Chemical Kinetics and Transition State Theory
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Lecture – 11
Problem solving session 1

Hello and welcome to module 11 of Chemical Kinetics and Transition State Theory. Last four modules or so, we have been looking at the collision theory for reactions. And we have went through its derivation very very carefully in great detail, and I have derived an equation. What I want to focus on today is to take a step back and calculate; so we will look at specific problems and actually calculate numbers out. And see how this collision theory actually works in to calculating the rate constant; so just a quick recap.

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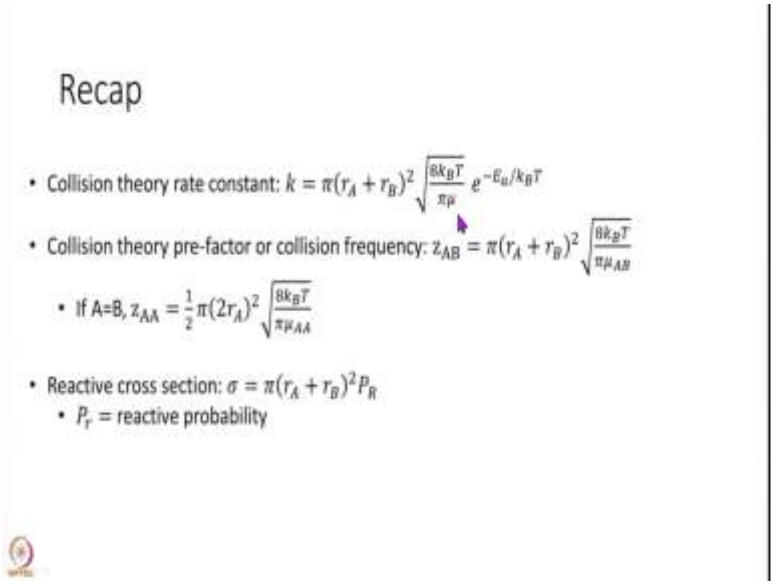

Recap

- Collision theory rate constant: $k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$
- Collision theory pre-factor or collision frequency: $z_{AB} = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu_{AB}}}$
    - If A=B, $z_{AA} = \frac{1}{2}\pi(2r_A)^2 \sqrt{\frac{8k_BT}{\pi\mu_{AA}}}$
- Reactive cross section: $\sigma = \pi(r_A + r_B)^2 P_R$
    - P_r = reactive probability

This is the final formula we derived for the collision theory; rA and rB are the radii of A and B. this is the average speed, mu is the reduced mass, Ea is the activation energy and T is the temperature. We actually, let me just make another notation, which is the pre-factor or collision frequency, to just this term without the exponential.

You will in books or literature often see this being called the pre-exponential factor, from the perspective of Arrhenius equation; or it can often called the collision frequency. One important note we met two modules ago, if A is equal to B; you have to be careful, the collision gets a factor of half and so will the rate. So, rA is equal to rB, you will get two rA; you will get mu as mu AA; but also you get this factor of half.

So, if you do not remember it how we got this factor half; go back to couple of modules and you will see the logic for that. In a last module we had introduced the idea of reaction cross section, as pi rA plus rB square into PR; where PR is the reactive probability. And we had went through and carefully argued, how to choose this PR to get this kind of an equation.

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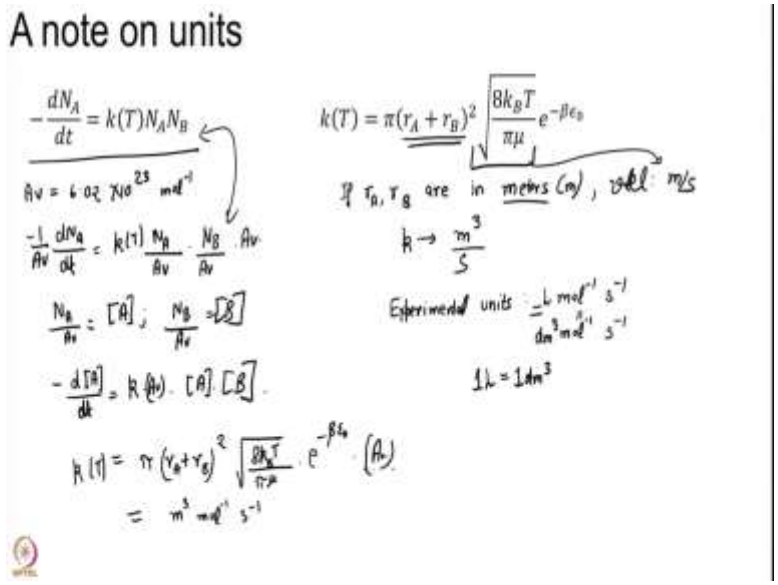

