MSc II nd SEMESTER : Course – CH 9 UNIT IV

Teacher : Prof. Kallol K Ghosh Lecture Slots : January 6 – 31st , 2015

Please Read this important Article also :

Historical perspective on: RRKM reaction rate theory for transition states of any looseness [Volume 110, Issue 3, 28 September 1984, Pages 230–234]

David M. Wardlaw, R.A. Marcus Chem Phys Letter 2013, 589,23-25

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Source of Literature : ***keszei.chem.elte.hu/rkinetika/unimol_draft.doc***

Theories of unimolecular reaction rates

1. Introduction.

I'll follow the chronological development of the theories, trying to emphasize how they were developed to answer experimental questions and how experiments were designed to help theory decide how to proceed so that it improves its description and gets closer to reality. I'll therefore start with a historical overview on the development of these theories, and then follows deeper explanations to relate each of these theories with experimental issues.

As soon as I reach the state of the art, namely RRKM, I will go more into the details and explain what its basic assumptions are and criticize them to have a better understanding of its limitations.

Finally I will introduce you shortly to alternative theories which can refine the theoretical description and be of great help when RRKM lacks a reliable description.

2. Definition.

A unimolecular reaction is in principle the simplest kind of elementary reaction since it involves the decomposition or isomerization of a single reactant (write ODE)…. ideally in gas phase, since in liquid phase it must involve the participation of surrounding molecules (apolar solvent, or be an ultrafast reaction completed within a few picoseconds, not having time to interact with surrounding molecules except for resolvation).

3. Historical overview.

Perrin initially suggested it to be caused by radiation (1919) but Langmuir showed that the density of infrared radiation available was not sufficient to account for the rates observed and Lindemann showed the disagreement of this hypothesis with experiment (inversion of sucrose would be enormously accelerated by sunlight).

Lindemann called attention to the fact that if the rates of activation and of de-activation are large compared to the rate of the reaction; the reaction may be unimolecular regardless of the order of the activation process (1922).

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow[k_2]{} B + C$$

Calculations were performed (separately by Christiansen and Kramers -1923-, by Lewis -1925- and by Tolman -1925-) making use of the simple collision theory developed by Langmuir in 1920 in order to conclude between the two activation processes but none of these were favorable to either method of activation.

Two arguments followed these calculations to help concluding on that topic:

- one came from experimental studies:

Hinshelwood & co found discrepancies in the slope of log k vs P at low and at high pressure for decomposition of propaldehyde and other ethers which are strictly unimolecular at high pressures but deviate at low pressure.

Decomposition of azomethane was studied experimentally by Ramsperger in 1927 who put into light much bigger discrepancies at low and at high pressure in the rate constant than in the Hinshelwood cases.

These experimental evidences are suggesting a collisionally controlled phenomenon.

- the second from the suggestion by Christiansen that the number of degrees of freedom of the molecule must be considered.

Hinshelwood then succeeded to show that the maximum rate was largely increased by Christiansen's assumption, and explained his experimental results fairly well but not the much faster decomposition of azomethane observed by Ramsperger (or only by considering an absurd number of degrees of freedom).

$$A + M \underset{k_{-1}}{\overset{k_1(E)}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow[k_2]{} B + C$$

Rice, Ramsperger and Kassel (separately) modified the assumption that the specific reaction rate of energized molecules is a constant to let it be an energy dependent step. They designed the now so-called RRK theory (1927).

$$A + M \xrightleftharpoons[k_{-1}]{\delta k_1(E \longrightarrow E+\delta E)} A^*_{(E \rightarrow E+\delta E)} + M$$

$$A^*_{(E)} \xrightarrow{k_2(E)} B + C$$

At that time no computer were available, therefore gross approximations were done in RRK theory (all oscillators treated as equivalent).

Marcus modified their theory to introduce the concept of TS and also developed a quantum statistical description of the energization step, relying on computational methods to evaluate density and sum of states of the energized molecule and the activated complex, and accounted for the conservation of angular momentum during the activation. This leaded to the actual RRKM theory (1952).

$$A + M \xrightleftharpoons[k_{-1}]{\delta k_1(E \longrightarrow E+\delta E)} A^*_{(E \rightarrow E+\delta E)} + M$$

$$A^*_{(E)} \xrightarrow{k_2(E)} A^{\#} \xrightarrow{k^{\#}} B + C$$

4. Lindemann mechanism.

Lindemann's theory forms the basis for all modern theories of unimolecular reactions, it was published almost simultaneously by Lindemann (1922) and Christiansen (PhD, 1921):

