

# Chemistry 4000 Fall 2012 Test 2 Solutions

- Intramolecular vibrational relaxation (IVR) is the random exchange of energy between normal modes of a molecule. IVR allows the energy initially stored in one part of a molecule to find its way to the reactive mode, allowing a reaction to occur, a central concept in RRK and RRKM theories.
  - A microcanonical rate constant is a rate constant associated with an ensemble of fixed energy. RRKM theory calculates a microcanonical rate constant in the first instance. The thermal (i.e. canonical, corresponding to an ensemble of fixed temperature) rate constant is calculated by averaging the microcanonical rate constant over a Boltzmann distribution.
  - In RRKM theory, an active mode is a mode that participates in IVR on the time scale corresponding to the time between collision events. Only the energy stored in these modes can be redistributed to the reactive mode before a collision deactivates the molecule.
  - The transition rate  $w_{ij}$  is the probability per unit time that a system in state  $i$  will jump to state  $j$ . This quantity appears in master equation treatments of, among other things, IVR.
  - Detailed balance is the principle that, in equilibrium, every process and its reverse are in dynamic equilibrium, i.e. the forward and reverse rates of a process are equal. Detailed balance has a number of applications. One important application is the demonstration that the transition rates in a master equation are related by Boltzmann factors.
- Apply the steady-state approximation to the intermediate:

$$\begin{aligned}\frac{d[A_2^*]}{dt} &= k_1[A]^2 - (k_{-1} + k_2)[A_2^*] \approx 0. \\ \therefore [A_2^*] &\approx \frac{k_1}{k_{-1} + k_2}[A]^2.\end{aligned}$$

The rate of reaction is  $v = k_2[A_2^*]$ , so we have

$$v \approx \frac{k_1 k_2}{k_{-1} + k_2}[A]^2.$$

This mechanism predicts a second-order rate law, regardless of pressure. This is inconsistent with experimental observations which show a first-order rate law at high pressures.

- (b) In Lindemann-type mechanisms,  $k_2$  corresponds to the RRK rate constant  $k_{2K}$ . From the equation

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

we see that  $k_2$  depends very strongly on  $s$ .  $A_2^*$  should have roughly twice as many active modes ( $s$ ) as  $A^*$ . For energies just above  $E^\ddagger$  (which dominate the reaction rate because of the Boltzmann decrease in probability with reaction energy), a larger  $s$  gives a much smaller value of  $k_{2K}$ . We would therefore predict the exciplex mechanism to be a minor contributor to the reaction rate compared to the normal Lindemann pathway.

Note: The exciplex mechanism might become important if IVR is not random, i.e. if the formation of the complex directs energy specifically to the reactive mode.

3.  $N$  is a possible composition vector.

$P(\mathbf{N}, t)$  is the probability that the system has composition  $\mathbf{N}$  at time  $t$ .

$a_r(\mathbf{N})$  is the propensity of reaction  $r$ , i.e. the probability per unit time that reaction  $r$  occurs.

$\nu_r$  is the stoichiometry vector of reaction  $r$ , i.e. the change in the composition when reaction  $r$  occurs.

**The first sum** represents the rate at which the probability of having composition  $\mathbf{N}$  increases due to reactions that start with compositions  $\mathbf{N} - \nu_r$  and result in composition  $\mathbf{N}$ .

**The second sum** represents the rate at which the probability of having composition  $\mathbf{N}$  decreases due to reactions which, starting from composition  $\mathbf{N}$ , take the system to a different composition.