A note on units

$$-\frac{dN_A}{dt} = k(T)N_AN_B$$

$$k(T) = \pi(r_A + r_B)^2\sqrt{\frac{8k_BT}{\pi\mu}}e^{-\beta\epsilon_0}$$

$Av = 6.02 \times 10^{23}\ mol^{-1}$

$$-\frac{1}{Av}\frac{dN_A}{dt} = k(T)\frac{N_A}{Av}\cdot\frac{N_B}{Av}\cdot Av$$

$\frac{N_A}{Av} = [A]$; $\frac{N_B}{Av} = [B]$

$$-\frac{d[A]}{dt} = k(Av)\cdot[A][B]$$

$$k(T) = \pi(r_A+r_B)^2\sqrt{\frac{8k_BT}{\pi\mu}}\,e^{-\beta\epsilon_0}\,(Av)$$

$$= m^3\ mol^{-1}\ s^{-1}$$

If r_A, r_B are in meters (m), vel: m/s

$k \rightarrow \frac{m^3}{s}$

Experimental units $L\ mol^{-1}\ s^{-1}$

$dm^3\ mol^{-1}\ s^{-1}$

$1L = 1dm^3$

One important thing before we solve problems is that of units; units is always very very important, any number you any anytime you calculate must always have units. So, what is the unit of k? So this k that is written here, if you look at it what is the unit right now? If rA comma rB are in let us say meters. And this thing is velocity, so velocity is let say in meters per second; then k is in units of meter cube per second.

So, I have this meter square multiplied by meter per second, so I get meter cube per second. But, the typical units of rate experimental units of rate are typically in liters mole inverse second inverse. So, first thing is that if we want to compare to experiment, these are the units we want to calculate in. By the way, often in literature you will also find dm cube mole inverse second inverse; we are liter and 1 liter is equal to 1 dm cube.

So, these two are identical, this is equal to this; so, let us go back to the basics on what we are doing. The k the way we have defined is via this equation; we are calculating dNA over dt as the rate constant here, into NA into NB. You can go back on our very basic derivation and you will see this is true. Remember typically the experimental rate is in the language of concentrations; so have to convert in the language of concentration first.

So, what I do is I defined this Avogadro number which is 6.02 into 10 to the power of 23 mole inverse. And let me write this as so we will note now that, well you can first verify that this equation really follows from this; that is almost trivial to proof. And then note that NA over Avogadro number equal to concentration of A; and NB divided by Avogadro number is concentration of B.

So, I get minus d concentration of A by dt equal to k, into Avogadro number into concentration of A into concentration of B in the language of concentrations. So, my new k of T becomes pi into e to the power minus beta epsilon naught, into the Avogadro number. So, if I do that the new units has been become meter cube mole inverse second inverse; because of Avogadro I get a mole inverse.

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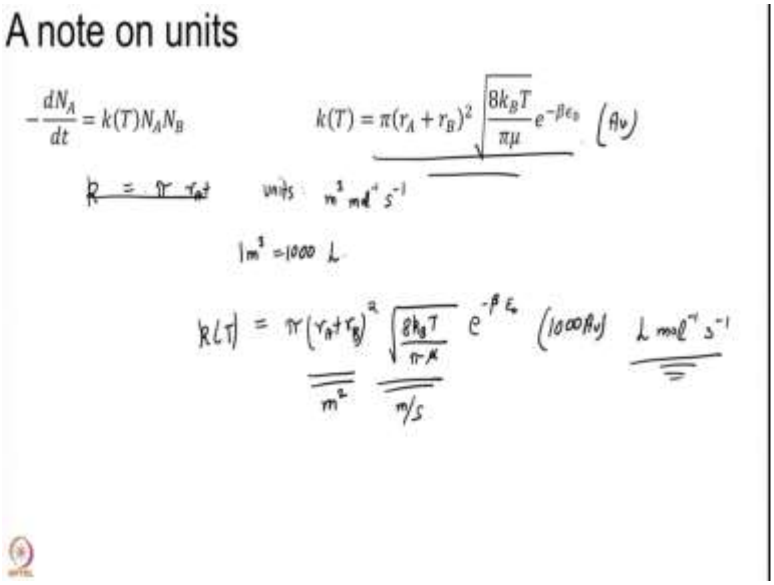

A note on units

$$-\frac{dN_A}{dt} = k(T)N_AN_B \qquad \underline{k(T) = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-\beta\epsilon_0}} \ (Av)$$

$\underline{k = \pi r_{A+}}$ units $m^3 mol^{-1} s^{-1}$

$1 m^3 = 1000\ L$

$$k(T) = \underbrace{\pi(r_A+r_B)^2}_{m^2} \underbrace{\sqrt{\frac{8k_BT}{\pi\mu}}}_{m/s}\, e^{-\beta\epsilon_0} \ (1000 Av) \ \underline{L\ mol^{-1} s^{-1}}$$

But, this still I have to be careful, I have to be careful of using pen first; and then the k that I have written is pi basically this thing into an Avogadro number. And the units is so far meter cube mole inverse second inverse; and what do I want it is I want it in liter into mole inverse second inverse. So, there is still a little bit of change I need; how do I do that? You remember? How is meter cube and liter related?