- by collision a fraction of molecules becomes energized and gain a critical energy quantity E°. The rate depends on the number of bimolecular collisions and is calculated from the simple collision theory (independent of energy content, Boltzmann distribution):

$$A + M \rightarrow A^* + M \quad (k_1)$$

- energized molecules are de-energized by collision, the rate is equated to the collision number only (every collision leads to de-energization, pre-exponential term Z):

$$A^* + M \rightarrow A + M \quad (k_{-1})$$

- there is a time-lag in the unimolecular dissociation process which occurs with a rate constant also independent of the energy content:

$$A^* \rightarrow B + C \quad (k_2)$$

the consequences of Lindemann theory are revealed when considering the concentration of energized molecules as constant in the course of the reaction (steady-state approximation) leading to the following expression of the overall rate of reaction:

$$v = k_2[A^*] \approx \frac{k_2 k_1 [M][A]}{k_{-1}[M] + k_2} \quad (1)$$

At high pressures we find the expected, and experimentally observed, unimolecular process

$$k_{-1}[\mathrm{M}] >> k_2 \qquad v = k_2[A^*] \approx \frac{k_2 k_1 [A]}{k_{-1}}$$

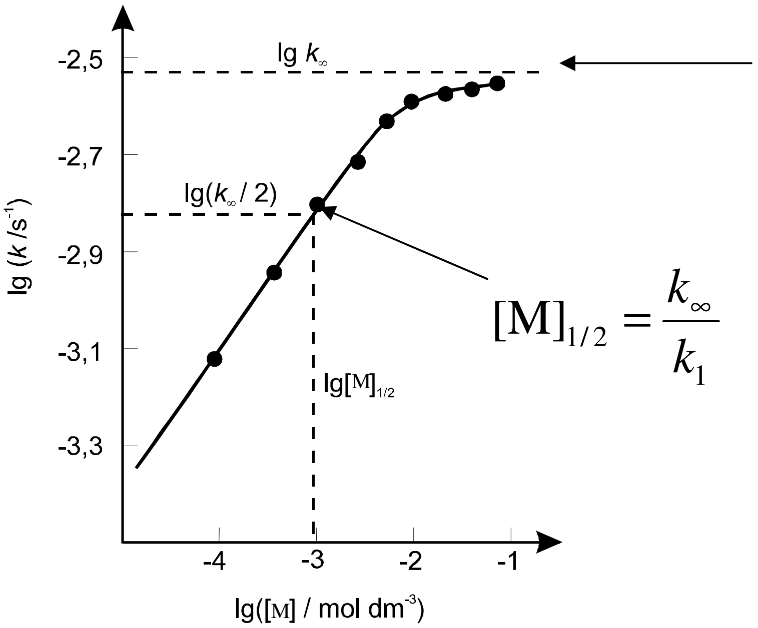
And at low pressures the reaction rate is then better described by a second order reaction:

$$k_2 >> k_{-1}[\mathrm{M}] \qquad v = k_2[A^*] \approx k_1[A][M]$$

This theory correctly predicts the rate constant fall-off at low pressures, but the values calculated are far from experimental results (early experimental tests were performed but it is now known that the examples chosen are not unimolecular processes …).

We can calculate the pressure at which the rate constant reaches half of its high pressure value (transition pressure):

$$\frac{k_2 k_1 [M]_{1/2}}{k_{-1}[M]_{1/2} + k_2} = \frac{k_\infty}{2} \quad \Rightarrow \quad [\mathrm{M}]_{1/2} = \frac{k_\infty}{k_1}$$

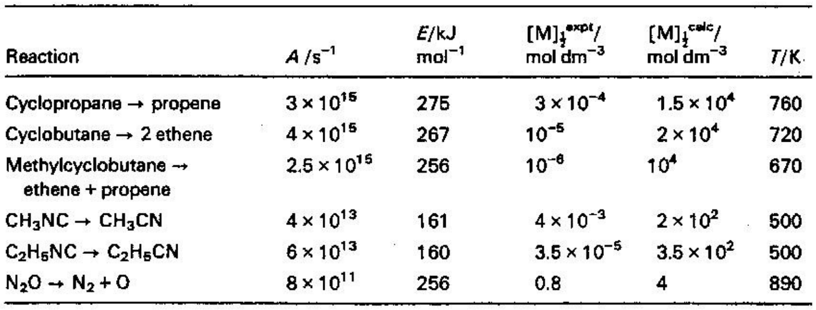


$$\mathrm{k}_\infty = \frac{k_2 k_1}{k_{-1}}$$

$$[\mathrm{M}]_{1/2} = \frac{k_\infty}{k_1}$$

where $[\mathrm{M}]_{1/2}$ is the “third body” concentration at which the experimental rate constant falls to half of its high pressure value.

Since no values for k_2 could be provided by the theory, k_{inf} was measured and k_2 derived from it. The goal was then to get good agreement for the transition pressure. But problems arose with experimental values of $[\mathrm{M}]_{1/2}$, discrepancies between experimental and calculated values can be as big as 10^8 !!!! …. especially for bigger molecules …..



