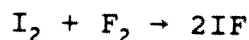


CHEMICAL KINETICS

1. Review of Elements of Chemical Kinetics.

1-1 Mechanism. Elementary Processes and Molecularity

When one writes a chemical reaction such as



It only describes the stoichiometric relation between reactants and products, but does not tell us the exact relation between molecular collisions and chemical change.

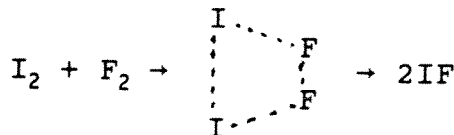
One can write the rate of change of this chemical reaction in the following way.

$$\begin{aligned} \text{Rate} &= -\frac{dP_{\text{I}_2}}{dt} - \frac{dP_{\text{F}_2}}{dt} = \frac{1}{2} \frac{dP_{\text{IF}}}{dt} \\ &= R(k_a, P_i) \end{aligned}$$

and the rate of chemical change depends on the concentrations of reactant as well as the mechanism.

Mechanism:

In the reaction of I_2 and F_2 , the inspection of orbital symmetry might suggest that a four-centered symmetric approach between I_2 and F_2 might have a potential energy barrier which is too high for collisions between I_2 and F_2 at thermal energy to produce IF products through a symmetric intermediate state.



The most likely mechanism might involve the dissociation of either I_2 or F_2 as the initiation step.



then followed by chain reactions



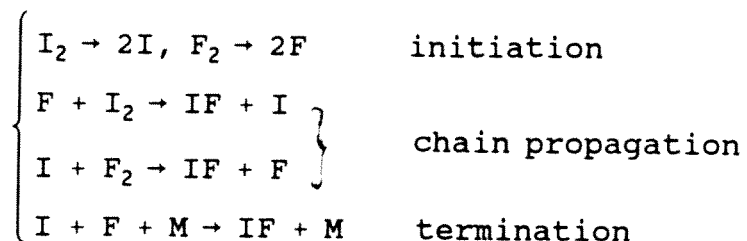


which are mainly responsible for the formation of most of IF.

Of course, when the concentration of I and F atoms build up, IF can also be formed by a three-body process with an inert participant, M, removing some of the energy between F and I to form the bond IF.

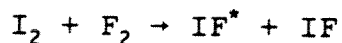


All these individual atomic and molecular processes which induce the chemical change are called elementary processes and the collections of all elementary processes which are responsible for a given stoichiometric chemical reaction are called mechanism.



The mechanism mentioned above might not be entirely correct. In the late 1960's, Professor Johnston's group found that when I_2 and F_2 were mixed, not only did reaction take place easily, but fluorescence from electronically excited IF^* were observed and the fluorescence intensity was proportional to the concentration of both I_2 and F_2 .

It seems to suggest



reaction must be taking place, but as mentioned earlier, four-centered reaction might not be responsible for the production of IF^* .

Apparently, there is something strange going on. The scientific knowledge (chemical knowledge) accumulated by mankind is far from perfect, there are many things we cannot explain or cannot understand, and that is exactly why we are doing research.

In the early 1970's, when Jim Farrar was studying $F + CH_3I \rightarrow IF + CH_3$ reaction as a function of collision energies in a molecular beam experiment, he observed an IF^* signal which

apparently was not from $F + CH_3I \rightarrow IF + CH_3$ reaction. His careful examination revealed that the new feature shown in the IF^* signal in the mass spectrometric detector was actually from the reaction of $CH_3I + F_2 \rightarrow CH_3IF + F$.

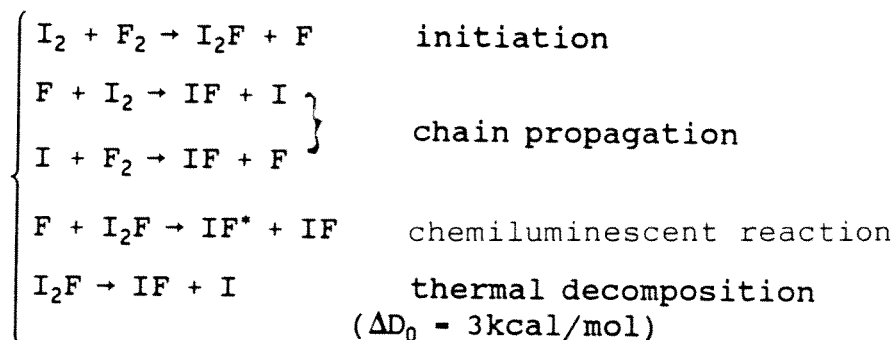
This reaction has a threshold of 11 kcal/mol, implying that CH_3I and F is bound by 26 kcal/mol, a really astonishing result. This reaction certainly suggests that for iodine-containing molecules, reaction with F_2 , not only forms radical product, but also has a threshold energy which is way below the dissociation energy of F_2 (~37 kcal/mol, energy required for the "initiation").

