

Where We Go From Here

Homework Problems

Paper Selection – Name and approximate title/subject to me by spring break

MidTerm Exam – one week take-home and short-in class part

in class part April 3, take home on web page week before and due April 3

Lecture topics next couple of weeks

- Collision Theory
- “Review” of statistical mechanics (review pchem)
- Activated Complex
- Theoretical Calculation Approach
- Gas Phase Reactions
- etc.

Course divided into 3 main parts

- Experimental Kinetics
- Kinetics Theory and Modeling
- Specialized Topics (gas phase, solution, catalysts, solid surface)

Why do theory and modeling, why not just experimental?

A model that “works” shows that we really understand what is going on

Collision Theory

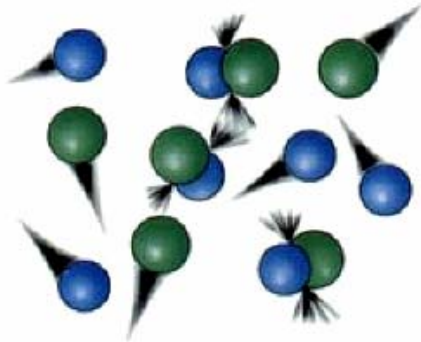
Simple models for chemical kinetics based on assumption that **atoms and Molecules must collide in order to react**. Collision allows contact between two reacting species (second order) or accumulation of energy by a single reacting species (first order) to acquire enough energy to get over activation energy barrier.

Modeling – attempt to develop mathematical expressions based on first principles of physics that describe a process or phenomenon. Then test the model by making predictions than can be verified by experimental data. Once the model is verified, it can be improved by making mathematical modifications. The model may be used to estimate results before or without experimental data. The model may be later mathematically incorporated as sub-sections to other more complex models. If the model works well (predicts experimental data) it indicates that the process is well understood and that assumptions are valid.

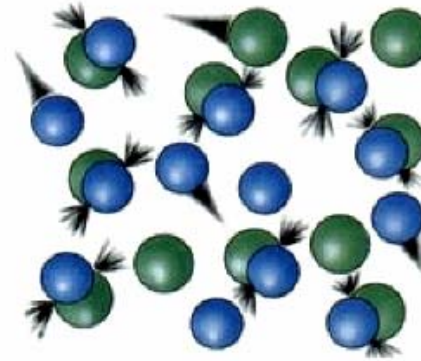
Collision Model Includes

- The faster molecules move the more frequently they collide
- The more molecules per unit volume (number density) the more frequently they collide
- The higher the partial pressure of a gas the higher the number density
- Number per unit volume calculated from Avogadro's number and ideal gas law
- The larger a molecule the higher the probability of collision with another molecule

Collision Theory



Low concentration = Few collisions



High concentration = More collisions

$$k(T) = Z\rho \exp\left(\frac{-E_a}{RT}\right)$$

$$Z = N_A^2 \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

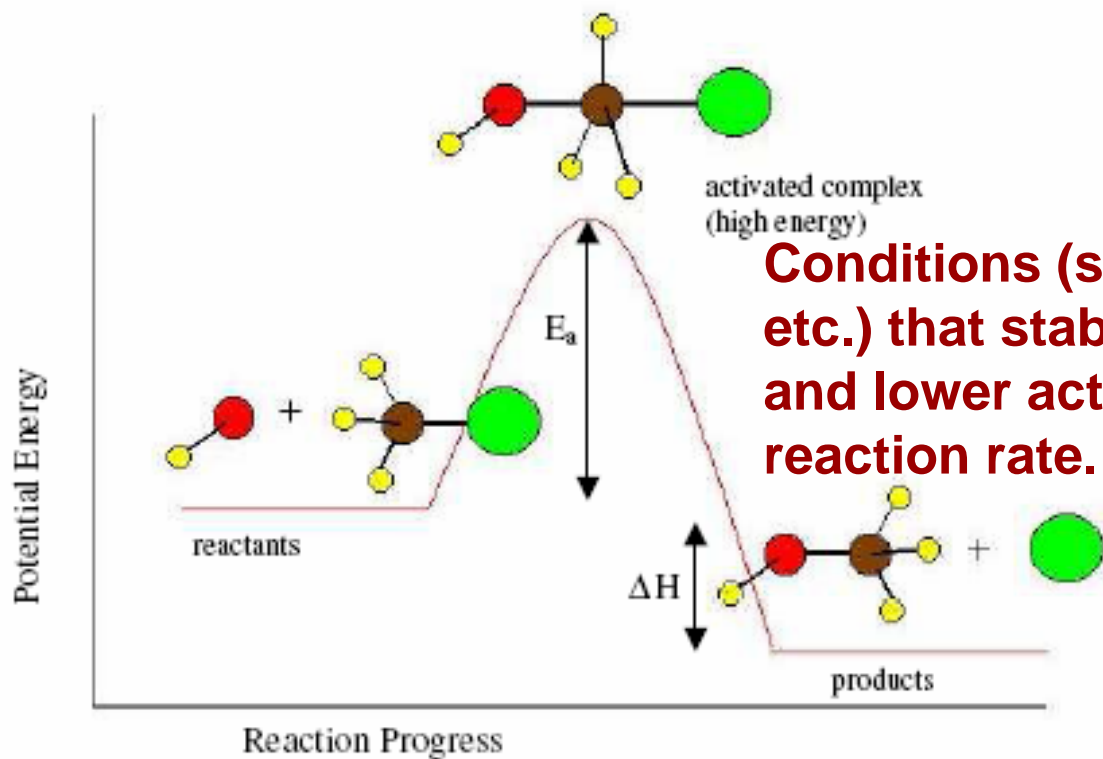
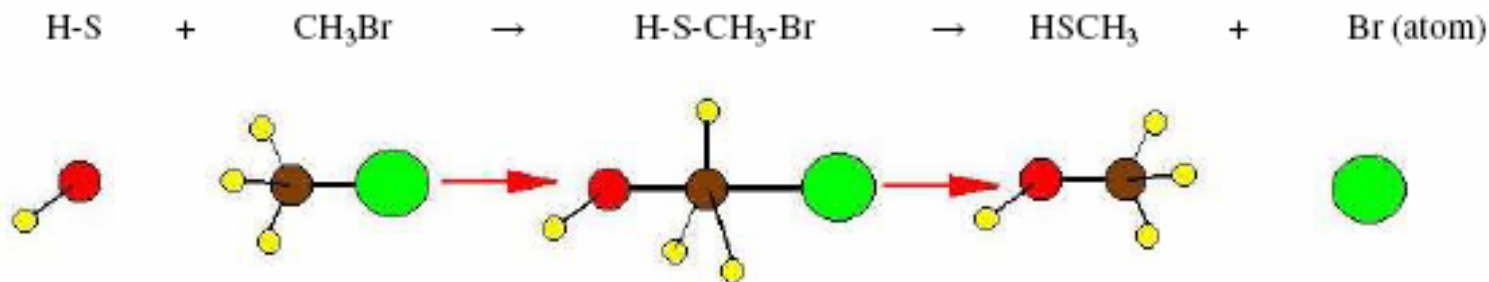
- N_A is number density (atoms or molecules/volume)
- σ_{AB} is the reaction cross section
- k_B is Boltzmann's constant
- μ_{AB} is the reduced mass of the reactants