So, one liter one meter cube is thousand liters. So, k of T becomes pi rA plus rB square root 8kT over pi mu e to the power minus beta epsilon naught, into thousand into Avogadro number. And this will be in liter mole inverse second inverse, if this is in meter square; this is a meter per second. If you want to use different units, obviously you are free to do so; but at the end you almost converted your units carefully enough to get finally in the experimental answer.

And in any case whenever you write calculate a number; the units should be mentioned. Without the unit if I calculate a rate constant and that give you rate constant 10 into 10 to the power of 7. What what do I understand from it? What 10 into 10 to the power of 7 elements; so without that you unit that number is completely meaningless, always remember that. So, you get your number and you get your units right.

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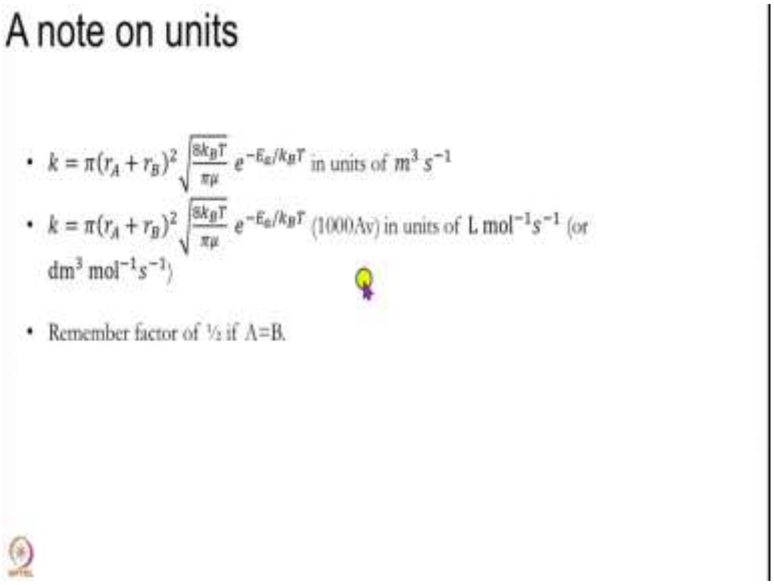

A note on units

- $k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$ in units of $m^3\, s^{-1}$
- $k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$ (1000Av) in units of L $\mathrm{mol}^{-1} s^{-1}$ (or dm^3 $\mathrm{mol}^{-1} s^{-1}$)
- Remember factor of ½ if A=B.

So, in summary what we have is the original expression that we had derived here, is basically in meter cube second inverse. Now, if I multiply that by thousand into Avogadro number; I will get in liter mole inverse second inverse, which is the same as dm cube mole inverse second inverse. And always remember if a bimolecular reaction if A is equal to B, then I must multiply by a factor of half.

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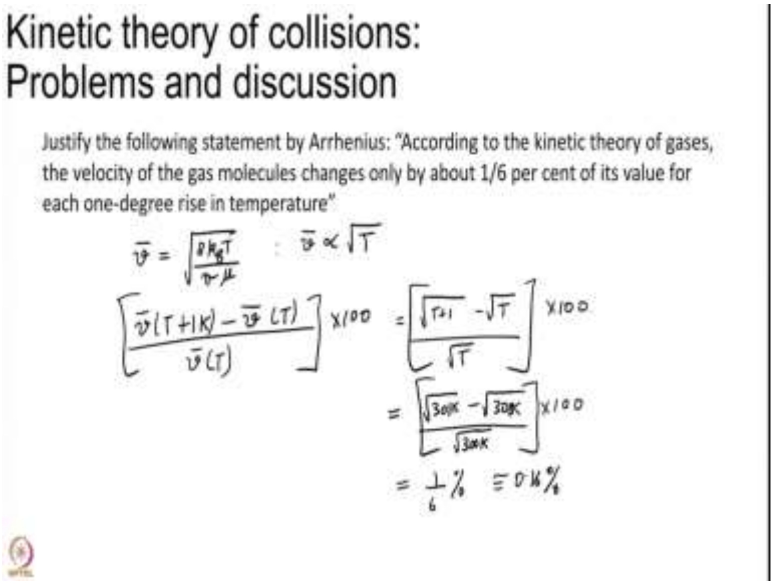

Kinetic theory of collisions: Problems and discussion

Justify the following statement by Arrhenius: "According to the kinetic theory of gases, the velocity of the gas molecules changes only by about 1/6 per cent of its value for each one-degree rise in temperature"

