*}}\cdot\frac{1}{\rho} \quad \text{—②}$$

$$\Omega^{(1,1)*} = \left[44.54\,T_{AB}^{*\,-4.9} + 1.91\,T_{AB}^{*\,1.58}\right]^{0.1}$$

$$T_{AB}^{*} = \frac{k_B T}{\epsilon_{AB}} \; ; \; \epsilon_{AB} = \sqrt{\epsilon_A\epsilon_B}$$

$$M_R = \frac{M_A M_B}{M_A + M_B} \; ; \; \sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

By simplification, Eq ② become

$$D_{AB} = 2.662\times10^{-2}\,\frac{\sqrt{T^3\,\frac{1}{2}\,\frac{(MW_A + MW_B)}{MW_A\times MW_B}}}{P\,\sigma_{AB}^2\,\Omega^{1.1*}}\;(m^2/s) \quad \text{—③}$$

P is in bar, T is in K,
σ = Molecular diameter in nm
MW is in g.

So, it is given all these datas, you can get from a table right by considering Lennard Jones model like potential model right.

We can derive you know like this thing, but I will just give you the final you know this answer for the diffusivity that is for diffusivity relationship, for diffusivity right D i it can be 3 by 8 pi m k B T root over divided by pi sigma square omega 1 coma 1 star right and 1 over rho.

So, if you look at it is similar in nature right is not it, like you know k B the Boltzmann constant is there, T is the temperature right and sigma is your diameter of the molecule, but there is a one term which is coming this is the term and that is known as the reduce collision integral correction fact, the sigma is basically reduced collision integral factor right and this is why it is given because it is given to include the effect of real gas right; that is a thing.

Student: Sir, ratios omega.

Ratio 1 coma 1 star right star, this is star and if you look at of course that is a some relationship for that. There might be several relation for this reduce collision triple factor, I am just giving you one of them right. Let us look at this. This will be basically this collision integral factor is a function of T star right. So, if you look at this T star right, this T star T star is equal to basically k B by T into epsilon.

If you look at this k B by epsilon already we can get from table, we have seen that just now like you know. So, and epsilon is what? Here well depth the depth of that value in that this thing right. So, therefore, this you can get and keep in mind that it is changing with the log 1 and log plot this is omega 1 by 1 start and this is being used for the generally diffusivity calculation and omega 2 by 2 star is used for viscosity and the conductivity calculation which will be doing and there will be some difference in that but it is similar in nature and for binary mixture right. As I consider, let us say this is for binary mixture diffusion coefficient right.

Equation 1 becomes right D A B 3 by 8 root over pi k B T m R divided by pi sigma A B square 1, 1 coma star now this is basically a function of this thing into rho. So, if you look at this sigma, you know sorry gamma 1 coma 1 star.

This is reduced collision integral of you can say this thing is equal to basically I can use a semi empirical relationship T A B star minus 4.9 plus 1.91 T A B 1.58 power to the 0.1. Now this T this is also tab and this tab I have already told you, but let me again tell you that t star k B is equal to k B by T by epsilon A B.

What is epsilon A B, epsilon A B is equal to epsilon A epsilon B. You know that A is a, molecule B is a another molecules are you getting and then this m R is the reduced mass which already we have defined earlier let me write down a M A M B divided by M A plus M B right and what is sigma A B? Sigma A B is equal to sigma A plus sigma B divided by 2. This already we have discuss I am just restating again now to if I say this is equation 2 to simplify you know that equation and in a manageable format which will be easier to use, we can do that we can actually put this k B values, pi values and you know kind of things and express this density in terms of pressure and temperature kind of thing using ideal gas.

Because if you look at the real gas is taken care by reduce which you know reduces collision integral which takes care of the effect of real gases. So, rest of the things are pretending to ideal gas are you getting. So, therefore, I can write down the equation 2 becomes by simplification, equation 2 D AB 2.662 10 power 2 minus 2 T cube half, molecular weight of A plus molecular weight of B, molecular weight of A into I can say multiplication M W B right divided by P sigma A B square star and this will be in unit of metre square per second and keep in pi. Mind that P is in bar P is in bar P is the pressure right in bar and T is in kelvin and molecular diameter sigma, this is molecular diameter; it can be A, can be B and I am just writing that way metre is in nanometre.

