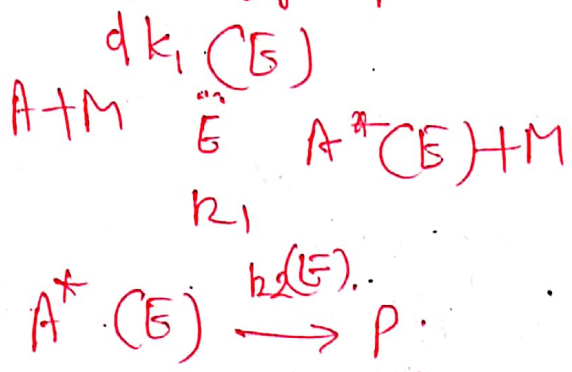## RRKM theory: [Rice-Ramsperger-Kassel-Marcus]

In RRKM theory, the energy of the molecule is partitioned into fixed and non-fixed components. Only the non-fixed component E^*, which can flow freely around the various modes of motion of the molecule, can contribute to reaction.

RRKM Theory → Based on the results of Hinshelwood and RRK theory, the reaction mechanism can be rewritten to take account of the fact that the rates of collisional activation and unimolecular dissociation are energy dependent.

$$A + M \underset{k_1}{\overset{dk_1(E)}{\rightleftharpoons}} A^*(E) + M$$

$$A^*(E) \xrightarrow{k_2(E)} P$$

Applying the steady state approximation to $[A^*(E)]$ leads to the rate expression.

$$\frac{d[P(E)]}{dt} = \frac{k_2(E)\, dk_1(E)[A][M]}{k_1[M] + k_2(E)}$$

The thermal rate coefficient is obtained by integrating over E from E_0 to ∞

$$k = \int_{E_0}^{\infty} \frac{k_2(E)\, dk_1(E)[M]}{k_1[M] + k_2(E)} = \int_{E_0}^{\infty} \frac{k_2(E)\, dk_1(E)[M]}{k_1(1 + k_2(E)/k_1[M])}$$

The various terms of the rate expression are now evaluated using statistical mechanics.

(i) $\dfrac{dk_1(E^*)}{k_1}$ is the equilibrium const. for energization of the A molecules into the energy range E^* to $E^* + dE^*$, and can be calculated from the partition function ratio

~~$Q_{A^*}(E^*)/Q_A$~~

$$Q_{A^*}(E^*)/Q_A.$$

(ii) $k_2(E^*)$ is obtained by applying the steady-state treatment to the activated complex. $A^{\ddagger}$ as in RRK theory ~~with the~~ with the modification that the overall reaction is broken down into energy contributions, from ~~both~~ translation and from rotation/vibration, the rate const. $k^{\ddagger}$ and ratio of concentrations $[A^{\ddagger}]/[A^*]$ are evaluated using partition functions ($k^{\ddagger}$ is treated as a translation along the reaction coordinate).

In the high pressure limit, RRKM theory reduces to transition state theory. In the general case, RRKM theory admits equilibrium between A^* and $A^{\ddagger}$, but not between A^* and A. However at high pressure A^* and A are also in equilibrium. Transition state theory assumes that the activated complex $A^{\ddagger}$ is in thermal equilibrium with the reactants. ~~Ie~~ This is equivalent to assuming that the thermal ~~Boltzmann~~ Boltzmann distribution is maintained at all energies which is true at sufficiently high pressures $\Rightarrow$ at high pressures the RRKM model becomes the same as the ~~tran~~ transition state theory model, and the results of the two theories coincide.