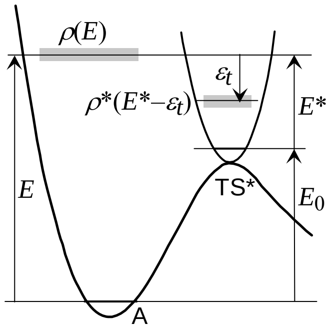
6. Microcanonical Statistics

· Why & where?

→ molecules about to dissociate have non-Boltzmann energy distribution

6.1 Microscopic rate constant

(= microcanonical form of TST)



· microcanonical equilibrium

$$\frac{[\mathrm{TS}(E^*,\varepsilon_t)]}{[\mathrm{A}(E)]}=\frac{\rho^*(E^*-\varepsilon_t)\rho_{trans}^{*(1\mathrm{D})}(\varepsilon_t)}{\rho(E)} \qquad (6.1)$$

ε_t : 1D translational energy on TS* ... from (3.2)

$$\rho_{\mathrm{trans}}^{*(1\mathrm{D})}(\varepsilon)=\frac{l^*}{h}\sqrt{\frac{2\mu^*}{\varepsilon_t}} \qquad (6.2)$$

· half of TS(E^*, ε_t) passes TS* (length l^*) with velocity $\upsilon_t=\sqrt{\frac{2\varepsilon_t}{\mu^*}}$ → rate: $\frac{1}{2}\frac{\upsilon_t}{l^*}=\frac{1}{l^*}\sqrt{\frac{\varepsilon_t}{2\mu^*}}$.

$$k(E,\varepsilon_t)=\frac{[\mathrm{TS}(E^*,\varepsilon_t)]}{[\mathrm{A}(E)]}\times\frac{1}{l^*}\sqrt{\frac{\varepsilon_t}{2\mu^*}}$$

$$=\frac{\rho^*(E^*-\varepsilon_t)}{\rho(E)}\frac{l^*}{h}\sqrt{\frac{2\mu^*}{\varepsilon_t}}\times\frac{1}{l^*}\sqrt{\frac{\varepsilon_t}{2\mu^*}}$$

$$=\frac{\rho^*(E^*-\varepsilon_t)}{h\rho(E)} \qquad (6.3)$$

· microscopic rate constant

$$k(E)=\int_0^{E^*}k(E,\varepsilon_t)d\varepsilon_t=\frac{W^*(E^*)}{h\rho(E)} \qquad (6.4)$$

where $W^*(E^*)$ is sum of states; $W^*(E^*)=\int_0^{E^*}\rho^*(\varepsilon)d\varepsilon$.

by taking adiabatic rotation into account;

$$k(E)=\frac{Q_{rot}^*}{Q_{rot}}\frac{W^*(E^*)}{h\rho(E)} \qquad (6.5)$$

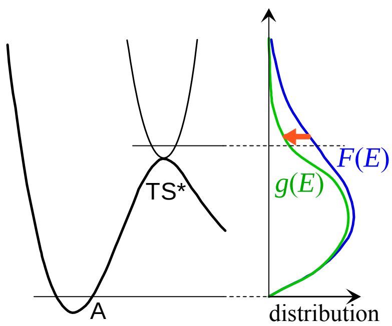
· $W(E)$ and $\rho(E)$ ← direct count algorithm [Stein & Rabinovitch, *J. Chem. Phys.* **58**, 2438 (1973).]

Problem-6.1 ... see handout-6

6.2 Unimolecular reactions

⟨RRKM concept⟩

· energy distribution $g(E)$ of A is distorted from Boltzmann distribution;



$$F(E)=\frac{\rho(E)}{Q}\exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \qquad (6.6)$$

$$k=\int_{E_0}^{\infty}g(E)k(E)\mathrm{d}E \qquad (6.7)$$

[HPL (High-pressure limit)] $g(E) = F(E)$

$$k_\infty = \frac{k_B T}{h}\frac{Q_{rot}^* Q^*}{Q_{rot} Q}\exp\left(-\frac{E_0}{k_B T}\right) \tag{6.8}$$

Problem-6.2

Derive eq. (6.8) from (6.7) using (6.6) and (6.5).

[LPL (Low-pressure limit) and FO (fall-off region)] $g(E) \neq F(E)$

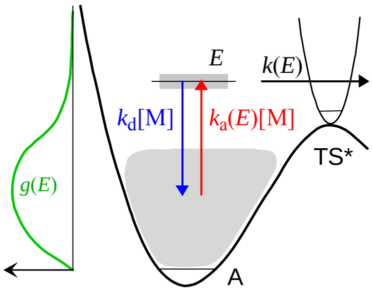
* methods of estimation of $g(E)$ → variations of RRKM theory

⟨Conventional RRKM⟩

· deactivation rate constant k_d

$$Z_{LJ} = \Omega_{A-M}^{(2,2)*}\pi\sigma_{A-M}^2\sqrt{\frac{8k_B T}{\pi\mu_{A-M}}}[M] \tag{6.9}$$

$$k_d \approx \beta\frac{Z_{LJ}}{[M]} \tag{6.10}$$



β: weak collision factor (0.1~1)

· activation rate constant (detailed balancing)

$$\frac{k_a(E)}{k_d} = \frac{\rho(E)}{Q}\exp\left(-\frac{E}{k_B T}\right) \tag{6.11}$$

· steady-state assumption for [A(E)] →

$$g(E) = \frac{[A(E)]_{ss}}{[A]} = \frac{\rho(E)\exp(-E/k_B T)}{Q\{1 + k(E)/k_d[M]\}} \tag{6.12}$$

[HPL] → (6.8)

[FO] → numerical integration of (6.7) with (6.12) and (6.5)

[LPL] $k_0 = \frac{1}{[M]}\lim_{[M]\to 0} k = k_d\int_{E_0}^{\infty} F(E)dE = \int_{E_0}^{\infty} k_a(E)dE$

⟨Master-equation RRKM⟩

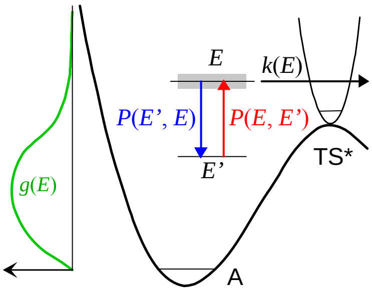
$$-k_{uni}\,g(E) = -k(E)g(E) + Z_{LJ}\int_0^\infty [P(E,E')g(E') - P(E',E)g(E)]dE' \tag{6.13}$$

k_{uni} : (steady-state) unimolecular reaction rate constant

$P(E, E')$ and $P(E', E)$: energy transfer probability from E' to E and E to E'

· using energy grain → eigenvalue problem

$$\mathbf{Mg} = k_{uni}\,\mathbf{g} \tag{6.14}$$



· exponential down model (for $E < E'$)

$$P(E,E') \propto \exp\left(-\frac{E'-E}{\alpha}\right) \tag{6.15}$$

· upward transfer → detailed balancing

$$\frac{P(E,E')}{P(E',E)} = \frac{\rho(E)}{\rho(E')}\exp\left(-\frac{E-E'}{k_B T}\right) \tag{6.16}$$

· $\alpha \approx \langle\Delta E_{down}\rangle$ ... independent of A

... dependent on M

· results do not strongly depend on the energy transfer model (such as eq. 6.15).