Be sure units match – best to use SI units (m, kg, s, J)

$e^{-E_{act}/RT}$ is the statistical fraction of molecules with energy above E_{act}

Collision Theory

The energy changes during a chemical reaction can be graphed as a “reaction pathway”:



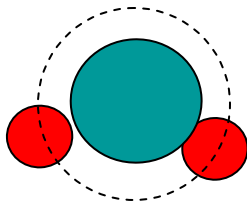
Conditions (solvent, temp, pressure, etc.) that stabilize activated complex and lower activation energy, increase reaction rate.

Collision Theory – model development

We need to know how large molecules are, how fast they move and how many there are per unit volume (number density)

Molecular Size

– what size sphere could represent the molecule? (effective diameter)



Water H₂O and effective diameter

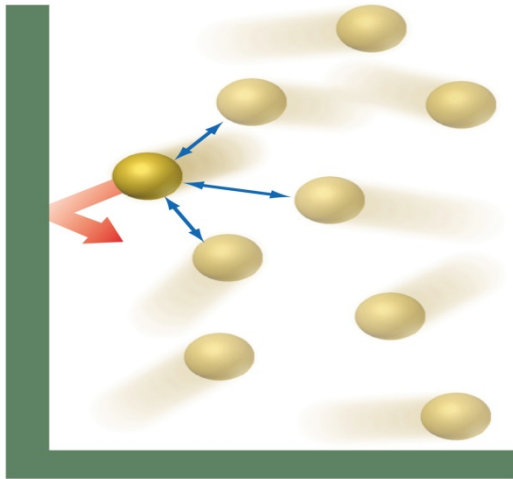
Assuming liquids have molecules closely packed, we can assume the volume is made up of packed spheres. So the number of spheres divided by the volume of the liquid is an approximation of the volume of the “effective” sphere. From volume of the sphere the radius and diameter may be calculated.

EXAMPLE

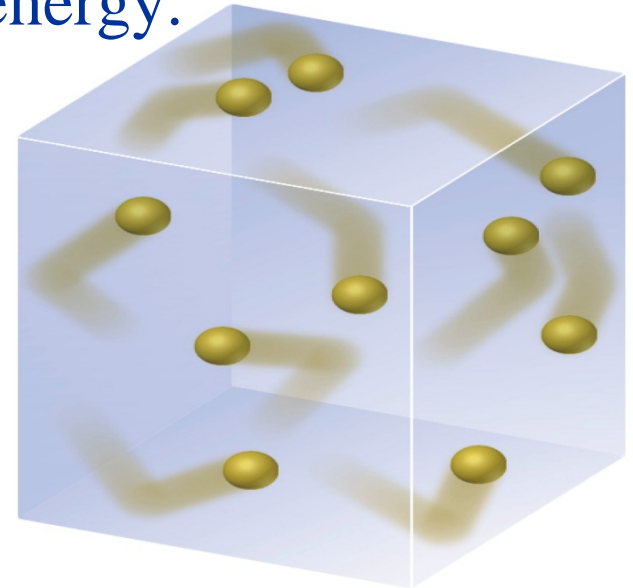
Water – 1 mole is 18 g and contains $6,02 \times 10^{23}$ molecules if the density of water is $0,998 \text{ g/cm}^3$ then 1 mole occupies $18/0.998 = 18.036 \text{ cm}^3$ (disregarding sig fig)
Effective spherical volume of 1 H₂O molecule = $18.036 / 6,02 \times 10^{23} = 2.006 \times 10^{-23} \text{ cm}^3$
Volume of sphere = $\frac{4}{3} \pi r^3$ now solve for effective radius and diameter

Kinetic Molecular Theory of Gasses

- Kinetic molecular theory provides an understanding of pressure and temperature on the molecular level.
- Pressure of a gas results from collisions per unit time on the walls of container (transfer of momentum)
- Magnitude of pressure given by how often and how hard the molecules strike.
- Gas molecules have an average kinetic energy.
- Each molecule has a different energy.