It was not surprising that the later research carried out by Valentini and Coggiola showed that the formation of I_2F from the reaction

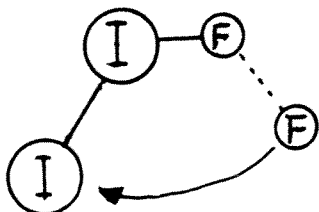


has a threshold as low as 4 kcal/mol. That is why I_2 and F_2 react so easily even at room temperature

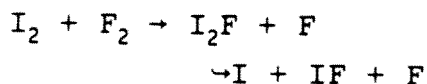
Consequently, if we were to update what we found, we will write



In the initiation step sometimes the departing F atom might bump into the end I atom in I_2F and form IF^* . Although the occurrence of such an event is only a small fraction of I_2F formation, it is responsible for the IF^* production through bimolecular reactions between I_2 and F_2 . The reaction intermediate is not symmetric



Since the dissociation energy of I_2F is only 3 kcal/mol, when the collision energy exceeds 7 kcal/mol, some vibrationally excited I_2F dissociate

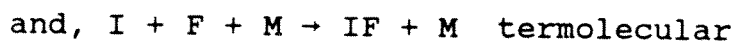
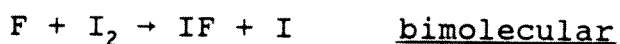


At higher energy, the dissociation of I_2F is so fast it might not be able to be separated by their formation and one should write



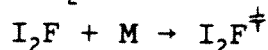
Molecularity:

The elementary chemical reactions are traditionally classified based on the number of molecules involved. For example, the following elementary reactions are called



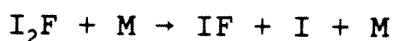
But, the distinctions among these three are not clear cut, especially when one examines the collisional dynamics between molecules and intramolecular dynamics involved.

For example, the unimolecular dissociation of I_2F involves the collisional energization of I_2F



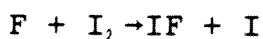
then followed by the dissociation of vibrationally excited I_2F^\ddagger .

For small molecules, the dissociation process might start to take place before colliding partners depart, and the lack of clear separation between energization and dissociation might make it more appropriate to write it in a single step

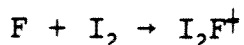


and consider it to be a bimolecular collision induced dissociation.

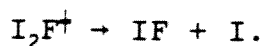
Likewise, for a bimolecular chemical reaction



if the reaction intermediate turns out to be very stable, then the process could be more accurately described as the bimolecular complex formation



followed by a unimolecular decay of I_2F^\ddagger



Again, in a termolecular recombination



if MF is a very stable intermediate, then the termolecular process can be written as



followed by a bimolecular reaction

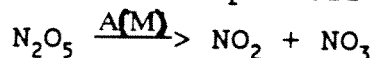


It seems clear that no matter whether the reaction is unimolecular, bimolecular, or termolecular, what we really have to understand is:

- (a) molecular scattering processes, including elastic, inelastic and reactive scattering, with detailed understanding of complex formations, $T \rightarrow V, R$ or $V, R \rightarrow T$ intermolecular energy transfers, and,
- (b) intramolecular dynamics.

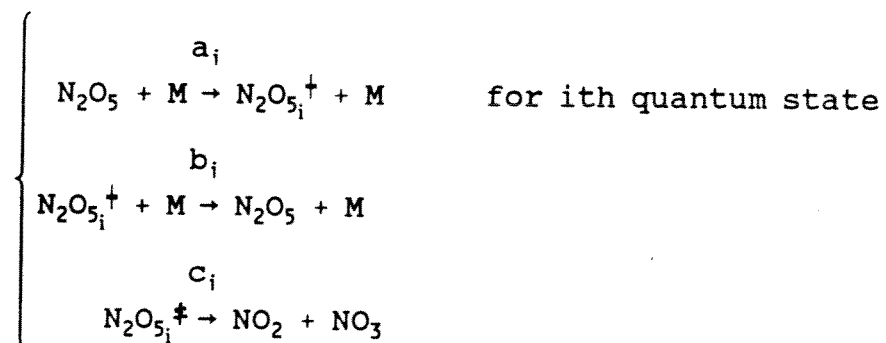
Rate Expression and Mechanism:

When we write a chemical rate process



and use $A(M)$ to describe the rate, $A(M)$ is not a constant.

The mechanism of this decomposition process involves the following step.



The rate of reduction of N_2O_5 is then

$$- \frac{d[N_2O_5]}{dt} = \sum_i \left\{ a_i [N_2O_5] [M] - b_i [N_2O_{5_i}^{\ddagger}] [M] \right\}$$

When steady state concentration of $[N_2O_5^\ddagger]$ is established

$$\frac{d[N_2O_5^\ddagger]}{dt} = a_i [N_2O_5] [M] - b_i [N_2O_5^\ddagger] [M] - c_i [N_2O_5^\ddagger] = 0$$

$$[N_2O_5^\ddagger] = \frac{a_i [N_2O_5] [M]}{b_i [M] + c_i}$$

$$\begin{aligned} -\frac{d[N_2O_5]}{dt} &= \sum_i c_i [N_2O_5^\ddagger] \\ &= \sum_i \frac{a_i c_i [M]}{b_i [M] + c_i} [N_2O_5] \\ &= A(M) [N_2O_5] \end{aligned}$$

$$A(M) = \sum_i \frac{a_i c_i [M]}{b_i [M] + c_i}$$

and it is not a constant

When $[M]$ is large

$$-\frac{d[N_2O_5]}{dt} = \sum_i \frac{a_i}{b_i} c_i [N_2O_5] = \sum_i k_i c_i [N_2O_5]$$

the rate is controlled by c_i , the unimolecular rate constant.