And M W is in gram to this unit 1 has to take care whenever you are using the, let us say equation 3. Equation 3 whenever you are using be careful about units otherwise it will be all (Refer Time: 24.20) means it will be you know complicated, it will be something garbage you will get number wise are getting my point. So, generally people use this one and then be happy with that and we may do some come calculation just have it free. Now having done this thing question arises, we make get the diffusivity for a particular mixture with respect to another may sorry, we may get the diffusivity of one molecule with another respect to another molecule, but; however, in combustion problem right, will have to handle mixture of gases.

That means mixture of several molecules. Now how will handle that because if I will go on doing that, then it will be life will be very miserable. It is I am having 23 species I am in 23 diffusivity (Refer Time: 25.13) and then others will be also moving with 11 different diffusivity is not it; however, how will take care that is important because will be learning how to take care of mixture.

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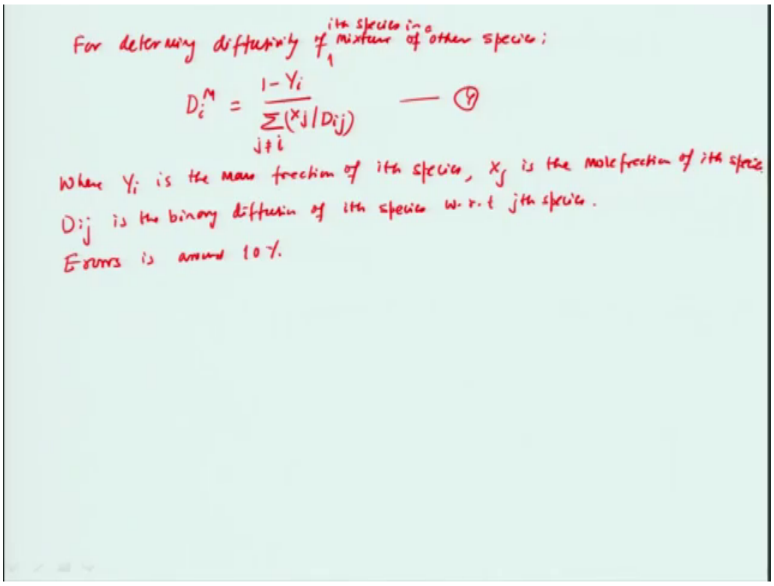

For determining diffusivity of ith species in a mixture of other species;

$$D_i^M = \frac{1-Y_i}{\sum_{j\neq i}(X_j/D_{ij})} \quad \text{—} \quad ⑨$$

Where Y_i is the mass fraction of ith species, X_j is the mole fraction of jth spec

D_{ij} is the binary diffusion of ith species w.r.t jth species.

Errors is around 10%.

So, for determining the diffusivity mixtures, we can use certain empirical formula of mixture of you know other compounders other species right.

Ah what we are doing, we are basically looking at diffusivity of you know right of particular species with respect to other specie, other species right of mixtures right in a mixture will be basically D i M is equal to 1 minus Y i divided by X j into D i j where j is not equal to i where Y i is the mass fraction of i-th species and the x j is the mole fraction of i-th species of course, the D i j is the binary diffusion i-th species with respect to what is that, j-th species and keep in mind that the you are basically calculating in the diffusivity of i-th species ok, did not diffusivity of i-th species in a mixture right in a mixture of other species are you getting.

And if you use this thing, there will some error and that errors will be in the range of something around you know 10 to 15 percent kind of thing. So, if you use this because this is let us say 4 right and the errors if you use this because formula and also other whatever you have done till now, the errors will be is around something 10 percent.

So, we will stop over here. And then in the next lecture will be discussing about how to handle this you know other properties kind of thing right.

Thank you very much.