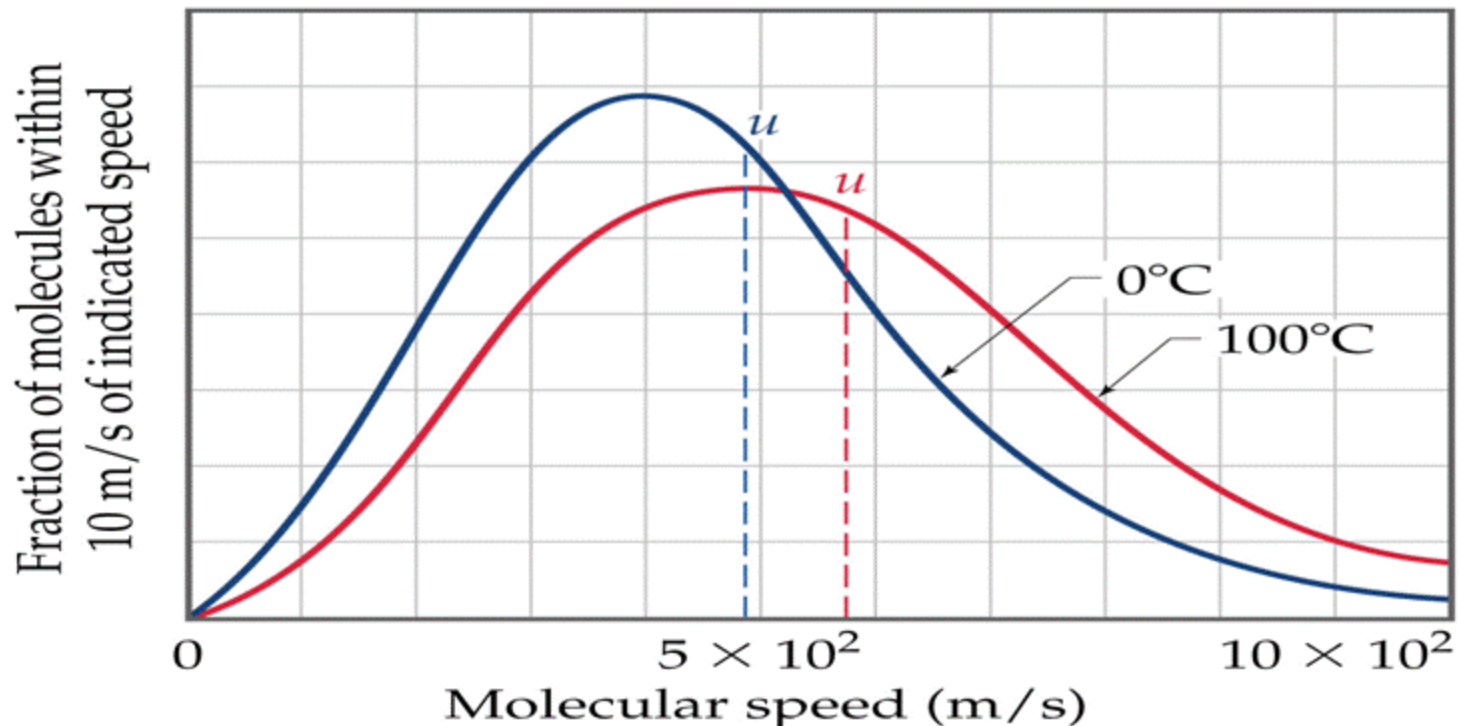


Review Physical Chemistry



Kinetic Molecular Theory of Gasses

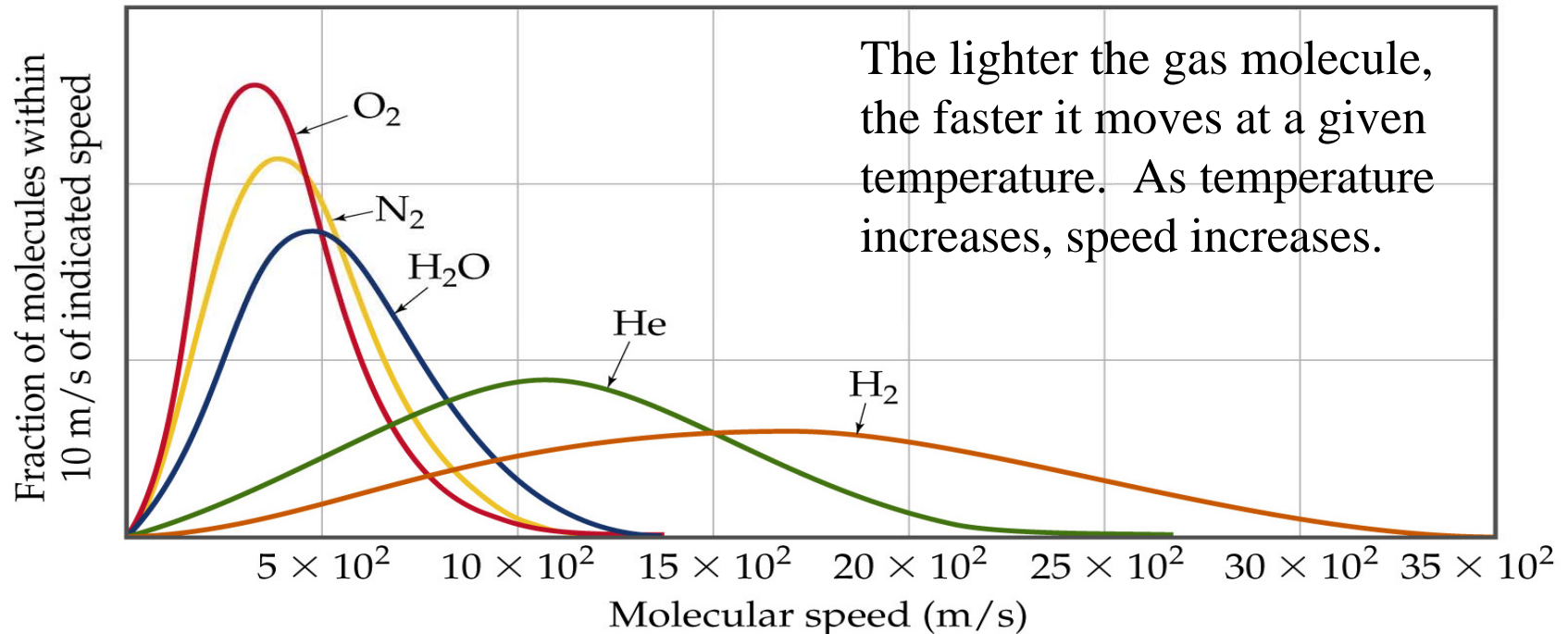
- There is a spread (statistical distribution) of individual energies (speeds) of gas molecules in any sample of gas.
- As the temperature increases, the average kinetic energy and speed of the gas molecules increases.