Reaction	A /s^{-1}	E/kJ mol^{-1}	$[\mathrm{M}]_{\frac{1}{2}}^{\mathrm{expt}}$/ mol dm^{-3}	$[\mathrm{M}]_{\frac{1}{2}}^{\mathrm{calc}}$/ mol dm^{-3}	T/K
Cyclopropane → propene	3×10^{15}	275	3×10^{-4}	1.5×10^{4}	760
Cyclobutane → 2 ethene	4×10^{15}	267	10^{-5}	2×10^{4}	720
Methylcyclobutane → ethene + propene	2.5×10^{15}	256	10^{-6}	10^{4}	670
$CH_3NC \rightarrow CH_3CN$	4×10^{13}	161	4×10^{-3}	2×10^{2}	500
$C_2H_5NC \rightarrow C_2H_5CN$	6×10^{13}	160	3.5×10^{-5}	3.5×10^{2}	500
$N_2O \rightarrow N_2 + O$	8×10^{11}	256	0.8	4	890

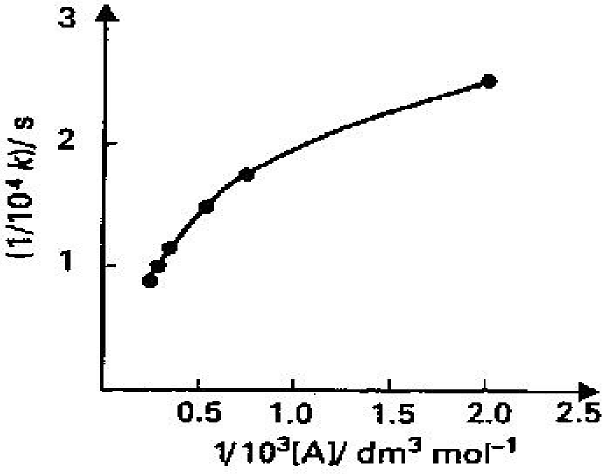
it is usually called the **first failure** in Lindemann mechanism.

We may also rewrite equation (1) to get:

so that plotting $1/k_{uni}$ vs $1/[M]$ should give a straight line from which we can extrapolate k_1 and k_∞ .

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2} \quad \Leftrightarrow \quad \frac{1}{k_{uni}} = \frac{1}{k_1[M]} + \frac{1}{k_\infty}$$

Here’s the plot[1] of the cis-trans isomerization of $C_2H_2D_2$ with the **second failure** in Lindemann mechanism (the expected linearity is not found !!):



by considering the activation energy to be constant, and the collision frequency to be the same in all steps, we can modify the following equation:

$$k_2 = \frac{k_{-1} k_\infty}{k_1}$$ to obtain: $k_2 \approx A_\infty$ of the order of a frequency ($10^{13}s^{-1}$)

which is actually contradictory with the time-lag concept introduced to consider the unimolecular step.
This is what made Hinshelwood try to modify this theory and especially the expression of the activation rate to account for a longer lifetime of the energized molecule ($\sim 1/k_2$) depending on the number of degrees of freedom (as said previously k_2 was not expected to be calculated but inferred from experimental data and especially the success of the theoretical description of the activation step).

Summary of Lindemann mechanism:

- the reaction occur in two steps, a bimolecular activation step and a unimolecular dissociation step.
- all the rate constants are independent of the internal energy of the molecules.
- the rate of energization is calculated on the basis of SCT.
- the rate of de-energization is simply the collision frequency (strong collision).
- the unimolecular step is said to be rate determining at high pressure and a fast step at low pressure.
- there are evident two failures:
    - the fall-off critical region is not well-described (discrepancies between theoretical data and experimental data diverge with molecules getting bigger).
    - the linear extrapolation of inverse plot expected is not found experimentally (low pressure description not correct, modification of bimolecular step description).

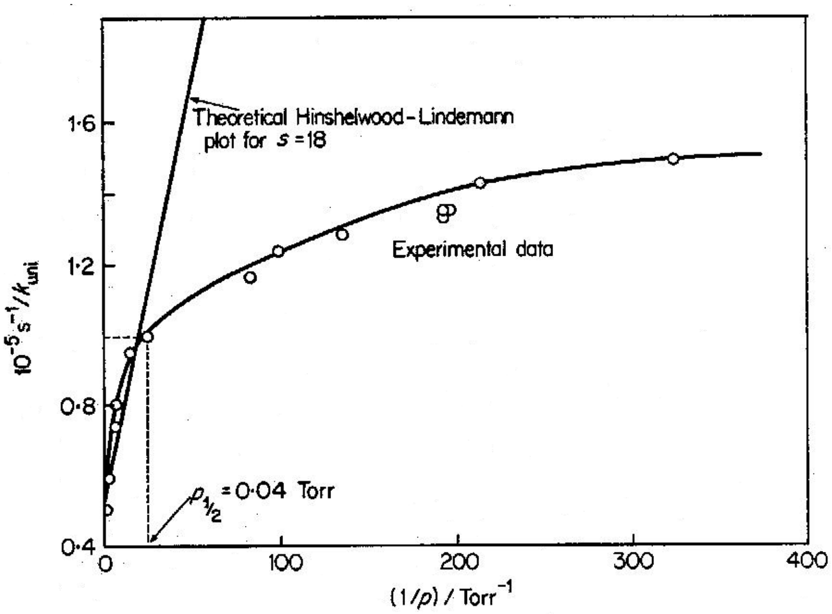
5. Hinshelwood theory.