When $[M]$ is small

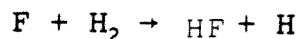
$$-\frac{d[N_2O_5]}{dt} = \sum_i a_i [M] [N_2O_5]$$

The rate is controlled by the excitation process.

1-2. Rate Constants and Cross Sections

1-2-1 Temperature Dependence of Rate Constants

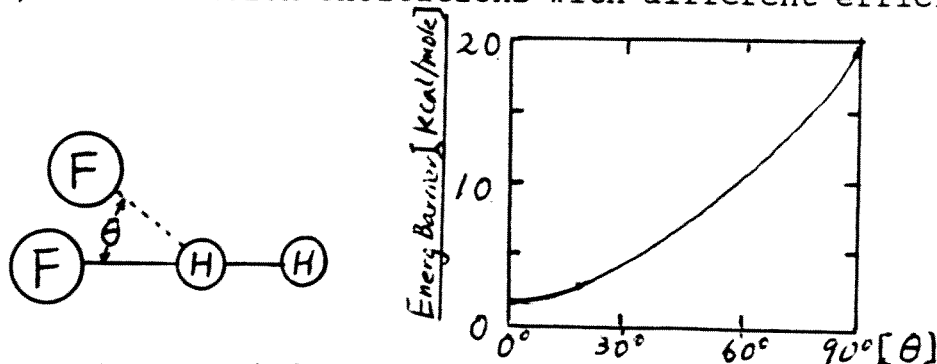
Even for an exothermic reaction like



there is a potential energy barrier between reactants and products. Namely, there is a minimum energy requirement in order for a reaction to proceed.

This potential energy barrier depends on the geometric

arrangement of reactants and can be overcome by translational, rotational, and vibration excitations with different efficiencies.



It is not surprising that at higher temperatures, with molecules moving at higher transitional energies, the acceptance angle, θ , for the reaction becomes wider and the rate of reaction becomes larger. At higher temperatures, as more molecules are in higher rotationally and vibrationally excited states, sometimes the rate might change drastically.

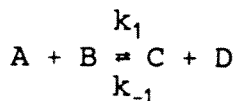
It was found empirically by Hood (1878) that the rate constant, k , of a reaction varies with absolute temperature, T , according to the law of the form

$$\log k = B - \frac{A'}{T}$$

where A' and B are constants.

In 1884, van't Hoff had given some theoretical significance to this law, argued on the basis of the effect of temperature on equilibrium constants. This idea was extended by Arrhenius and was successfully applied by him to the data for a number of reactions.

Arrhenius Law:



$$K_c = \frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]}$$

$$\frac{d \ln K_c}{dT} = \frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{\Delta E}{RT^2}$$

Which may be split into two equations

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + I$$

$$\frac{d \ln k_2}{dT} = \frac{E_{-1}}{RT^2} + I$$

where $E_1 - E_{-1} = \Delta E$

Experimentally it was found that I can be set equal to zero

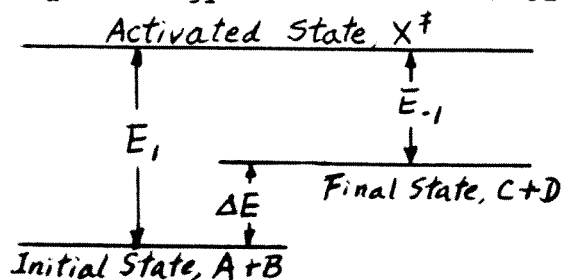
$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Consequently, $k = A e^{-\frac{E_a}{RT}}$

The well-known Arrhenius expression:

A = preexponential factor or frequency factor

E_a = energy of activation or activation energy



Very often after k was measured at a wide range of temperature and plot $\ln k$ as a function of $\frac{1}{T}$.

Since

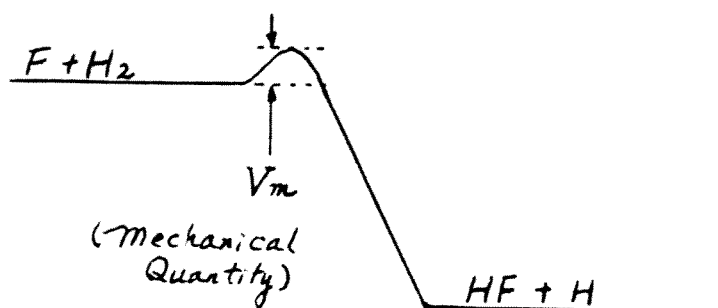
$$\ln k = \ln A - \frac{E_a}{RT}$$

then the slope will be E_a and the intercept will be $\ln A$, or

$$E_a = RT^2 \frac{d(\ln k)}{dT}$$

E_a is a phenomenological quantity. It is not a mechanical quantity.

1-2-2 The Relation Between the Activation Energy, E_a , and the Potential Energy Barrier, V_m



Activation energy, E_a , is closely related to the potential energy barrier, V_m , of a given reaction, but they are not the same. E_a is derived from macroscopic experiments and V_m is a mechanical quantity.

If one uses a simple collision theory and derives the rate constant for a system having a potential energy barrier, V_m , one obtains an expression

$$k(T) = B(T) e^{-\frac{V_m}{kT}}$$

Suppose $B(T) = CT^n$, and let us derive activation E_a from this.