Molecular Speeds

- Consider two gases at the same temperature: the lighter gas has a higher speed (rms) than the heavier gas.
- Mathematically:

$$u = \sqrt{\frac{3RT}{M}}$$



How Far Apart are Gas Molecules?

For Water we showed a few slides back that 18 g liquid water occupies a little over 18 cm³

At 0 C (273.15 K) & 1 atm pressure (STP) 18 g water gas occupies 22400 cm³

Gas molecules are thousands of times further apart than molecular diameters

They move very fast so there are frequent collisions

The kinetic energy of a molecule is $\frac{1}{2} mv^2$

Since velocity v is square root of $3RT/M$

Then kinetic energy is proportional to absolute temperature (K)

How Far Do Molecules Move Between Collisions?

• Average distance of a gas molecule between collisions is called **mean free path**.

• At sea level, mean free path is about 6×10^{-6} cm.

• The higher the pressure the shorter the mean free path

• At low pressure (partial vacuum like space) mean free path is short

• Chemical reaction requires molecules to bump into each other

• Molecules gain energy overcome activation energy by collision

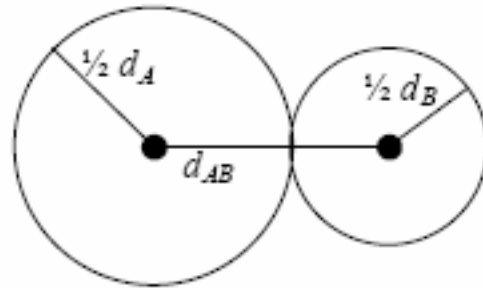
$$\text{Mean free path estimate} = \frac{\text{Distance traveled}}{\underbrace{\pi d^2}_{\text{Volume of interaction}} \underbrace{\bar{v} t}_{\text{Mean distance per collision}} n_V} = \frac{1}{\pi d^2 n_V}$$

Labels in the diagram:
- Distance traveled: $\bar{v} t$
- Mean distance per collision: $\frac{1}{\pi d^2 n_V}$
- Volume of interaction: πd^2
- Number of molecules per unit volume: n_V

Collision Theory – model development

Simple, not-so-rigorous derivation of hard sphere collision rate

Molecules A and B have diameters and corresponding collision cross-section d_A , d_B , $\sigma_A = \pi d_A^2$, and $\sigma_B = \pi d_B^2$. Note that the collision cross-section is not the cross-sectional area of the molecule itself, but the cross-sectional area of a cylinder whose radius is equal to the diameter of the molecule (see below). An A and B molecule collide whenever their centers of mass come within a distance $d_{AB} = (d_A + d_B)/2$ of each other.



The molecules of an ideal gas move with the *Maxwell-Boltzmann* distribution of velocities (vector velocity) and speeds (scalar velocity). The probability that a molecule has a speed between c and $c+dc$ is given by

$$f(c)dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} c^2 \exp\left(\frac{-mc^2}{2kT} \right) dc .$$

Collision Theory - model

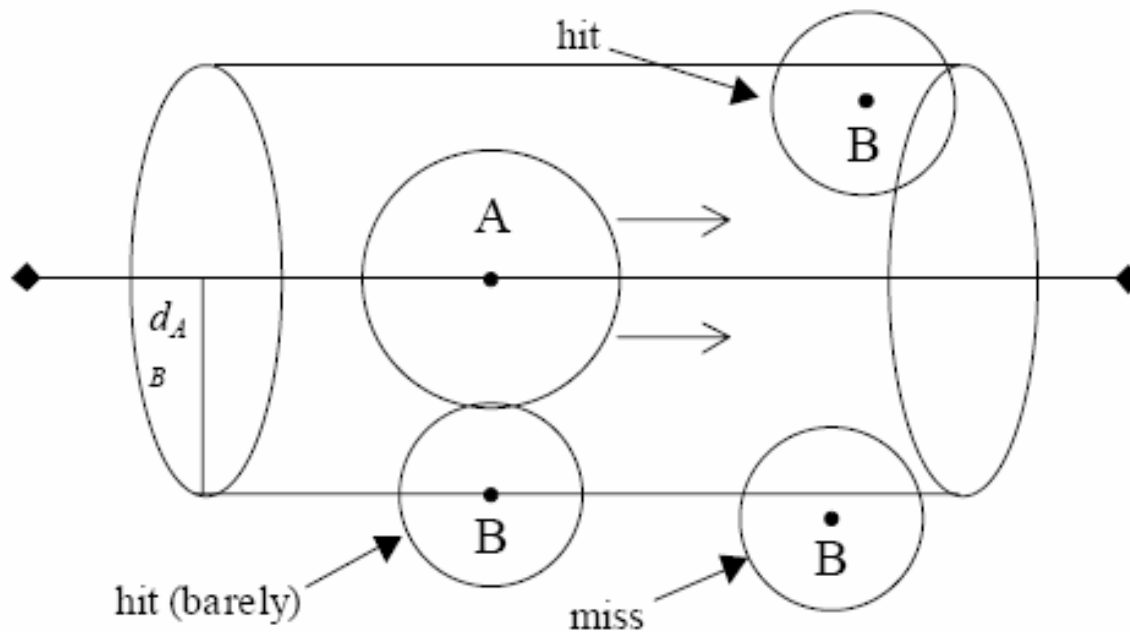
In this expression, m is the particle mass, c is the speed, T is the temperature, and k is Boltzmann's constant ($=R/N_A$). The Maxwell-Boltzmann distribution is derived in most physical chemistry textbooks, so I won't repeat the fairly lengthy derivation here. The average speed is given by

$$\bar{c} = \int_0^{\infty} cf(c)dc = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

A simplified derivation of the collision frequency is as follows. Suppose that a molecule of type A is moving through a box of randomly distributed B molecules. It then sweeps out a 'collision tube' with cross-sectional area $\sigma_{AB}=\pi(d_{AB})^2$. All B molecules that lie within this 'collision tube' will get hit.