Accounting for suggestions made by Christiansen and Lindemann, Hinshelwood modified the previous mechanism to account for internal degrees of freedom during the activation process. He then modeled the internal modes of A by a hypothetical molecule having s equivalent classical harmonic oscillators, and by considering thermal equilibrium and the strong collision assumption (meaning that the probability of deactivation is equal to the collision frequency, each collision is efficient to deactivate), he obtained:

$$\boxed{k_1 = \frac{Z}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} \exp\left(-\frac{E_0}{k_B T}\right)}$$

since $E_0 >> k_B T$ the new factor in the expression of the rate constant is very much greater than unity, which is giving a higher rate constant for larger molecules and is exactly what is required to overcome the problem with the too short time-lag in the unimolecular step (the probability for a molecule to have the energy E0 needs to be the product of Boltzmann distribution -with different energy mean- for each oscillator, here the rate constant represents the chance for a molecule to reach an energy greater than E0, but it is actually energy-dependent !!!).

Satisfactory fits to experimental data could always be done with this theory at the transition pressure but not on the whole range of pressure (cis -> trans-but-2-ene):



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Moreover the fits were always obtained by considering a number of degrees of freedom different to the one expected for the molecule, without a priori method of calculation of s for a particular reaction.

These results can be quite puzzling, since the description of the bimolecular step was improved but still at low pressure, it seems to be more problematic than at high pressure (inverse plot presented here !!); this can be explained by the fact that, at low pressure the distribution of energy is not kept constant, because the dissociation process may be faster for highly energized molecules and lower for less energized ones. The highly energized molecules will dissociate very fast and since the thermal equilibrium is not maintained, only the molecules with low energy remain … slowing down the dissociation process. This is what made RR and K modified that theory to account for energy dependence of the dissociation step's rate as well !!

6. RRK theory.

Rice and Ramsperger (1927[3]), and later but independently Kassel who introduced at the same time a quantum formulation of the theory (1928[4]), recognized that the rate of the unimolecular step should depend on the vibrational energy of the energized molecule as well. For that purpose, they introduced the idea that a minimum of energy must be localized in specific modes of molecular motion in order for the dissociation to take place, and that the newly calculated rate constant must be proportional to that probability.

They did not explicitly mention an activated complex intermediate (TST did not exist at that time!!! this theory appeared during the 30's) but instead considered the energy localization process to compute the rate constant.

(I will then not speak about a new intermediate step introduced in RRK even if you will find this consideration in many books or articles, e.g. in Pilling)

Both of them kept the Hinshelwood-Lindemann theory in its state and modified the expression of the unimolecular step to account for their new idea. They started by considering that energy can flow freely among the different oscillators (which is a rather good approximation as long as the energy involved is big enough compare to the number of oscillators, they can thus be considered as behaving non linearly and being strongly coupled to each other, the strong coupling speeding up the process of transfer, but the oscillators are not harmonic any more …), then Kassel (in its quantum calculations) computed the number of ways to distribute $(\mu - m)$ quanta over the s oscillators (since m quanta will be located on the critical oscillator) to get (the quantum calculation is much easier than the classical one, Kassel demonstration will therefore be presented here):

$$\frac{(\mu - m + s - 1)!}{(\mu - m)!(s-1)!}$$

and the probability to have one of this configuration should be divided by all the possible ways of arranging the μ quanta, leading to:

$$P_m^\mu = \frac{\mu!(\mu - m + s - 1)!}{(\mu - m)!(\mu + s - 1)!}$$

explanation with balls and boxes and reference to the documents on website http://keszei.chem.elte.hu/2.felev/manko.doc

considering the classical limit which consists in having a very large number of quanta compare to the number of oscillators, Kassel got:

$$\left.\begin{array}{l}\mu >> s\\ m >> s\end{array}\right\} \longrightarrow \left.\begin{array}{c}\dfrac{(\mu - m + s - 1)!}{(\mu - m)!} \approx (\mu - m)^{s-1}\\[2ex] \dfrac{\mu!}{(\mu + s - 1)!} \approx \mu^{-(s-1)}\end{array}\right\} \quad P_m^\mu = \left(1 - \frac{m}{\mu}\right)^{s-1}$$

the rate constant was then said to be proportional to that quantity, and by introducing energy, it leads to the following expression for the dissociation rate constant (classical RRK expression):