Now we have

$$k = CT^n e^{-\frac{V_m}{kT}}$$

$$\ln k = \ln C + n \ln T - \frac{V_m}{kT}$$

$$\frac{d \ln k}{dT} = \frac{n}{T} + \frac{V_m}{kT^2}$$

$$\text{and } E_a = kT^2 \frac{d \ln k}{dT} = \underline{nkT + V_m}$$

In the case when $n = 0$, then $B(T)$ is constant and $E_a = V_m$. But for most of gas phase elementary reaction,

$$-2 \leq n \leq 2$$

depends on whether attractive forces or repulsive forces play more important roles before reaching the transition state.

When we are considering chemical reactions of a compound, we must realize that these molecules are in different quantum states and molecules in different quantum states behave differently. They have different specific rate constants.

The fraction of a molecule in i th quantum state

$$\chi_i = \frac{n_i}{n} = \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}}$$

↙
partition function

If the rate of establishing equilibrium among the reactants is faster than the rate of depletion of molecules in a given quantum state due to chemical reaction (equilibrium assumption), then

$$k = \sum_i \chi_i k_i = \frac{\sum_i k_i e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}}$$

$$\ln k = \ln \left(\sum_i k_i e^{-\frac{\epsilon_i}{kT}} \right) - \ln \left(\sum_i e^{-\frac{\epsilon_i}{kT}} \right)$$

$$E_a = RT^2 \frac{d \ln k}{dT} = \frac{\sum_i \epsilon_i k_i e^{-\frac{\epsilon_i}{kT}}}{\sum_i k_i e^{-\frac{\epsilon_i}{kT}}} - \frac{\sum_i \epsilon_i e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}}$$

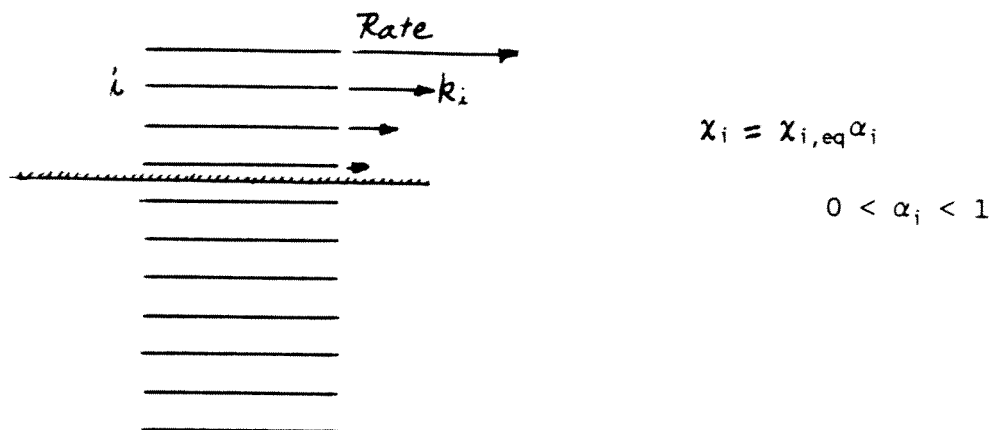
average energy of those
molecules which react

average energy of
all molecules

Thus, E_a is the difference between two averaged quantities, and it is not surprising that it is not exactly equal to the barrier height. [Johnston and Berks, Acc. Chem. Res. 5, 327 (1972)]

Now, suppose we have deviations from equilibrium. Suppose

upperstates react very fast such that the population could be depleted from equilibrium distribution.



Usually, the higher the i state or the higher the ϵ_i , the smaller the α_i . That will occur when intermolecular energy transfer to higher i state is slower than the reaction rate of i state.

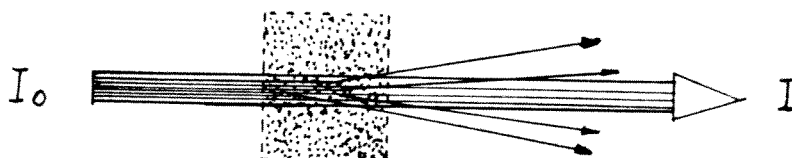
As a result of this, the average energy of molecules which react decreases as a non-equilibrium effect occurs.

$$E_{a,ne} < E_{a,eq}$$

and sometimes $E_{a,ne}$ may, in fact, be less than the endoergicity of reactions. In shock tube studies of the dissociation of alkali halides using Ar as a driver gas, measured activation energies, ~105 kcal/mol, were significantly lower than the dissociation energies, ~120 kcal/mol.

