

Foundations of Chemical Kinetics Lecture 12:
Unimolecular reactions in the gas phase:
RRK(M) theory

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Review of an important problem: Balls and walls

- Suppose that we have j indistinguishable balls that we want to place in s distinguishable rooms. We want to know how many different ways there are to do this.
- Rather than placing the balls in rooms with fixed walls, think about a situation with movable walls:



To make s rooms, we need $s - 1$ movable walls. (The outer walls don't move.)

The movable walls are indistinguishable objects.

An important problem: Balls and walls

- If the balls and walls were distinguishable, there would be $(j + s - 1)!$ arrangements of the balls and walls.
- However, the j balls are indistinguishable, so we are overcounting the number of arrangements by the number of permutations of j objects.
Similarly, we are overcounting the number of arrangements by the number of permutations of the $s - 1$ walls.
- The actual number of different arrangements of j balls in s urns is therefore

$$W = \frac{(j + s - 1)!}{j!(s - 1)!}$$

Stirling's approximation

- In chemical theory, we often want to evaluate $N!$ for large values of N .
- In that case, the factorial can be approximated as follows:

$$\ln N! \approx N \ln N - N$$

Density of states for s harmonic oscillators

- In lecture 2, we derived the following expression for the density of states of a harmonic oscillator:

$$g(\epsilon) = (\hbar\omega_0)^{-1}$$

- Because the density of states is constant, the total number of states with energies between 0 and ϵ is

$$G(\epsilon) = \epsilon(\hbar\omega_0)^{-1}$$

- Recall: Roughly speaking, the partition function counts the number of states with energies below $k_B T$.

Therefore,

$$q_{\text{vib}} \approx \frac{k_B T}{\hbar\omega_0}$$

Note: You can also derive this equation from the harmonic oscillator partition function by assuming that $\hbar\omega_0/k_B T$ is small.

Density of states for s harmonic oscillators

(continued)

- If we have s distinguishable, independent harmonic oscillators whose natural frequencies are ω_i , the partition function should therefore be

$$q_s \approx \prod_{i=1}^s \frac{k_B T}{\hbar \omega_i}$$

- From the definition of the classical partition function, we have

$$q_s = \int_0^{\infty} g_s(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

Density of states for s harmonic oscillators

(continued)

$$q_s = \int_0^{\infty} g_s(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon \approx \prod_{i=1}^s \frac{k_B T}{\hbar \omega_i}$$

- The problem now is to find the density of states corresponding to our partition function q_s .

This problem turns out to be solved by taking a mathematical operation called an inverse Laplace transform of q_s .

The result is

$$g_s(\epsilon) = \frac{\epsilon^{s-1}}{(s-1)! \prod_{i=1}^s \hbar \omega_i}$$

Vibrational energy distribution

- For simplicity, we assume that the s vibrational modes of a molecule have a common vibrational frequency ω_0 .

Then,

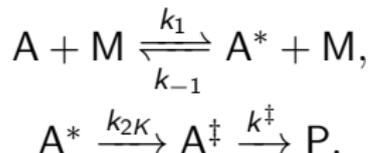
$$q_s \approx \left(\frac{k_B T}{\hbar \omega_0} \right)^s$$
$$g_s(\epsilon) \approx \frac{\epsilon^{s-1}}{(s-1)! (\hbar \omega_0)^s}$$

- The probability that a molecule has vibrational energy between ϵ and $\epsilon + d\epsilon$ is thus

$$\frac{g_s(\epsilon)}{q_s} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon = \frac{\epsilon^{s-1}}{(k_B T)^s (s-1)!} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

RRK theory

- Developed independently by Rice and Ramsperger and by Kassel in the late 1920s, hence the name.
- Modify the Lindemann mechanism to take into account the formation of the transition state:



- Why?
A* represents an energized molecule, but getting to the transition state requires that the energy stored in its vibrations move to the correct bond(s). The step with rate constant k_{2K} represents this process, which is known in the literature as **intramolecular vibrational relaxation** (IVR).