Collision Theory - model

A simplified derivation of the collision frequency is as follows. Suppose that a molecule of type A is moving through a box of randomly distributed B molecules. It then sweeps out a 'collision tube' with cross-sectional area $\sigma_{AB} = \pi(d_{AB})^2$. All B molecules that lie within this 'collision tube' will get hit.



The average length of 'collision tube' swept out by an A molecule in a time Δt is given by $\bar{c}_A \Delta t$, so the volume swept out per unit time is (area)*(length)/(time) = $\sigma_{AB} \bar{c}_A$. If there are N_B molecules of B per unit volume, then the collision rate for a single A molecule is given by

Collision Theory - model

In fact the B molecules are not stationary, but are also moving, and this increases the collision frequency. To correct for this, we need to replace the average velocity of an A molecule (\bar{c}_A) with the average *relative* velocity between an A molecule and a B molecule. The relative velocity is also given by the Maxwell-Boltzmann distribution, but with the molecular mass replaced by the reduced mass of the pair of molecules. The average relative velocity is given by

$$\bar{c}_{AB} = \left(\frac{8kT}{\pi\mu} \right)^{1/2}, \text{ where } \mu = \frac{m_A m_B}{m_A + m_B}$$

which is the same expression as before, with the mass of A replaced by the reduced mass of A + B. The collision rate *for a single A molecule with moving B molecules* is then given by

$$r_{coll} = \sigma_{AB} \bar{c}_{AB} N_B = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_B$$

Collision Theory - model

This has been derived as the collision rate for one A molecule with all B molecules. To get the total collision rate (total number of A-B collisions per unit volume per unit time) we simply multiply by the number of A molecules per unit volume. This total collision rate is then

$$Z_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A N_B$$

If the A and B molecules are identical, then we must divide the collision rate by 2 to avoid double counting. So, in a mixture of A and B molecules, the collision rates for each type of collision are given by

$$Z_{AA} = \sigma_A \left(\frac{4kT}{\pi m_A} \right)^{1/2} N_A^2, \quad Z_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A N_B, \quad Z_{BB} = \sigma_B \left(\frac{4kT}{\pi m_B} \right)^{1/2} N_B^2$$

In addition to dividing by 2 for the AA and BB collisions, we have used the fact that the reduced mass of 2 identical molecules is $\frac{1}{2}$ the mass of one molecule. The rate constants for the collision processes are then defined as

$$k_{AA} = \sigma_A \left(\frac{4kT}{\pi m_A} \right)^{1/2}, \quad k_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2}, \quad k_{BB} = \sigma_B \left(\frac{4kT}{\pi m_B} \right)^{1/2}$$

A first approximation – model can be improved and made more rigorous

Collision Theory – model improvement

A slightly more rigorous derivation of the collision rate

Another way to look at this is as follows. The fraction of the A molecules with speeds, relative to a particular B molecule, that are between c_{rel} and $c_{rel}+dc_{rel}$ is given by the Maxwell-Boltzmann distribution with the reduced mass of the colliding pair

$$f(c_{rel})dc_{rel} = 4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} c_{rel}^2 \exp\left(\frac{-\mu c_{rel}^2}{2kT} \right) dc_{rel}$$

Considering the same ‘collision tube’ discussed above, the collision frequency of a particular A molecule (with velocity between c_{rel} and $c_{rel} + dc_{rel}$ relative to a particular B molecule) is

$$r_{coll}(c_{rel}) = (\text{B molecules per volume}) * (\text{tube volume per time}) = N_B c_{rel} \sigma_{AB}$$

Integrating this over the distribution of relative velocities gives

$$r_{coll} = \int_0^{\infty} (N_B c_{rel} \sigma_{AB}) \left(4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} c_{rel}^2 \exp\left(\frac{-\mu c_{rel}^2}{2kT} \right) \right) dc_{rel} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_B$$

Collision Theory – model improvement

This gives the same expression for the collision rate as before, and is somewhat more rigorous than the previous, simpler derivation. The derivation presented by Benson (in *Foundations of Chemical Kinetics*, p. 148-155) even more rigorously demonstrates that this is the correct result, and that the same result is obtained when the separate Maxwell-Boltzmann velocity distribution of the two types of molecules is explicitly taken into account.

Derivation of the reaction rate

So far, we have just obtained the total rate of all collisions. What we would really like is the reaction rate, which is the rate of collisions that lead to reaction. A simple assumption that can be made is that reaction occurs if the kinetic energy of the particles along the direction of the collision is greater than some critical value. That is,

$$E_k = \frac{\mu c_{rel}^2}{2} > E_o$$

where the critical energy has been denoted E_o . This is equivalent to requiring that the relative velocity be greater than the corresponding critical velocity, which we may call c_o . That is,

$$c_{rel} > c_o = \sqrt{\frac{2E_o}{\mu}}$$

Collision Theory – model improvement

We can get the rate of these collisions by changing the lower limit of the integral given above to c_o . Doing so, and carrying out the integration gives

$$\begin{aligned}r_{\text{react}} &= \int_{c_o}^{\infty} (N_B c_{\text{rel}} \sigma_{AB}) \left(4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} c_{\text{rel}}^2 \exp\left(\frac{-\mu c_{\text{rel}}^2}{2kT} \right) \right) dc_{\text{rel}} \\ &= \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_B \left(1 + \frac{\mu c_o^2}{2kT} \right) \exp\left(-\frac{\mu c_o^2}{2kT} \right) \\ &= \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(1 + \frac{E_o}{kT} \right) \exp\left(-\frac{E_o}{kT} \right) N_B\end{aligned}$$

This is the rate per A molecule, so the total rate is obtained by multiplying by the concentration of A molecules to get

$$Z_{AB,\text{react}} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(1 + \frac{E_o}{kT} \right) \exp\left(-\frac{E_o}{kT} \right) N_A N_B$$

Collision Theory – model improvement

So, the predicted rate constant is now

$$k_{AB,react} = \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(1 + \frac{E_o}{kT} \right) \exp\left(-\frac{E_o}{kT} \right)$$

Arrhenius Equation

- “A” pre-exponential term
- Activation Energy term

which is the Arrhenius form with a slightly temperature dependent pre-exponential factor. This result is sometimes presented in textbooks without the $\left(1 + \frac{E_o}{kT} \right)$ term. I believe the correct form is the one that includes this term as derived here. In any case, this is not a reliable means of calculating rate constants, but does begin to relate rate constants to the molecular processes that are occurring.