$$\boxed{k_2(E) = A\left(1 - \frac{E_0}{E}\right)^{s-1}}$$

where E0 is the activation energy

E the overall vibrational energy of the molecule,

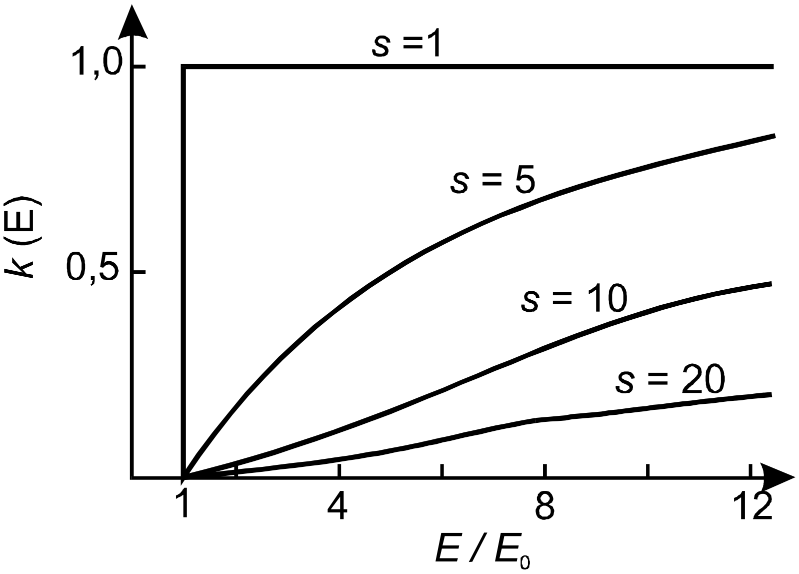
A is a constant, which seems to be an ad hoc term, but is actually the pre-exponential term in the Arrhenius expression when we extrapolate the expression for high pressures.

and the overall rate constant is therefore given by (considering the energy dependence of k_1 derived in Hinshelwood's theory):

$$\boxed{k_{uni} = \int_{E_0}^{\infty} \frac{k_2(E)dk_1(E \to E + dE)/k_{-1}}{1 + \frac{k_2(E)}{k_{-1}[M]}}}$$

in which k_2 should be replaced by the RRK expression derived above.

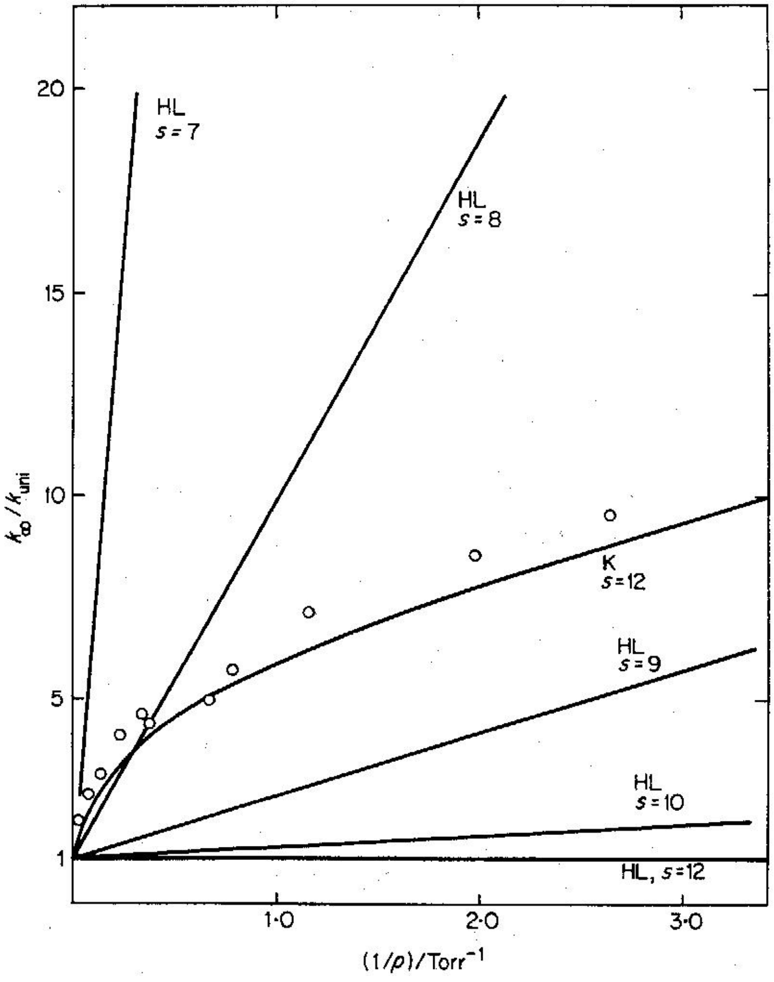
The following plot shows how the rate k_2 increases with respect to vibrational energy with the number of oscillators available as a parameter ($s = 1$ corresponds to the case described by Hinshelwood).



which is actually exactly what we need to have a better description at low pressure !!! (low energized molecules will have lower dissociation rate)

It should be explained here that the expression derived was initially derived by R and R by considering only classical case all along the calculation. The initial expression given here of the probability P was derived in Kassel's quantum calculations, which were shown to give the same result as RR in the classical limit (μ and m much bigger than s).

We will not develop Kassel quantum theory here (it is just a discrete summation of the expression of $k_2(E)$ before doing classical limit study), since it was not widely used despite his much better description than classical RRK of the fall-of.



Although Kassel's theory was giving better agreement to experiments, gross approximations were made (all equivalent classical harmonic oscillators) leading to results for which the number of oscillators couldn't be predicted a priori (as in Hinshelwood theory).