1-2-3 Cross Sections from a Phenomenological Approach

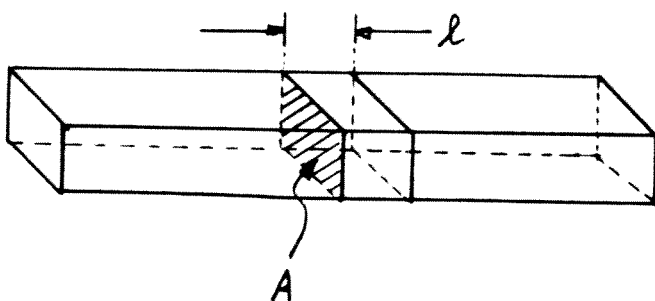
Imagine a beam of molecules of intensity $I_0 \frac{\text{molecules}}{\text{cm}^2 \text{ sec}}$ impinging on a dilute scattering gas



Some of the molecules in the beam may be removed from the beam due to scattering processes (elastic, inelastic or reactive scattering) and the intensity of beam which pass through the scattering gas is I .

$$\text{Fraction scattered is } \frac{I_0 - I}{I_0}$$

If the beam has an area A , the scatterer gas contained in a length l acts as if it had blanked out an effective area



$$\text{Then, } \frac{I_0 - I}{I_0} = \frac{\text{Effective area of scatterer gas}}{A} = \frac{A'}{A}$$

If $A' \ll A$. then effective area of scatter gas

A' = the effective area of a molecule \times number of molecules in scattering zone

$$= \sigma \times n \underbrace{\ell A}_{\text{Volume}}$$

\uparrow
 Number density

$$\sigma \underset{\text{number density}}{n} \underset{\text{volume}}{\ell} A = \frac{I_0 - I}{I_0} A$$

This relation only holds when $\frac{I_0 - I}{I_0}$ is very small, namely $I \approx I_0$.

$$\sigma = \frac{I_0 - I}{I} \frac{1}{n\ell} = -\frac{dI}{I} \frac{1}{nd\ell}$$

or $I = I_0 e^{-n\sigma\ell}$

This defines a total cross section, σ

The relation between a cross section and mean free path is

$$\lambda = \frac{1}{n\sigma} \quad \text{i.e., } I = I_0 e^{-\frac{\ell}{\lambda}}$$

At 1 atm $n = 2 \times 10^{19}$, if $\sigma = 25 \times 10^{-15} \text{ cm}^2$, then $\lambda = \frac{1 \text{ cm}}{5 \times 10^5} = 200 \text{ \AA}$

Of course, it doesn't matter how the concentration n is maintained. It may be by another beam. Flux and density is

related by $v_B \times n_B = J_B$, so $n_B = \frac{J_0}{v}$

In this type of attenuation measurement, we measure the total cross section. Namely, the effective area of molecules which cause momentum transfer to cause the deviation of molecules from their trajectories, but we do not know what happened; how much of these scattering events cause reaction, etc. But, in a crossed molecular beam experiment, one measures the number of scattered molecules per second at some solid angle and one can distinguish the nature of scattering process by identifying the product, and measuring velocity as functions of scattering angle. (Dynamics informations are really in the differential cross sections.)

Then by definition $I_0 - I = i$, the total number of molecules scattered away

$$i = \int_{\Omega} i(\Omega) d\Omega = n\ell I_0 \sigma \quad \left(\text{when } \frac{i}{I_0} \text{ is small}\right)$$

$$= n\ell I_0 \int \sigma(\Omega) d\Omega$$

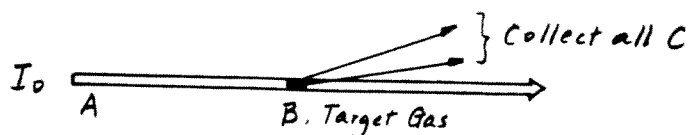
$\sigma(\Omega)$ is the differential cross section (scatter into angle Ω).

$$\sigma(\Omega) d\Omega = \frac{i(\Omega) d\Omega}{n\ell I_0}$$

Consequently, just like the derivation of the total cross section σ from the total flux of scattered molecules (a total alternation), one can derive the differential cross section $\sigma(\Omega)$ from the measurement of the flux of scattered molecule arriving at angle Ω .

$$\left\{ \begin{array}{l} \sigma = \frac{I_0 - I}{I_0} \frac{1}{n\ell} = \frac{i}{I_0} \frac{1}{n\ell} \\ \sigma(\Omega) = \frac{i(\Omega)}{I_0} \frac{1}{n\ell} \end{array} \right.$$

Now, lets imagine a reaction $A + B \rightarrow C + D$ and instead of measuring the attenuation of A (Total) let's collect all C (reaction products).



$$\frac{dN_C}{dt} = I_A \left(\frac{\#}{\text{cm}^2 \text{ sec}} \right) n_B A l \sigma_D$$

of C produced per second

$$\frac{dn_C}{dt} = \frac{1}{Al} \frac{dN_C}{dt} = \sigma_D I_A n_B$$

of C produced per second per unit volume.

Since $I_A = n_A v_A$

$$\therefore \frac{dn_C}{dt} = \frac{v_A \sigma_D}{k} n_A \cdot n_B$$

Now, we have assumed for simplicity that B was standing still. In general, it is found experimentally that dn_C/dt depends on both v_A and v_B in the combination $|v_A - v_B| = v_{rel} = g$

$$\text{Thus, } \begin{cases} k(g) = g \sigma(g) \\ k(T) = \int f(g) k(g) dg = \int g \sigma(g) f(g) dg \end{cases}$$

Thus our mechanical problem is defined if we know $\sigma(g)$ and $f(g)$, we can evaluate the rate constant $k(T)$ at a given temperature, T , easily.