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi\mu}} \quad : \quad \bar{v} \propto \sqrt{T}$$

$$\left[\frac{\bar{v}(T+1K) - \bar{v}(T)}{\bar{v}(T)}\right] \times 100 = \left[\frac{\sqrt{T+1} - \sqrt{T}}{\sqrt{T}}\right] \times 100$$

$$= \left[\frac{\sqrt{301K} - \sqrt{300K}}{\sqrt{300K}}\right] \times 100$$

$$= \frac{1}{6}\% \cong 0.16\%$$

So, with that let us start solving problems; let us start with an easy one. If you go back several modules, I had read a statement from Arrhenius. According to kinetic theory of gases which what we are discussing now, the velocity of the gas molecules changes only by about one sixth percent of its value, for each one-degree rise in temperature.

So, now actually we are in a position to test whether Arrhenius was right or not; maybe he was bluffing. But, we have a equations now, we will test; will put Arrhenius to the acid test, nobody is above mathematics. So, what as…the velocity is what he is talking about; and what we have shown that the velocity the average velocity is, root 8 kT over pi mu.

So, basically nu velocity is proportional to root T. So, if I change temperature how much will average speed change that is the question; that is what Arrhenius is commenting on. So, what I want to find is nu at T plus 1 Kelvin, minus nu at T Kelvin divided by nu at T; and convert to two percent into 100.

So, this is what I have to find and show to check whether this is equal to 1 over 6 or not. So, you can substitute this nu above here, and what you will quickly show is this is equal to root T plus 1, minus root of T; divided by root of T into 100. And basically what Arrhenius was talking of was that of room temperature. This is not always true, it will be close to true; but what he was discussing is it room temperature.

So, this becomes equal to root of 301, I am sorry root 300 Kelvin, divided by root 300 Kelvin; so, room temperature is 300 Kelvin or close by. So, you can work this out and show that this is equal to one sixth percent, which comes to very one sixth percent. So, this is a very simple numeric's, you can plug it plug it into your calculator; and you will you can prove this out, which is roughly equal to 0.16 percent.

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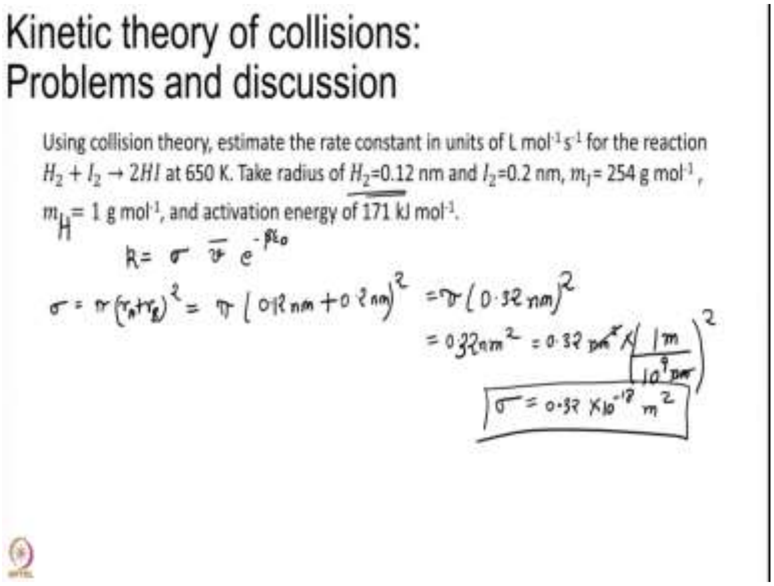

Kinetic theory of collisions: Problems and discussion

Using collision theory, estimate the rate constant in units of L mol^{-1} s^{-1} for the reaction $H_2 + I_2 \rightarrow 2HI$ at 650 K. Take radius of $\underline{H_2}$=0.12 nm and I_2=0.2 nm, m_I= 254 g mol^{-1}, m_H= 1 g mol^{-1}, and activation energy of 171 kJ mol^{-1}.

$$k = \sigma \, \bar{v} \, e^{-\beta \varepsilon_0}$$

$$\sigma = \pi (r_A + r_B)^2 = \pi (0.12\,\text{nm} + 0.2\,\text{nm})^2 = \pi (0.32\,\text{nm})^2$$

$$= 0.32\,\text{nm}^2 = 0.32\,\text{nm}^2 \times \left(\frac{1\,\text{m}}{10^9\,\text{nm}}\right)^2$$

$$\boxed{\sigma = 0.32 \times 10^{-18}\,\text{m}^2}$$

So, now let us look at a real reaction. So, kinetic theory of gases was actually particularly successful for the reaction of H2 plus I2 going to HI and its reverse; 2HI going to H2 plus I2. So, let us try to calculate a reaction for that; also we have given you a few units. This often when you look at this have a physical feel as well; look H2 is going to be small. H2 is roughly of the size of a few Armstrong, which is point 2 nano meter; so that is a size of H2.