Collision Theory – model improvement

The first modification that is usually made to this approach is to introduce a ‘steric factor’ or ‘reaction probability’ that absorbs the difference between the measured pre-exponential factor and the prediction given above. This gives

$$k_{AB,react} = P\sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(1 + \frac{E_o}{kT} \right) \exp\left(-\frac{E_o}{kT} \right)$$

where P is this ‘steric factor’. Physically, it may be thought of as reflecting the requirement that the molecules have a specific relative orientation before the collision. It could also be made energy dependent so that the reaction probability would depend on the kinetic energy of the collision in a smooth manner rather than being 0 below the critical energy (E_o) and some constant value above the critical energy.

Collision Theory – testing the model

Example: Calculation of a collisional rate constant

Use collision theory to estimate the pre-exponential factor for the reaction $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$ at 298 K. Use a hard-sphere collision diameter of 3.50 Å for HI. Report your result in $\text{mol}^{-1} \text{L s}^{-1}$ and compare your result to the experimental value of $3 \times 10^{10} \text{ mol}^{-1} \text{L s}^{-1}$. If we were to assign a ‘steric factor’ or ‘reaction probability’ for this reaction, what would it be?

An upper limit for the pre-exponential factor is given by the gas-kinetic collision rate divided by the concentration of HI squared. We saw in the derivations given above that for the simple hard-sphere collision theory (for collisions of identical molecules), this is given by

$$Z_{AA} = \sigma_A \left(\frac{4kT}{\pi m_A} \right)^{1/2} N_A^2, \text{ or } k_{AA} = \sigma_A \left(\frac{4kT}{\pi m_A} \right)^{1/2}$$

Collision Theory – testing the model

Putting in the numbers for this problem

$$\sigma_A = \pi d_A^2 = \pi (3.50 \times 10^{-10} \text{ m})^2 = 3.85 \times 10^{-19} \text{ m}^2$$

$$k = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

$$T = 298 \text{ K}$$

$$m_A = 127.9 \text{ g mole}^{-1} = 2.12 \times 10^{-25} \text{ kg molecule}^{-1}$$

so

$$k_{AA} = 6.05 \times 10^{-17} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

or

$$k_{AA} = 3.64 \times 10^{10} \text{ L mole}^{-1} \text{ s}^{-1}$$

Upper limit or maximum rate assumes every collision is oriented effectively (sterically)

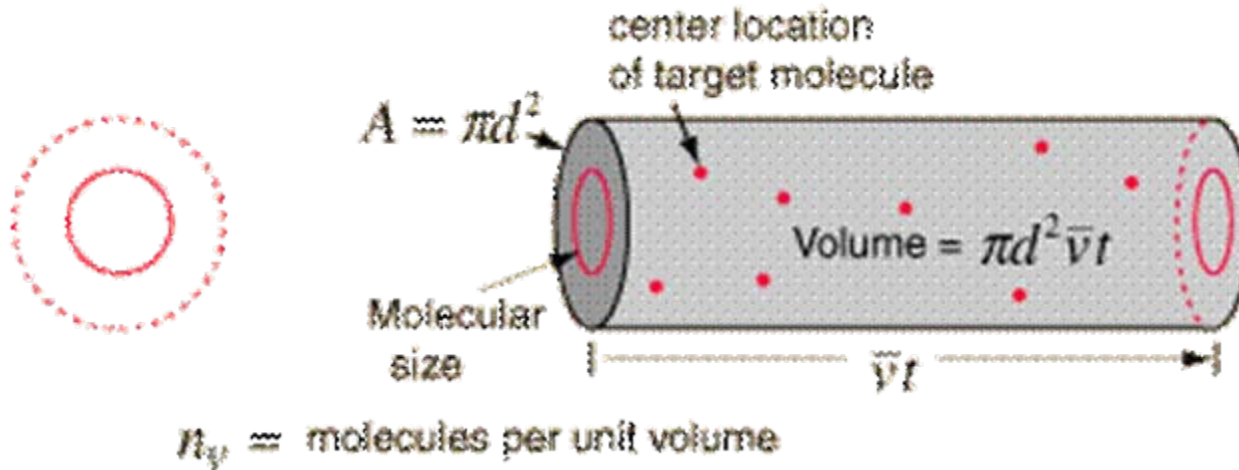
This collision rate constant is an upper limit for the pre-exponential factor for the reaction – we expect that

$$A \sim 3.6 \times 10^{10} \text{ L mole}^{-1} \text{ s}^{-1}$$

This is only slightly larger than the experimental value. If we were to assign a reaction probability, it would be $P = (3.0/3.64) = 0.82$. The observed pre-exponential factor is 82% of the gas-kinetic collision rate constant.

That is – it has been observed by experiment that about 82% of the collisions are effective and lead to reaction. This was determined by temp vs. rate data and the intercept of an Arrhenius plot and comparison with kinetic theory and the frequency of collisions.