RRK theory (continued)

- A^\ddagger should be the fastest decaying species in this mechanism since it isn't even a stable molecule.
- Apply the steady-state approximation for $[A^\ddagger]$, and **solve for k_{2K}** .
(You'll see why later.)

$$\frac{d[A^\ddagger]}{dt} = k_{2K}[A^*] - k^\ddagger[A^\ddagger] \approx 0$$
$$\therefore k_{2K} = k^\ddagger \frac{[A^\ddagger]}{[A^*]}$$

Note: $p^\ddagger = [A^\ddagger]/[A^*]$ is the probability that the energy stored in an energized molecule is in the reactive mode, so $k_{2K} = k^\ddagger p^\ddagger$.

RRK theory (continued)

- Applying the steady-state approximation the normal way, we get

$$[A^\ddagger] = \frac{k_{2K}}{k^\ddagger}[A^*]$$

- Since $v = k^\ddagger[A^\ddagger]$, we get $v = k_{2K}[A^*]$.
(This says that the step $A^* \rightarrow A^\ddagger$ is rate limiting once A^* has been formed.)
- In the original Lindemann mechanism, $v = k_2[A^*]$.
Comparing the two, we conclude that k_2 from the Lindemann mechanism is k_{2K} in the more detailed RRK mechanism.

RRK theory (continued)

- For simplicity, assume that all normal modes have the same frequency.

Note: All that is really required is that energy be able to flow from one vibrational mode to another. The simplification of equal frequencies just makes the math easier.

- Suppose that a particular energized molecule has energy $E = j\hbar\omega_0$ spread over s normal modes. The degeneracy of energy level E is just the number of different ways of storing j quanta in s modes:

$$G^* = \frac{(j + s - 1)!}{j!(s - 1)!}$$

RRK theory (continued)

- Suppose that we need at least m quanta in the reactive mode in order for the reaction to occur, with $\epsilon^\ddagger = m\hbar\omega_0$.
 The degeneracy of the set of molecules that have at least m quanta in the reactive mode is the number of ways of storing $j - m$ quanta in the s modes (which allows for some of the extra quanta to also be in the reactive mode):

$$G^\ddagger = \frac{(j - m + s - 1)!}{(j - m)!(s - 1)!}$$

- The probability that a molecule with j quanta has at least m of them in the reactive mode is therefore

$$p^\ddagger = \frac{G^\ddagger}{G^*} = \frac{j!(j - m + s - 1)!}{(j + s - 1)!(j - m)!}$$

RRK theory (continued)

$$p^\ddagger = \frac{G^\ddagger}{G^*} = \frac{j!(j - m + s - 1)!}{(j + s - 1)!(j - m)!}$$

- Usually, the transition state corresponds to a large $m \gg s$.
 Since $j > m$, j is also large.
- Apply Stirling's approximation:

$$\begin{aligned} \ln p^\ddagger &= \ln j! + \ln(j - m + s - 1)! - \ln(j + s - 1)! - \ln(j - m)! \\ &\approx j \ln j - j + (j - m + s - 1) \ln(j - m + s - 1) \\ &\quad - (j - m + s - 1) - [(j + s - 1) \ln(j + s - 1) \\ &\quad - (j + s - 1)] - [(j - m) \ln(j - m) - (j - m)] \\ &= j \ln j + (j - m + s - 1) \ln(j - m + s - 1) \\ &\quad - (j + s - 1) \ln(j + s - 1) - (j - m) \ln(j - m) \end{aligned}$$

RRK theory (continued)

- Two of the terms involve $s - 1 \ll m < j$. Use a Taylor expansion for $(a + x) \ln(a + x)$ with $x = s - 1$:

$$(a + x) \ln(a + x) \approx a \ln a + x (\ln a + 1)$$

- Therefore

$$\begin{aligned} \ln p^\ddagger &\approx j \ln j + (j - m) \ln(j - m) + (s - 1) [\ln(j - m) + 1] \\ &\quad - [j \ln j + (s - 1) (\ln j + 1)] - (j - m) \ln(j - m) \\ &= (s - 1) [\ln(j - m) - \ln j] \\ &= (s - 1) \ln \left(\frac{j - m}{j} \right) = \ln \left(\frac{j - m}{j} \right)^{s-1} \\ \therefore p^\ddagger &= \left(\frac{j - m}{j} \right)^{s-1} \end{aligned}$$