I2 is bigger, I2 is a huge molecule; so you get point 2 nano meter which is a bigger size. I have given you the masses of I and oh my god this is should be hydrogen; iodine is not 1 kilogram per mole. And in activation energy has been given, activation energy is nothing but Ea. And I am asking you if collision theory is true, what will be the rate constant? So, the rate constant a comprises of three factors clearly: sigma, average speed.

We are going to calculate each of these three separately; pi rA is 0.12 nano meter always be super careful with units. You can do this math, I have done this math; this comes out to equal to 0.32 nano meter square. But, I want to convert to meter square Si units; so what I do is 1 meter has 10 to the power of 9 nano meters whole square. So, multiply by that, nano meter square will cancel with this; so I will get 0.32 into 10 to the power of minus 18 meter square, one component down; second component new.

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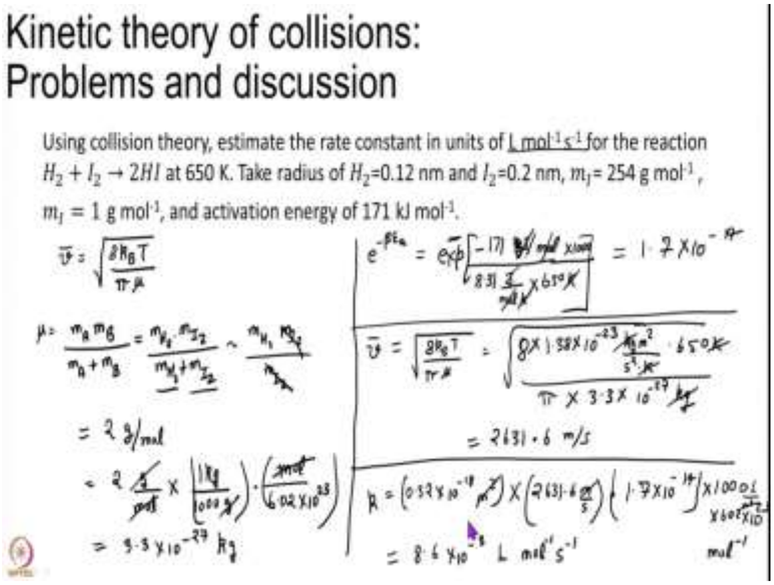

Kinetic theory of collisions:
Problems and discussion

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$$\bar{v} = \sqrt{\frac{8k_BT}{\pi\mu}}$$

$$\mu = \frac{m_A m_B}{m_A+m_B} = \frac{m_{H_2} \cdot m_{I_2}}{m_{H_2}+m_{I_2}} \sim \frac{m_{H_2} \cancel{m_{I_2}}}{\cancel{m_{I_2}}}$$

$$= 2\ g/mol$$

$$= 2\frac{\cancel{g}}{\cancel{mol}} \times \left(\frac{1\,kg}{1000\,\cancel{g}}\right)\cdot\left(\frac{\cancel{mol}}{6.02\times10^{23}}\right)$$

$$= 3.3\times10^{-27}\ kg$$

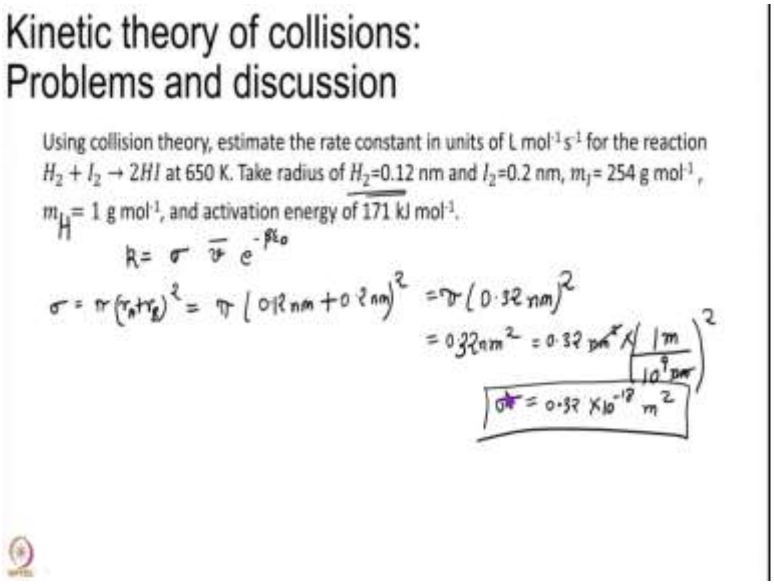
$$e^{-\beta E_a} = \exp\left[\frac{-171\,\cancel{kJ}/\cancel{mol}\times1000}{8.31\frac{J}{\cancel{mol}\,\cancel{K}}\times650\,\cancel{K}}\right] = 1.7\times10^{-14}$$