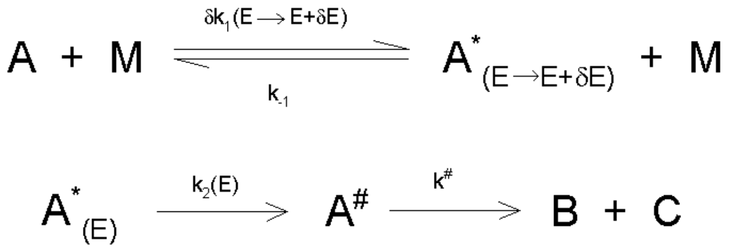
Here's the plot for azomethane decomposition at 603K. s=12 and collision cross-section 150A ... which are irrelevant (azomethane has 24 degrees of freedom and is not as big as 150A).

7. RRKM theory.

The RRK theory was an important development in the treatment of unimolecular reactions, but gross approximations were made at that time due to a lack of computational methods (actually no computers were available !!). Marcus, with Rice's help, developed the now called RRKM theory in 1952. Its main new features with respect to RRK are as follows:

- the energization rate constant k_1 is evaluated as a function of energy by quantum-statistical mechanical treatment.
- it considers explicitly the concept of Transition State^5 in the unimolecular process as an intermediate step (and converges to ART at the high pressure limit) and deals with the real frequencies of the energized molecule as well as of the TS, and treats explicitly the rotational degrees of freedom in the course of the dissociation.

The new reaction scheme is therefore:



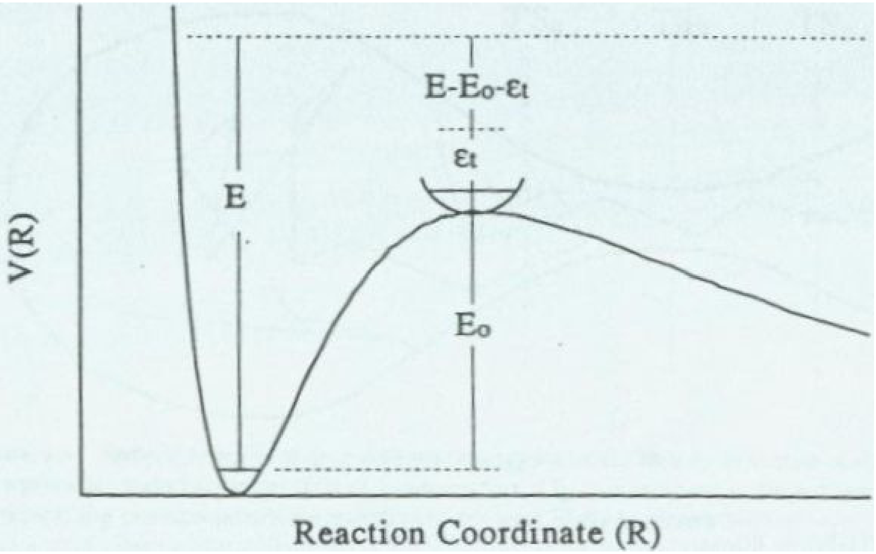
$$A + M \underset{k_{-1}}{\overset{\delta k_1(E \rightarrow E+\delta E)}{\rightleftharpoons}} A^*_{(E \rightarrow E+\delta E)} + M$$

$$A^*_{(E)} \xrightarrow{k_2(E)} A^\# \xrightarrow{k^\#} B + C$$

Its main goal is to use quantum statistical mechanics for calculating the equilibrium concentrations of A^* and $A^\#$. It is thus concerned with evaluating the number of ways of distributing the energy among the various degrees of freedom.

It should first be distinguished between the fixed and non-fixed energy:

- Fixed energy consists in ZPE and overall translational energy, they are of no interests in the following description.
- The remaining energy, the non-fixed one is assumed to be involved completely in redistribution during the reaction (IVR hypothesis discussed in the next chapter), even if Marcus dealt with non-active modes in his original paper, that consideration did not show any real importance in predicting rates constant.



i) Expression for the energy-dependence of the bimolecular step rate constant.

The quantity dk_1/k_{-1} used in the expression of the overall rate constant is actually an equilibrium constant which expression is given by statistical mechanics:

$$K(E)dE = \frac{Q(A^*_{(E\to E+dE)})}{Q(A)}$$

(explanation with ground state equivalence and general formula)

where Q is the partition function:

$$Q = \sum_{\mu=0}^{\infty} g_\mu \exp\left(-\frac{E_\mu}{k_B T}\right)$$

if dE is small the exponential term is the same in this range and we get:

and finally:

$$Q(A^*_{E\to E+dE}) = \left(\sum_{\mu=0}^{\infty} g_\mu\right).\exp\left(-\frac{E}{k_B T}\right) = \rho(E)dE.\exp\left(-\frac{E}{k_B T}\right)$$

$$\frac{dk_1(E \to E+dE)}{k_2} = \frac{Q(A^*_{(E\to E+dE)})}{Q(A)} = \frac{\rho(E)dE}{Q(A)}.\exp\left(-\frac{E}{k_B T}\right)$$

which is in fact the quantum Boltzmann distribution giving the thermal equilibrium proportion of molecules in the given energy range.

ii) Expression for the energy dependence of the dissociation step.