RRK theory (continued)

$$p^\ddagger = \left(\frac{j-m}{j} \right)^{s-1}$$

- Since $j = \frac{E}{\hbar\omega_0}$ and $m = \frac{E^\ddagger}{\hbar\omega_0}$, we have

$$p^\ddagger = \left(\frac{E - E^\ddagger}{E} \right)^{s-1}$$

- Since $k_{2K} = k^\ddagger p^\ddagger$,

$$k_{2K} = k^\ddagger \left(\frac{E - E^\ddagger}{E} \right)^{s-1}$$

- If we think of the reactive mode as a vibration, we can replace k^\ddagger by the frequency of that mode, ν^\ddagger .

RRK theory (continued)

- We previously found that the probability that s oscillators have a total energy between ϵ and $\epsilon + d\epsilon$ is

$$\frac{\epsilon^{s-1}}{(k_B T)^s (s-1)!} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

- If we assume that the first step is in quasiequilibrium, we have

$$\frac{[A^*]}{[A]} = \frac{k_1}{k_{-1}}$$

- A^* represents molecules with a range of different energies above ϵ^\ddagger .

If we, instead, think of A^* as representing molecules with energy between ϵ and $\epsilon + d\epsilon$ for any $\epsilon > \epsilon^\ddagger$, then

$$\frac{[A^*]}{[A]} = \frac{k_1}{k_{-1}} \frac{\epsilon^{s-1}}{(k_B T)^s (s-1)!} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

RRK theory (continued)

- The Lindemann rate constant is

$$k_L = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2} = \frac{(k_1/k_{-1}) k_2 [M]}{[M] + k_2/k_{-1}}$$

- We now have equations for k_1/k_{-1} and for $k_2 = k_{2K}$. Substituting them in, we get

$$dk_{\text{RRK}} = \frac{\nu^\ddagger [M] \left(\frac{\epsilon - \epsilon^\ddagger}{\epsilon}\right)^{s-1} \frac{\epsilon^{s-1}}{(k_B T)^s (s-1)!} \exp\left(-\frac{\epsilon}{k_B T}\right)}{[M] + \frac{\nu^\ddagger}{k_{-1}} \left(\frac{\epsilon - \epsilon^\ddagger}{\epsilon}\right)^{s-1}} d\epsilon$$

where we write dk_L since this represents the rate constant only for reactants with energies between ϵ and $\epsilon + d\epsilon$.

RRK theory (continued)

- To get the total rate constant, we just integrate. After a little simplification, we get

$$k_{\text{RRK}} = \int_{\epsilon^\ddagger}^{\infty} \frac{\nu^\ddagger [\text{M}]}{k_B T (s-1)!} \left(\frac{\epsilon - \epsilon^\ddagger}{k_B T} \right)^{s-1} \exp\left(-\frac{\epsilon}{k_B T}\right)}{[\text{M}] + \frac{\nu^\ddagger}{k_{-1}} \left(\frac{\epsilon - \epsilon^\ddagger}{\epsilon} \right)^{s-1}} d\epsilon$$

- This integral can't be evaluated analytically. Instead, we evaluate it numerically for given values of the constants, and typically making the **strong collision assumption**, which is the assumption that k_{-1} is strictly collision limited, i.e. that every collision of an A^* deenergizes it.

RRK theory in practice

- The number of modes participating in IVR, s , is used as a fitting parameter. We typically get the best results when s is about half the number of normal modes of A , although the best value of s is temperature dependent.
- Provided we are allowed to adjust s as we vary T , RRK theory agrees reasonably well with experiment.