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi\mu}} = \sqrt{\frac{8\times1.38\times10^{-23}\frac{\cancel{kg}\,m^2}{s^2\,\cancel{K}}\cdot650\,\cancel{K}}{\pi\times3.3\times10^{-27}\,\cancel{kg}}}$$

$$= 2631.6\ m/s$$

$$k = (0.32\times10^{-18}\,\cancel{m^2})\times\left(2631.6\frac{\cancel{m}}{s}\right)\left\{1.7\times10^{-14}\right\}\times1000\frac{L}{\cancel{m^3}}\times6.02\times10^{23}\,mol^{-1}$$

$$= 8.6\times10^{-8}\ L\,mol^{-1}s^{-1}$$



Kinetic theory of collisions:
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$$k = \sigma\,\bar{v}\,e^{-\beta E_a}$$

$$\sigma = \pi(r_A+r_B)^2 = \pi(0.12\,nm+0.2\,nm)^2 = \pi(0.32\,nm)^2$$

$$= 0.32\,nm^2 = 0.32\,\cancel{nm^2}\times\left(\frac{1\,m}{10^9\,\cancel{nm}}\right)^2$$

$$\boxed{\sigma = 0.32\times10^{-18}\,m^2}$$

Not new, speed that is given by 8 kT over pi mu; if you solve enough problems, you will memorize all of this. But, again do not go end up memorizing these equations; that is not the point of this course at all. Any equations that are needed in a exam situation, I will provide you all equations. So, first I have to find mu; mu remember is defined to be the reduced mass; so this is m of H2 into m of I2, divided by m of H2 plus m of I2.

You can actually go ahead and solve this, but I will be a bit smarter; I will note that m of I is way more than m of H, 250 times more. Then what I can do is this is just being a bit smart. If I add an H2 and I2, it is a little bit more than mI2 just 2 mole; I can as well ignore it. And I noticed this it is equal to m of H2, which is nothing but 2 gram per mole; but I want it in kilograms, I want it in SI units.

So, 2 grams per mole into 1 kilograms per thousand grams into Avogadro's number, 23 moles; So, Avogadro's number is mole inverse on dividing by Avogadro number. Mole cancels with mole, gram cancels with gram and therefore kilogram; and I have simplified this again and I have written the answer before hand with me. This comes out equal to 3.3 into 10 to the power of minus 27 kilograms. So, please go ahead and verify this number; I may have making mistakes.

If you make mistakes in the exam, you loose points; be sure that the number I am doing is right, punch it in the calculator. And finally I want to calculate e to the power minus beta Ea that is equal to the e to the power of minus; so let me just write exponential minus 171 kilo joules per mole, divided by rT. rT is 8.31 joules per mole Kelvin into temperature 650 Kelvin. So, you note this is kilo joule, this is joule; so I better multiply by a thousand here and I make this joule.

So, now all the units will cancel, K cancels with K, mole cancels with mole, joules cancels with joules. Again when R is required I will give you the value of r in an exam situation; do not go about memorizing, and this comes out equal to 1.7 fourteen. I have forgotten to calculate nu, I calculated a nu very happily; but I forgot to plug it in here.

This is equal to 8 kT over pi mu, so 8 what kB? kB is 1.38, into 10 to the power of minus 23 kilogram meter square per second square; into Kelvin into 650 Kelvin's, divided by pi. And mu I found to be 3.3 into 10 to the power of minus 27 kilograms. So, kilogram cancels with kilogram, Kelvin cancels with Kelvin. And this it will plug everything in to get 2631. 6 meters per second.

So, finally k is a product of sigma, sigma be calculated to be 0.32 into 10 to the power of minus 18 meter square, into nu bar 2631.6 meter per second; into e to the power minus beta Ea. And I wanted the answer in liter mole second inverse; so I multiply by thousand into Avogadro number. So, this is thousand of liter per meter cube; I will cancel the cube here with meter cube.

I will cancel I will cancel nothing else and I will calculate this is equal to at the end of the day; I have this number with me, 8.6 into 10 to the power of minus 3 liter mole inverse second inverse. So, at every step you have to be very careful, particularly of units. There is nothing very well hard here. I took this formula this one here and I am calculating each number very carefully; I calculated sigma here, I calculated this average speed here.

To calculate the average speed, I needed mu; mu I calculated here. I made a little approximation; you can make it more accurate and see if what I have said is right or not. Maybe I have made a mistake, maybe this quite hard to check whether that is right; I got mu and finally I calculated e to the power of minus beta Ea here. And then I plugged all of these in and for units I used thousand into Avogadro number; I plugged every number in. I have a calculator with me; I had plugged all those Avogadro's number.