By applying the SSA to $A^{\#}$ of the reaction scheme:

$$A^*_{(E)} \xrightarrow{k_2(E)} A^{\#} \xrightarrow{k^{\#}} B + C$$

we get: $$k_2(E) = \frac{1}{2}k^{\neq}\frac{[A^{\neq}]}{[A^*]}$$

the factor ½ coming from the fact that half of the molecules cross the extremum on the reverse direction. Then following a similar development to the TST we get the expression for the rate of dissociation:

$$k^{\neq} = \left(\frac{2x}{m\delta^2}\right)^{1/2}$$

with x the translational energy of the molecule at the top of the barrier, m its mass, and δ the length of the “box”

Considering again the two species to be at thermal equilibrium, the ratio of their concentrations is then expressed as the ratio of their partition function (they have the same ground state energy), both these species have the total energy in the same range $E \to E + dE$ and the ratio of their partition function reduces to the ratio of the sum of the degeneracies, which at the energy of interest, chemical energies, can be approximated by the ratio of their density of states:

$$\left(\frac{[A^{\neq}]}{[A^*]}\right)_{eq} = \frac{P(E^{\neq})N^{\neq}(x)}{\rho^*(E^*)}$$

where $P(E^{\#})$ represents the number of vibrational-rotational quantum states of $A^{\#}$ with its non-fixed energy $E^{\#}$.
$N^{\#}(x)$ the number of translational quantum states of $A^{\#}$ at the energy x.

By using the expression of the number of states given in our lecture on TST, and by considering all the calculated expression, we get the for the activation rate constant:

$$k_2(E) = \frac{1}{h\rho^*(E^*)}\sum_{E'^+=0}^{E^+} P(E'^+)$$

with E'^+ being the non-fixed energy of the TS not involved in the translation ($E^+ = E'^+ + x$).

We did not actually consider the effect of adiabatic rotations in these calculations (explanation here of adiabatic rotations), and to converge to ART at the high pressure limit, we should take them into account. This can be simply done by multiplying the above expression by the ratio of the rotational partition functions (this idea has only limited validity at low pressure where another procedure is required).

Another point has been omitted, is the problem of multiple reaction paths. The example of dissociation of H2O leads to two equivalent paths, and to account for that we should include another factor called *statistical factor* or *reaction path degeneracy* $L^{\#}$ (short explanation here).

We finally get the more general expression:

$$k_2(E) = L^{\neq} \frac{Q_1^{+}}{Q_1} \frac{1}{h\rho^{*}(E^{*})} \sum_{E'^{+}=0}^{E^{+}} P(E'^{+})$$

At high pressure limit, we don't get equilibrium only between A^+ and A^* but also for the collision step and the reaction scheme can be modified to:

$$\mathrm{A} + \mathrm{M} \xrightleftharpoons{\text{equilibrium}} \mathrm{A}^{+} + \mathrm{M}$$

$$\mathrm{A}^{+} \longrightarrow \mathrm{B} + \mathrm{C}$$

which leads to the same results as in ART !!!

8. Major approximations in RRKM.

i) Intramolecular Vibrational Relaxation:

IVR assumption says that the energy flows freely among the different modes of the molecule before it can dissociate. It is an essential statement to allow the use of thermal distribution and equilibrium assumptions in RRKM theory.

As mentioned previously, Marcus made provision for some of the degrees of freedom to be completely inactive and which could therefore not participate to the dissociation process. This energy can however be redistributed randomly between these modes and affects the density of states of the energized molecule as well as the activation rate constant.

There is little evidence that energy is rapidly redistributed between all vibrational modes involved within a time not greater than 10^{-11} s.

This assumption may reach his limits when considering e.g. huge molecules (fragmentation of polymers or biomolecules), or very low energy barrier (isomerization of rather big enough molecules). It is usually called non-ergodic process (no time for energy to explore the complete phase space), but you may find this term in publications whenever there is something not understood …..

ii) Strong collisions assumption:

This assumption means that relatively large amounts of energy are transferred in molecular collisions (>> kT). RRKM assumes then the energization step to be single-step on contrary to ladder-climbing processes. This assumption also assumes that the molecule after collision is in a state completely independent as the one before, no dynamical details of the collision are thus necessary within that description.

A more detailed study of energization step can be done involving accurate description of the dynamics of collision, and it seems relatively important for small molecules. However it was shown that multiplying the de-energization rate constant by a constant λ less than unity, leading to shift of the curve $\log(k_{uni})$ vs. $\log(p)$ by $\log(\lambda)$, is sufficient to give rather good agreement with experimental data.

iii) The equilibrium hypothesis:

In the unimolecular step it was assumed as in ART that the TS is crossed as if there would be equilibrium between energized and activated molecules (SSA as if no net reaction is occurring, total equilibrium of reverse reaction).