Now let us look at $f(g)$

We know that when the system is in equilibrium, the velocity distributions of atoms or molecules should have Maxwell-Boltzmann distribution:

$$f(\vec{v}_1) = \left(\frac{m_1}{2\pi kT} \right)^{3/2} e^{-\frac{m_1 v_1^2}{2kT}}$$

but what we are interested in is the relative motion between molecules, not the motion in the lab coordinate system itself. It means that we are interested in $f(\vec{v}_1 - \vec{v}_2) = f(\vec{g})$ rather than

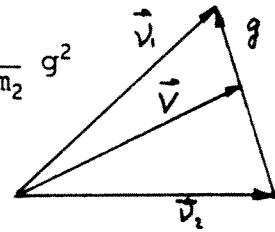
$f(\vec{v}_1)$ and $f(\vec{v}_2)$.

$$f(\vec{v}_1, \vec{v}_2) = f(\vec{v}_1) \cdot f(\vec{v}_2) = \left(\frac{m_1}{2\pi kT} \right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{1}{2}(m_1 v_1^2 + m_2 v_2^2)/kT}$$

define, $\vec{g} = \vec{v}_2 - \vec{v}_1$, $\vec{V} = \frac{m_1 \vec{v}_1 + m_2 \vec{v}_2}{m_1 + m_2}$

If we transform the coordinates and express \vec{v}_1, \vec{v}_2 in terms of \vec{g} and \vec{V} , it is easily shown

$$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} (m_1 + m_2) V^2 + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} g^2$$



So, if we rearrange the equation

$$f(\vec{v}_1, \vec{v}_2) = \left(\frac{m_1 + m_2}{2\pi kT} \right)^{\frac{3}{2}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \frac{M v^2}{kT}} \cdot e^{-\frac{1}{2} \frac{\mu g^2}{kT}}$$

$$= \left(\frac{M}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \frac{M v^2}{kT}} \cdot \left(\frac{\mu}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \frac{\mu g^2}{kT}}$$

here $M = m_1 + m_2$

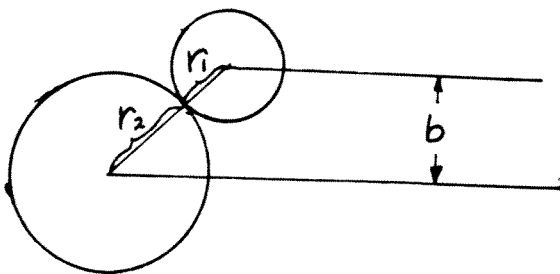
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$f(\vec{g}) = \left(\frac{\mu}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \frac{\mu g^2}{kT}}$$

$$f(g) = 4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} g^2 e^{-\frac{1}{2} \frac{\mu g^2}{kT}}$$

1-2-4 Hard Sphere Collisions:

Atoms and molecules are not hard spheres, but it is nice to have a framework of limiting case that one can make the comparison of a real system with.



Hard sphere scattering cross section = $\pi(r_1 + r_2)^2$. There is collision when $b \leq r_1 + r_2$; r_1 and r_2 are the radii of hard spheres b is known as the impact parameter.

If every collision lead to a chemical reaction, then

$$\begin{aligned} k(T) &= \int_0^{\infty} \pi(r_1 + r_2)^2 \cdot gf(g) dg \\ &= \pi(r_1 + r_2)^2 \int_0^{\infty} gf(g) dg \\ &= \pi(r_1 + r_2)^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} = \pi(r_1 + r_2)^2 \cdot \bar{g} \end{aligned}$$

For atoms and small molecules: $r_1 + r_2 = 4 \text{ \AA} = 4 \times 10^{-8} \text{ cm}$

$$\pi(r_1 + r_2)^2 = 50 \text{ \AA}^2$$

$$\bar{g} = 4 \times 10^4 \text{ cm/sec (for O}_2 \text{ at 300 K)}$$

$$k(T) = 50 \times 10^{-16} \times 4 \times 10^4 = 2 \times 10^{-10} \text{ cc/sec mol.}$$

If a rate constant of an elementary reaction is $\sim 10^{-10}$ cc/sec mol, it is a fast reaction, almost every gas kinetic collision leads to reaction. Some atom-molecule reactions, e.g., $F + I_2$, and $F + H_2$, have this magnitude of rate constants. Only ion-molecule reactions have rate constants larger (10^{-9} cc/sec. mol), mainly due to the long range charge induced dipole interactions pull them together from a large distance.

Since collision rate between particle A and particle B is

$$\frac{dn}{dt} = \bar{\sigma} \bar{g} n_A \cdot n_B$$

For identical particle $\frac{dn}{dt} = \frac{1}{2} \sigma g n_A^2$

At 1 atm, 1 cc contains 2×10^{19} mol/cc and since $\sigma g = 2 \times 10^{-10}$ cc/sec.mol

$$\begin{aligned} \frac{dn}{dt} &= \frac{1}{2} \times 2 \times 10^{-10} \times (2 \times 10^{19})^2 \\ &= \underline{4 \times 10^{28} \text{ mol/cc sec}} \end{aligned}$$

of collisions for each molecule per sec

$$= \frac{4 \times 10^{28}}{2 \times 10^{19}} = 2 \times 10^9 \quad [2 \times 10^9 \text{ sec} : 65 \text{ years}]$$

1-2-5 Reactants Having Velocity Distributions at Two Temperatures

If two reactant species on a bimolecular reaction, each has a Maxwell-Boltzman distribution of velocities corresponding, respectively, to temperatures T_1 and T_2 . The problem of converting the velocity dependent cross section to a statistical rate coefficient is somewhat more difficult. Such a situation is most likely to occur, if the masses of reactant species are very different. Especially in a gaseous plasma form by electric discharge, the electron temperature is usually much higher than the temperatures of ions or molecules.