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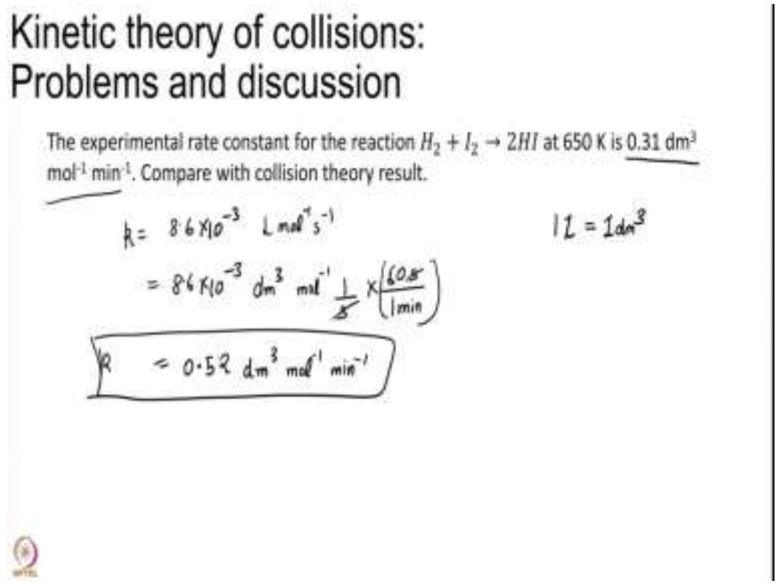

Kinetic theory of collisions: Problems and discussion

The experimental rate constant for the reaction $H_2 + I_2 \rightarrow 2HI$ at 650 K is 0.31 dm^3 mol^{-1} min^{-1}. Compare with collision theory result.

$$k = 8.6 \times 10^{-3} \ L\, mol^{-1} s^{-1}$$

$$= 8.6 \times 10^{-3} \ dm^3\, mol^{-1} \frac{1}{\cancel{s}} \times \left(\frac{60\, \cancel{s}}{1\, min}\right)$$

$$\boxed{k = 0.52 \ dm^3\, mol^{-1}\, min^{-1}}$$

$$1L = 1 dm^3$$

Now, I actually responded to provide you a little context, so the number that we have calculated is 8.6 into 10 to the power of minus 3 liter mole inverse second inverse. And the experiment that were done back in that day more than a hundred years ago from now, was point three one dm cube mole inverse minute inverse; so, I want to check whether my number matches or not.

We, first thing I noticed that this has in minute inverse, not a big deal. Remember that liter is the same as dm cube, I have 1 over second; but I will multiply by 60 second divided by 1 minute.

Second cancels, I get this multiplied by 60 and I will get 0.52; so this is my k for a collision theory and this is my experimental.

This is not bad at all, given that this is such an approximate theory does not have even bonds. So, if I have to think of H2 plus I2; H has a bond and I has a bond and it is it is does not look like a sphere at all, H2 is not a sphere. But, you see that the comparison is not bad within a factor of 2. In your assignment you will be solving more problems; I will solve whenever problem here.

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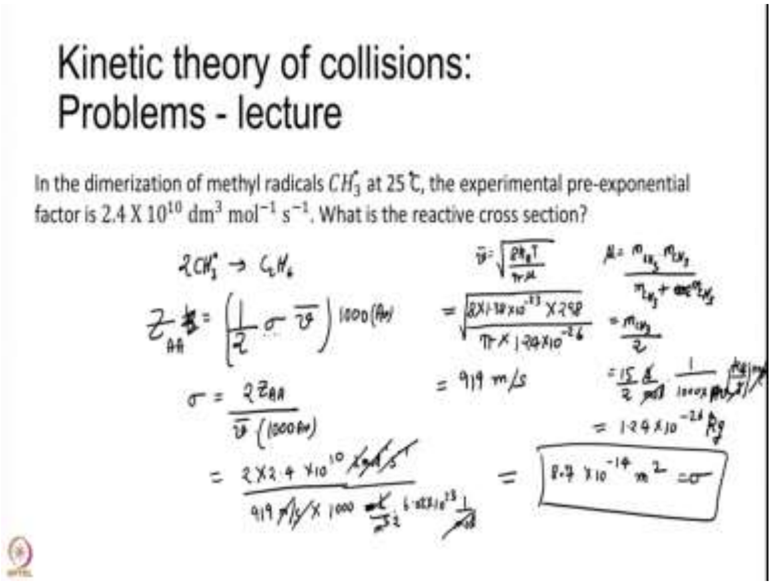

Kinetic theory of collisions: Problems - lecture

In the dimerization of methyl radicals $CH_3^\bullet$ at 25 °C, the experimental pre-exponential factor is 2.4 X 10^{10} $dm^3\ mol^{-1}\ s^{-1}$. What is the reactive cross section?