This assumption has been proven to work well by non-statistical calculations, providing that the energy barrier is not too low. In the case where E0/kT is less than 10, it starts to be problematic, and it has been shown that when the ratio has a value of 5, approximately 8% error is introduced in the results.

iv) Continuous distribution function of state density:

The approximation of continuous density of states for the activated complex can be cumbersome, since most of the energy available is fixed to overcome the barrier and a part of it stored in the translational motion. This approximation holds very well for highly excited molecules (density of states becomes a continuous function of energy) but can become problematic when the energies involved are just above chemical energies.

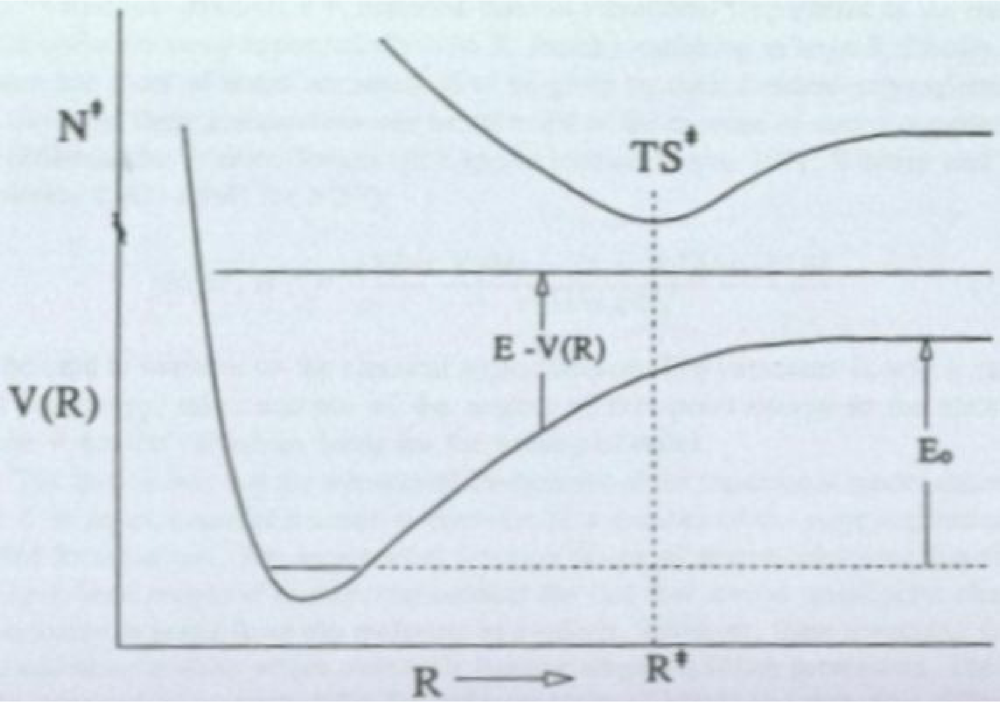
An example is given for cyclopropane with excitation energy E^*=70kcal/mol and $E^\#$=5kcal/mol, A* has 4.10^9 vibrational quantum states/kcal and $A^\#$ has only 10^2 … a continuous approximation of density of states is thus less valid for activated complex …

9. Other theories.

i) VTST:

This variant of the theory is very useful when no TS can be explicitly identified (for Morse-like potential, e.g. direct bond dissociation), where there is no saddle point (no energy barrier to overcome). It is based on the idea that there is a "bottleneck" in the phase space during the dissociation (TS is the surface which divides reactants from products and for which the phase space is the minimum). This can be explained by the fact that during the dissociation process the molecule needs to reach at a certain point a very specific conformation without which it cannot go further to dissociate. Arrhenius equation can be written in terms of exponential of Gibbs free energy and exponential of entropy (which is the equivalent of the pre-exponential ratio of partition functions !!!) which characterize the number of distinct states reachable with that amount of energy. Therefore when the conformation is more restrictive, the entropy is less and the pre-exponential factor is also less, leading to a smaller value for the rate constant.

To identify that state we can simply calculate the sum of states at different point of the PES and consider the point where it is the lowest (give formula of RRKM).



This is the idea of VTST[6]. This type of calculations can be performed with the help of the software TheRate[7].

ii) Phase Space theory:

The statistical dissociation rate constant can be calculated from the point of view of the reverse reaction. Again this procedure is limited to reaction without energy barrier (called loose TS reaction).

It is considering that the decomposition is governed only by the phase space available under strict energy and angular momentum conservation. Considering equilibrium between reactants and products, we get:

$$\frac{k_{uni}}{k_{bim}} = \frac{[A][B]}{[AB]} \Leftrightarrow k_{uni} = k_{bim} \frac{\rho(E-E_0, j_A) * \rho(E-E_0, j_B)}{\rho_{AB}(E, J)}$$

for which there is no need of informations on the TS.

iii) Other theories:

Other theories exists, Orbiting Phase Space Theory, SACM (Statistical Adiabatic Channel Model), the TST Switching Model (there are 2 TS at short and at long range, similar theory to VTST but seems to deviate for ionic dissociation) … which are all based on a statistical description of unimolecular reactions.

10. REFERENCES.

Software available on the web: MassKinetics[8], TheRate[7]

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