Mean Free Path of a Gas Molecule



The mean free path could then be taken as the length of the path divided by the number of collisions.

$$\text{Mean free path estimate} = \frac{\text{Distance traveled } \bar{v} t}{\underbrace{\pi d^2 \bar{v} t}_{\text{Volume of interaction}} n_v} = \frac{1}{\underbrace{\pi d^2}_{\text{Mean distance per collision}} n_v}$$

Distance traveled

Mean distance per collision

Volume of interaction

Number of molecules per unit volume

Using this Rate Constant

Problem Example---

Our collision theory model applied to the second order reaction



Gives a second order rate constant of 3.6×10^{10} M/sec at 25°C

Graph the fraction of I_2 remaining as a function of time when 1 mole each of H_2 and I_2 are placed in a 22.4 liter container at 25°C

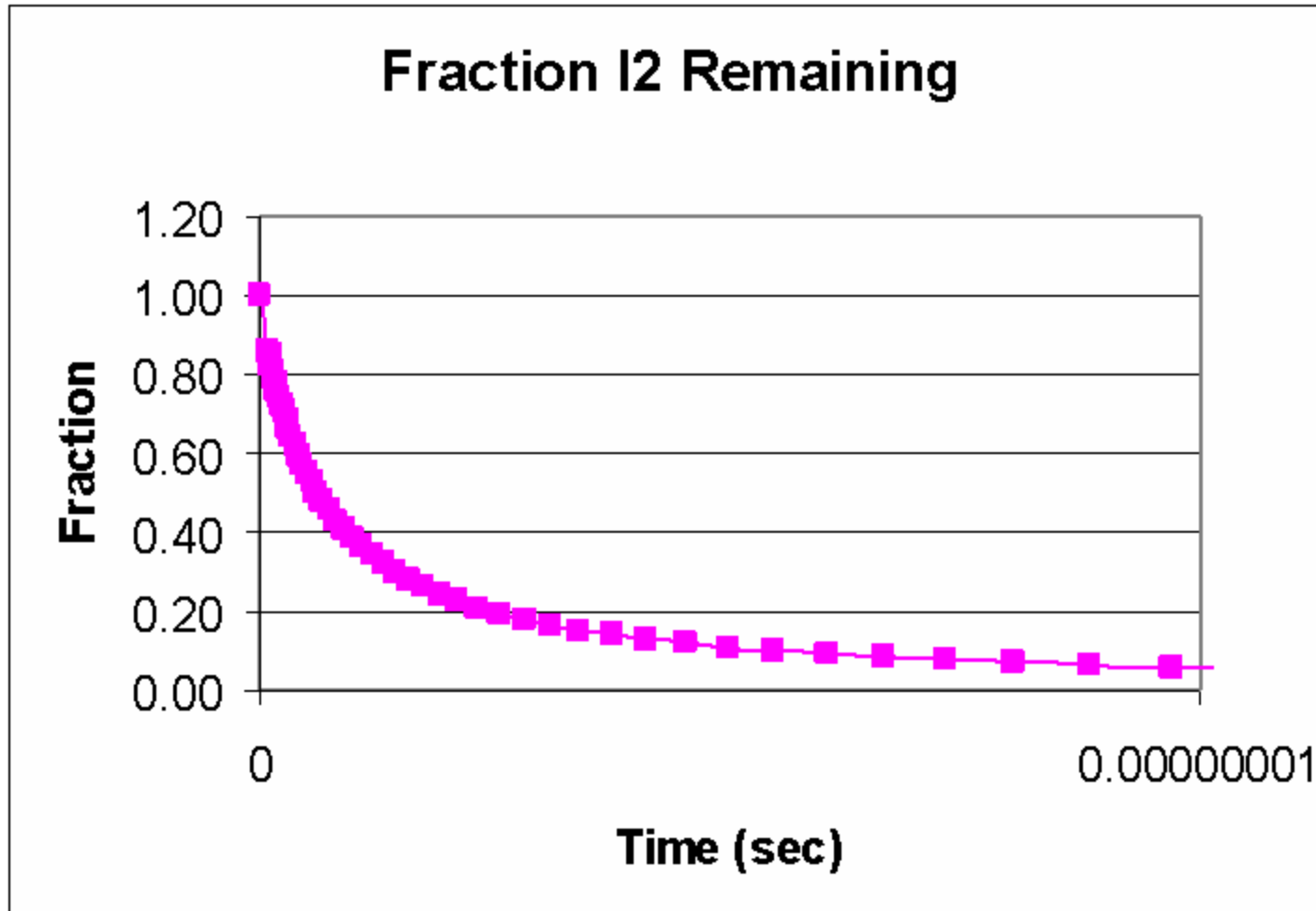
$$\text{initial conc of } \text{I}_2 \text{ and } \text{H}_2 = 1/22.4 = 0.0446 \text{ M}$$

$$d[\text{A}]/dt = -k[\text{A}]^2 \quad (\text{A}_t) = (\text{A}_o)/[1+kt(\text{A}_o)]$$