$2CH_3^\bullet \rightarrow C_2H_6$

$Z_{AA} = \left(\frac{1}{2}\sigma\bar{v}\right)1000(A_v)$

$\sigma = \frac{2Z_{AA}}{\bar{v}(1000A_v)}$

$= \frac{2\times2.4\times10^{10}\ L/mol/s}{919\ m/s\times1000\ \frac{L}{m^3}\ 6.023\times10^{23}\frac{1}{mol}}$

$\bar{v} = \sqrt{\frac{8k_BT}{\pi\mu}}$

$= \sqrt{\frac{8\times1.38\times10^{-23}\times298}{\pi\times1.24\times10^{-26}}}$

$= 919\ m/s$

$\mu = \frac{m_{CH_3}m_{CH_3}}{m_{CH_3}+m_{CH_3}}$

$= \frac{m_{CH_3}}{2}$

$= \frac{15}{2}\frac{g}{mol}\ \frac{1}{1000\times mol}\ kg/g$

$= 1.24\times10^{-26}\ kg$

$= \boxed{8.7\times10^{-14}\ m^2 = \sigma}$

So, in the dimerization of CH3 radical, pen here; 2CH3 dot, this is the reaction we are looking at 25 degree C. Somebody had figured out the pre-exponential factor and the question is here we have to find the reactive cross section; so how do I find that. So, I note k is half that remember because here A is equal to B; so I get a factor of half into sigma into nu, that is my pre factor.

So, let me not write that as let me write that as Z; so I have to calculate this sigma. So, sigma and the unit that they have provided is in liter mole inverse second inverse; so I multiply this by thousand into Avogadro number. So, sigma is 2 ZAA divided by nu bar into thousand Avogadro number. So, I have to calculate nu bar now, again is 8 kT over pi mu; mu is equal to m into CH3 into m of CH3, divided by m of CH3 plus m of CH3.

This is nothing but m of CH3 divided by 2, which is close to how much; I have this written down here 15. So, the mass of carbon is 12 and hydrogen's are 1; so this is 15 by 2 grams per mole, into 1 by thousand into Avogadro number; which will converted into kilograms per gram into moles. Just like we did in the last slide, mole cancels here, grams cancel with this; and this I can have found already.

And this is equal to mass mass here 1.24 into 10 to the power of minus 26 kilograms. So, I substitute that here, I get 8 into kB everything in Si units; I am not going to write this all the units as explicitly as last. Remember temperature must be written in Kelvin's, never forget that; do not write 25 degree c here at temperature at 273 Kelvin's. pi into mu so everything is in SI units and this comes out to be then 919 meters per second.

So, I have all the factors here, Z is 2.4, nu I have calculated 919; this thing was in liter mole inverse second inverse, thousand liter in meters cube into Avogadro number. So, a lot of things cancel, liter cancels with liter, moles cancels with mole, seconds cancels with second. And I will be left with meters square, 1 meter will cancel with square; and these are all numbers that I can just plug in. And I get that is equal to 8.7 into 10 to the power of minus 14 meter.

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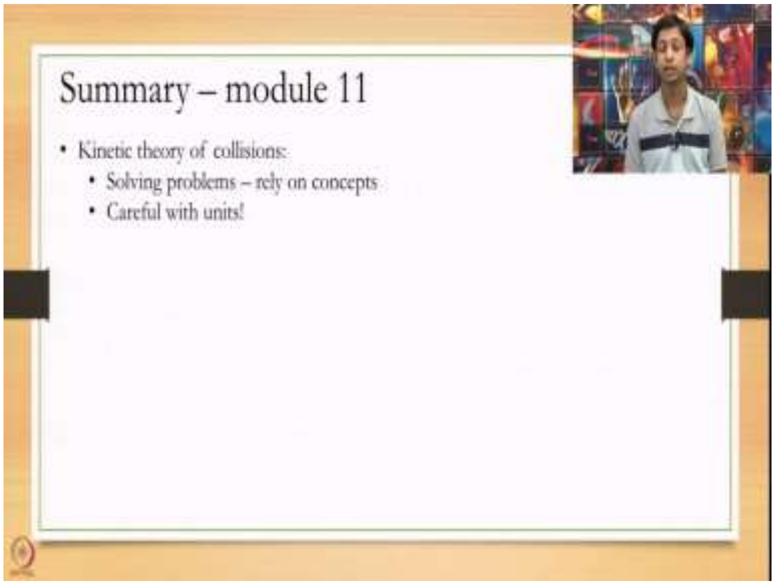

Summary – module 11

- Kinetic theory of collisions:
  - Solving problems – rely on concepts
  - Careful with units!

So, we will end here, so today we had looked at practical applications of a kinetic theory; and how to calculate numbers out, with proper units. I can promise you if you do not practices on your own enough problems; you will never get units right correctly. We are tricky and it takes practice; so with that I will stop here. In assignments you can solve more problems; the textbooks that I have referred to, also has more problems practice. Thank you very much.we w