So, if we have

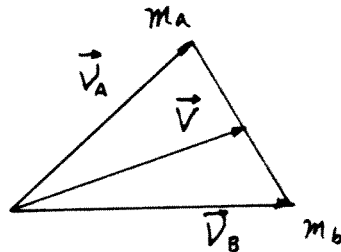
$$f_A(\vec{v}_A) = \left(\frac{m_A}{2\pi kT_A} \right)^{\frac{3}{2}} \exp \left[-\frac{m_A v_A^2}{2kT_A} \right]$$

$$f_B(\vec{v}_B) = \left(\frac{m_B}{2\pi kT_B} \right)^{\frac{3}{2}} \exp \left[-\frac{m_B v_B^2}{2kT_B} \right]$$

$$k = \iiint g \sigma(g) f(\vec{v}_A) f(\vec{v}_B) d\vec{v}_A d\vec{v}_B$$

If we now set $\vec{g} = \vec{v}_A - \vec{v}_B$, $\vec{V} = \frac{m_A \vec{v}_A + m_B \vec{v}_B}{m_A + m_B}$

We note that, when $T_A = T_B$ then \vec{V} is the velocity vector of c.m of the system



$$\vec{V} = \frac{m_A \vec{v}_A + m_B \vec{v}_B}{m_A + m_B}$$

$$f_A(\vec{v}_A) f_B(\vec{v}_B) = \left(\frac{m_A}{2\pi kT_A} \right)^{\frac{3}{2}} \left(\frac{m_B}{2\pi kT_B} \right)^{\frac{3}{2}} \exp \left[-\frac{\mu g^2}{2kT^*} - \left(\frac{m_A}{T_A} + \frac{m_B}{T_B} \right) \frac{V^2}{2k} \right]$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$T^* = \frac{m_A T_B + m_B T_A}{m_A + m_B}$$

$$k_{\sigma}(T^*) = 4\pi \left(\frac{\mu}{2\pi kT^*} \right)^{\frac{3}{2}} \int_0^{\infty} g^3 \sigma(g) \exp \left(-\frac{\mu g^2}{2kT^*} \right) dg$$

This equation is essentially the same as the one we derive for all specimens in the same temperature except the definition of temperature.

Here we have "reduced temperature"

$$T^* = \frac{m_A T_B + m_B T_A}{m_A + m_B}$$

Example: The ionization of neutral atoms on a plasma characterized by an electron temperature T_e and a neutral atom temperature, T_n . Assume the cross-section for single ionization near the threshold has the form

$$\begin{aligned} \sigma(g) &= 0 \text{ for } \frac{\mu g^2}{2} < I : \text{ ionization potential} \\ &= a \left(\frac{\mu g^2}{2} - I \right) \text{ for } \frac{\mu g^2}{2} \geq I \end{aligned}$$

$$k(T^*) = 4\pi a \left(\frac{\mu}{2\pi kT^*} \right)^{\frac{3}{2}} \int_{\left(\frac{2I}{\mu}\right)^{\frac{1}{2}}}^{\infty} g^3 \left(\frac{\mu g^2}{2} - I \right) \exp \left(-\frac{\mu g^2}{2kT^*} \right) dg$$

we find

$$k(T^*) = 2a \left(\frac{2kT^*}{\mu} \right)^{\frac{3}{2}} (I + 2kT^*) \exp \left(-\frac{I}{kT^*} \right)$$

$$\text{where } T_* = \frac{m_e T_n + m_n T_e}{m_e + m_n} = \left(\frac{m_e}{m_n} \right) T_n + T_e$$

For an atom-electron plasma system with $T_e > T_n$, one then has $T^* = T_e$

when $I \gg kT_e$; i.e. in a low temperature plasma (microwave discharge).

$$k(T_e) = 2a \left(\frac{2kT_e}{m_e} \right)^{1/2} I \exp \left(- \frac{I}{kT_e} \right)$$

1-3 State to State Cross Sections: $\sigma(m, l | i, j; g)$

Now we have some concept of $\sigma(g)$. The effective area of molecule for special events, lets look at it more precisely. When we wrote $\sigma(g)$, we neglected the dependence of initial and final quantum states of molecules involved in chemical reaction. Usually, it is understood that all quantum states populated are summed over.

But, we can be more specific and look at quantum state dependence, since very often, this is extremely important.

$$A_i(\vec{V}_A) + B_j(\vec{V}_B) \rightarrow C_m(\vec{V}_C') + D_l(\vec{V}_D')$$

i, j, m and l are the quantum numbers of A, B, C and D molecules.

The reaction cross section of this process could be written down for a given relative velocity

$$\sigma(m, l | i, j, g) = \int_{\Omega} d\Omega' \sigma(m, l | i, j; g, \Omega')$$

total reactive cross section from i, j to m, l with relative velocity g

differential reactive cross section from i, j, g to m, l and to specific solid angle Ω

This integration on angle is necessary because of the distributions of impact parameters.