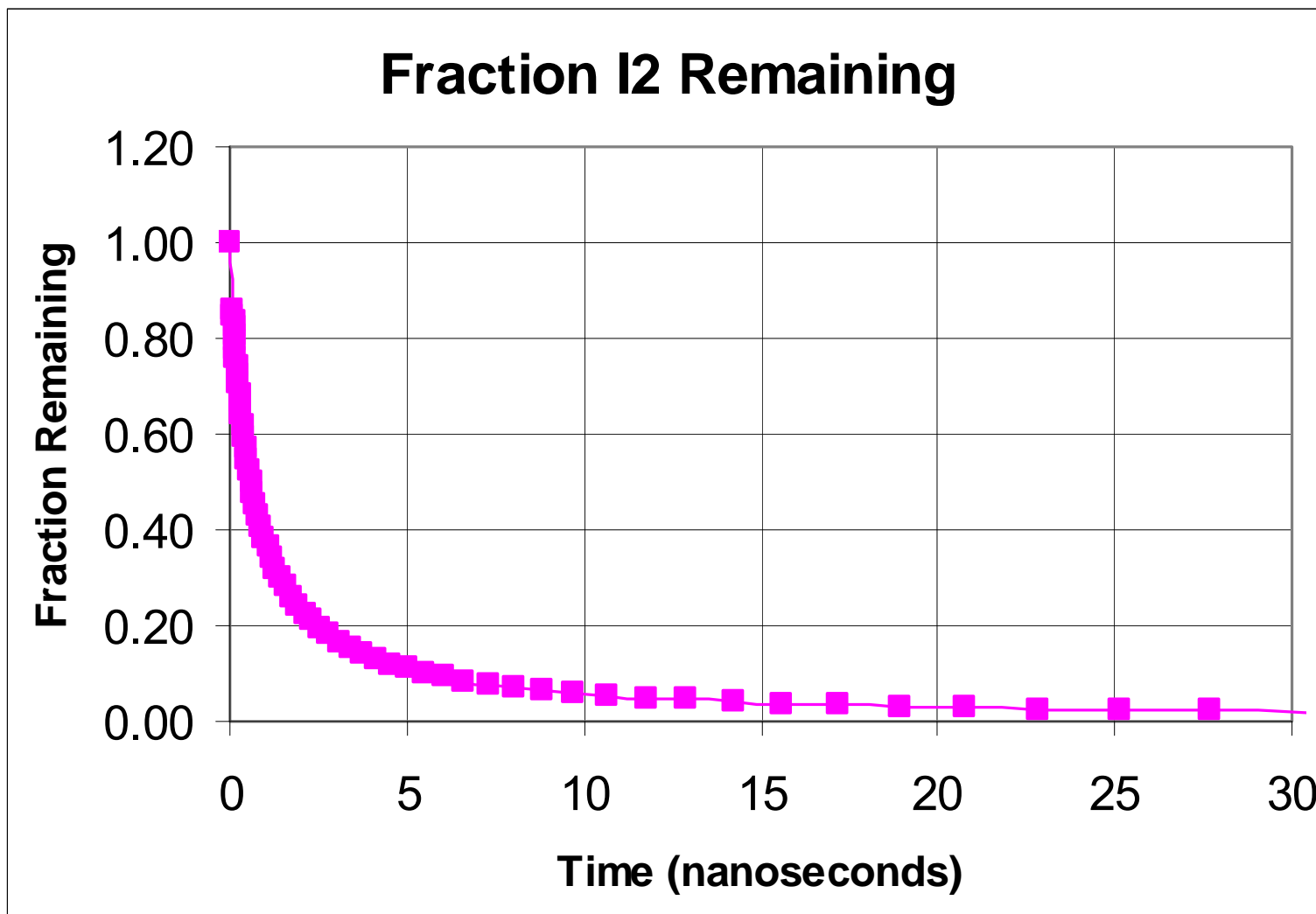
$$\text{fraction remaining} = \text{A}_t / \text{A}_o = 1/[1+kt(\text{A}_o)]$$

Generate an Excel Spread Sheet and Graph

Example Problem



Example Problem



Collision Theory – sample problem

Calculate the approximate “frequency factor” A for the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ at 0 °C (273 K). Data from tables – collision radius H = diameter/2 = 0.68×10^{-10} m for O_2 collision radius = 1.5×10^{-10} m gas constant $R = 8.31$ J/mol/K or $\text{kg m}^2/\text{s}^2/\text{K}/\text{mol}$ Avogadro’s number = N_0 molecules per mole reduced mass = $m_1 m_2 / (m_1 + m_2)$ Boltzmann’s constant = $k = R/N_0 = 1.3806503 \times 10^{-23}$ $\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$ Watch Units! don’t mix moles and molecules 1 Angstrom is 10^{-8} cm or 1×10^{-10} m Best to use SI units then change to desired units.

Frequency of Collisions between H and $\text{O}_2 = Z = \text{cross section area} \times \text{avg speed} \times N_0$

$$Z_{AA} = \sigma_A \left(\frac{4kT}{\pi m_A} \right)^{1/2} \quad Z_{AB, \text{react}} = \sigma_{AB} \left(\frac{8kT}{\pi \mu} \right)^{1/2}$$

$$\mu = M_1 M_2 / (M_1 + M_2) = 1 \times 32 / (1 + 32) = 32 / 33 = 0.97 \text{ g/mol} = 9.7 \times 10^{-4} \text{ kg/mol (reduced mass)}$$

$$\text{avg speed} = [8kT / \pi \mu]^{1/2} = 244 \text{ m/sec (this is a “relative” speed since base on } \mu)$$

$$\text{collision cross section area} = \pi r^2 = 3.14159 \times (1.5 \times 10^{-10} \text{ m})^2 = 15.6 \times 10^{-20} \text{ m}^2/\text{molecule}$$

$$\text{solve for } Z \text{ (or } A) = 3.8 \times 10^{-14} \text{ Angstrom}^3/\text{molecule/sec (could convert to L/mole/sec)}$$

$$\text{(experimental measurement} = 1.5 \times 10^{-14} \text{ Angstrom}^3/\text{molecule/sec (not bad for simple model)}$$

Molecule	Average Velocity, (meters/second) at 0 deg C	Molecular Diameter (Å)
H ₂	1687	2.74
CO	453	3.12
Xe	209	4.85
He	1200	2.2
N ₂	450	3.5
O ₂	420	3.1
H ₂ O	560	3.7
C ₂ H ₆	437	5.3
C ₆ H ₆	270	3.5
CH ₄	593	4.1
NH ₃	518	4.4
H ₂ S	412	4.7
CO ₂	361	4.6
N ₂ O	361	4.7
NO	437	3.7

Problem Example – Collision Theory

Predict the Arrhenius pre-exponential term for $\text{Cl}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{H}(\text{g})$

Data – Atomic mass g/mol Cl = 35.453, $\text{H}_2 = 2.01594$

effective or collision diameter σ Cl = 0.200 pm and $\text{H}_2 = 0.150$ pm ??

Watch units

changing mol weight to kg and concentrations from molecules/ m^3 to mol/Lit
for unlike molecules colliding

$$A = (\text{probability factor}) \times [8\pi RT(M_1 + M_2)/M_1 M_2]^{1/2} \sigma_{12}^2 (1000\text{L})$$

$$\text{rate} = A e^{-E_{\text{act}}/RT} (\text{conc } 1)(\text{conc } 2)$$

where fraction with enough energy = $e^{-E_{\text{act}}/RT}$

$$\text{Frequency of collision} = [8\pi RT(M_1 + M_2)/M_1 M_2]^{1/2} \sigma_{12}^2 (1000\text{L})$$

for this reaction the probability factor experimentally found to be ~ 0.11