RRK theory in practice (continued)

$$k_{\text{RRK}} = \int_{\epsilon^\ddagger}^{\infty} \frac{\nu^\ddagger [\text{M}]}{k_B T (s-1)!} \left(\frac{\epsilon - \epsilon^\ddagger}{k_B T} \right)^{s-1} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

$$[\text{M}] + \frac{\nu^\ddagger}{k_{-1}} \left(\frac{\epsilon - \epsilon^\ddagger}{\epsilon} \right)^{s-1}$$

- At large pressures, we get

$$k_{\text{RRK}} \approx \int_{\epsilon^\ddagger}^{\infty} \frac{\nu^\ddagger}{k_B T (s-1)!} \left(\frac{\epsilon - \epsilon^\ddagger}{k_B T} \right)^{s-1} \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

$$= \nu^\ddagger \exp\left(-\frac{\epsilon^\ddagger}{k_B T}\right)$$

- Since vibrational frequencies are never much larger than 10^{14} s^{-1} , the high-pressure preexponential factor should never be much larger than this either, but in practice it is often found to be much larger (values of up to 10^{17} s^{-1} are not unusual).

Canonical and microcanonical ensembles

Canonical (constant T)
ensemble

↑ Average over a
Boltzmann distribution

Microcanonical (constant E)
ensemble

The M in RRKM

- RRKM theory is an extension of RRK theory developed by R. A. Marcus (Canadian, Nobel Prize winner 1992).
- RRKM theory is intended to improve on RRK theory by eliminating arbitrary assumptions.
- RRKM is a **microcanonical transition state theory**:

Microcanonical: Rate constant calculated at fixed energy ϵ

Canonical rate constant (i.e. the normal

temperature-dependent k) recovered by averaging over a Boltzmann distribution

Transition-state theory: RRKM connects TST with statistical theories

Assumptions of RRKM theory

- The assumed mechanism is the same as in RRK theory:
 - Collisional activation, followed by
 - Intramolecular vibrational relaxation leading to the transition state
- As in RRK theory and TST, it is assumed that energized molecules pass through the transition state just once.

Note: There is a variational version of RRKM theory in which we try to ensure that this is so.

Assumptions of RRKM theory

- Internal degrees of freedom of the energized molecules are designated as either
 - Adiabatic: quantum state doesn't change during reaction,
or
 - Active: energy exchanged between active modes during reaction
- Adiabatic modes are often associated with conserved quantities, e.g.
 - Rotation around system centre of mass
 - 
 - conservation of angular momentum
- Most internal (normal) modes would be active.

Assumptions of RRKM theory

- Proper quantum mechanical treatment of vibration and rotation
- No assumptions about frequencies of normal modes
- Harmonic approximation normally used, but not necessary
- Exact counting of states possible (i.e. no approximation of partition functions)

RRKM theory vs experiment

- RRKM theory has passed two different types of tests:
 - 1 Calculation of the thermal $k(T)$ and comparison to experiment
 - 1 Using experimental frequencies, geometries, etc.
 - 2 Using parameters obtained from *ab initio* calculations
 - 3 Fitting some parameters of model using experimental data
 - 2 Calculation of the microcanonical rate constant $k(E)$ and comparison to experiment
 - Experiments involve preparation of reactants in known states and subsequent measurement of reaction rate

Non-RRKM behavior

- The central assumption of RRKM theory is a division of modes into adiabatic and active, with energy redistribution between active modes being fast enough that a random distribution results on a time scale much faster than that for reaction.
- In some reactions, there are modes that are not adiabatic, but from which energy flows slowly.
- Possible causes:
 - Strictly harmonic vibrational modes would truly be normal. Accordingly, modes that are only weakly anharmonic tend not to equilibrate with the others quickly.
 - Rotational modes can couple weakly to the vibrational modes.

Non-RRKM behavior (continued)

- Imagine a non-reactive mode that contains excess energy which is only slowly released to the other modes.
- As a result, the probability that the reactive mode acquires sufficient energy would increase with time, leading to a **time-dependent rate constant**.

Review of unimolecular reaction rate theories

Lindemann mechanism:

- Starting point for all theories of gas-phase unimolecular reactions
- Assumes that molecules are energized by collision

RRK theory:

- Brings “transition-state thinking” into statistical theories
- Assumes that energy is rapidly exchanged between internal modes
- Requires sufficient energy to accumulate in reactive mode in order for reaction to occur

Review of unimolecular reaction rate theories

RRKM theory:

- A microcanonical transition-state theory
- Allows for a proper quantum-mechanical treatment of all internal modes
- Divides modes into active (rapidly equilibrating) and adiabatic