As you may have noticed, the specification of i, j and g is not really enough since one needs additional mechanical conditions. The specification of angular momentum (a very important factor in chemical reaction). So $\sigma(m, l | i, j, g)$ is really average over impact parameter (or angular momentum). Thus, we have to integrate over $d\Omega$. Or if one introduces an impact parameter, b , (it means we pay our attention more to the reactant side).

$$\sigma(m1 | ij; g) = 2\pi \int_0^{\infty} P(m1 | ij; gb) b db$$

$\int_{\Omega} I_{c_m}(\Omega) d\Omega =$ total number of c_m formed/sec with relative

velocity g from $i \cdot j$

$$= \tau \int_{\Omega} d\Omega \sigma(m, 1 | i \cdot j; g\Omega) g n_{A_i} f_A(\vec{v}_A) \cdot n_{B_i} f_B(\vec{v}_B) d\vec{v}_A d\vec{v}_B$$

Now, $\frac{dn_c}{dt} = \sum_{i,j,lm} \int_{v_A, v_B} \sigma(m, 1 | i, j \cdot g) g n_{A_i} f_A(v_A) n_{B_i} f_B(v_B) dv_A dv_B$

So, since $\frac{dn_c}{dt} = k n_A \cdot n_B$ and $n_{A_i} = \chi_{A_i} \cdot n_A$

$$k = \sum_{i,j,lm} \underbrace{\chi_{A_i} \chi_{B_i}}_{\text{internal}} \int g \sigma(lm | ij; g) \underbrace{f_{A_i} f_{B_i}}_{\text{translational}} dv_{A_i} dv_{B_i}$$

So, the "statistical" macroscopic rate constant is the rate of individual detailed chemical reactions, averaged over some distribution of states and relative velocities

$$(\sum \chi_{A_i}, \chi_{B_i}, \int g^2 f_A f_B dv_A dv_B).$$

It is customary to assume $(\chi_{A_i}, \chi_{B_i}, f_A dv_A f_B dv_B)$ are equilibrium distributions (appropriately weighted Boltzman). This is the "equilibrium" assumption of chemical kinetics.

It is clear that if a net reaction is proceeding, there cannot be an equilibrium distribution of states, since the "reactive" states of the reactant tend to be "drained" off by reaction. States "drained" can be repopulated by: (1) *inelastic* collisions; (2) "reverse" reactive collisions.

1-4. Relaxation of a Chemical System

Among the methods of the determination of rate

constants, the "relaxation" method is one of the commonly used methods. Just as the equilibrium constant is determined by the ratio of forward and backward rate constants. How fast a system thermalizes (or relaxes) on moving from non-equilibrium to equilibrium is determined by specific rate constants ($k_1, k_2; k_{-1}, k_{-2}$). Of course, if the system is a one-component non-reactive system, the relaxation process only depends on the transition probability of individual quantum states.

Define P_{ij} as probability per unit time that $i \rightarrow j$ transition occurs.

$P_{ij}n_i$ is the number of such transitions per unit time. The net rate of change is $\frac{dn_i}{dt} = \sum_j (P_{ji}n_j - P_{ij}n_i)$.

A whole set of such equations describe the system.

The solutions to those equations are expressed as

$$n_i = n_i(\infty) + \sum_{\ell} C_{i\ell} e^{-\lambda_{\ell} t}$$

where $n_i(\infty)$: equilibrium population.

$C_{i\ell}$: initial condition.

the amount deviated from equilibrium.

The significance of the λ_{ℓ} and C_{ℓ} and the ℓ subscript is as follows.

The system has linear combinations of concentration (imagine, the normal modes in molecular vibration)

$$q_{\ell} = \alpha_{1\ell} n_1 + \alpha_{2\ell} n_2 + \dots$$

such that

$$q_{\ell} = q_{\ell}(t=0) e^{-\lambda_{\ell} t} + q_{\ell}(\infty).$$

Thus, the time dependence of the concentrations is given by the sum over all normal modes

$$n_i = n_i(\infty) + \sum C_{i\ell} e^{-\lambda_{\ell} t}$$

Now, in the simplest case, take two state systems

$$\frac{dn_2}{dt} = P_{12}n_1 - P_{21}n_2$$

$$\begin{cases} n_2 = n_2(\infty) + C_2 e^{-\lambda t} \\ n_1 = n_1(\infty) + C_1 e^{-\lambda t} \end{cases}$$

only one decay mode has $\lambda \neq 0$ (n_1 and n_2 are related since the decrease of n_1 will be the increase of n_2). Then, by substitution using

$$P_{12}n_1(\infty) = P_{21}n_2(\infty)$$

one gets

$$-C_2\lambda = P_{12}C_1 - P_{21}C_2$$

Since $n_1 + n_2 = n_1(\infty) + n_2(\infty)$, C_1 and C_2 should have the same magnitude with opposite sign, namely,

$$C_1 = -C_2$$

One obtains a simple relation

$$\lambda = P_{12} + P_{21}$$

It means that the relaxation rate constant is the sum of transition probabilities P_{12} and P_{21} .

Combining λ with equilibrium constant $k = \frac{P_{21}}{P_{12}}$

It is possible to derive the values of both P_{12} and P_{21} .