Outline

• From macroscopic observables to a microscopic description of chemical reactions (reading Steinfeld et al. Chapter 6 & 7)
  • Potential energy surfaces
    • Long-range potentials
    • Empirical potentials
    • Molecular bonding potentials
    • Internal coordinates and Normal Modes of vibration
• Ab Initio calculation of potential energy surfaces
  • Analytic potential energy functions
  • Reaction path and introduction to transition state theory
  • Potential energy surfaces of electronically excited molecules
Outline

• Statistical approach to reaction dynamics transition state theory
  • Motion on the potential surface
  • Basic postulates and derivation of transition state theory
  • Dynamical derivation of transition state theory
  • Quantum mechanical effects in transition state theory
  • Thermodynamic formulation of transition state theory

• Application of transition state theory
  • Evaluating partition functions by statistical mechanics
  • Electronic partition function
  • Translational partition function
  • Vibrational partition function
  • Rotational partition function
  • Symmetry and statistical factors
  • Collision between atoms

Motion on the potential surface
Motion on the potential surface

\[ \frac{\partial U}{\partial s} = 0, \quad \frac{\partial^2 U}{\partial s^2} < 0 \]

Motion on the potential surface

\[ \frac{\partial U}{\partial \xi} = 0, \quad \frac{\partial^2 U}{\partial \xi^2} > 0 \]
Motion on the potential surface

Taylor's series expansion in the vicinity of the saddle point

\[ U(\xi, s) = \frac{1}{2} C_1(\xi - 2r_0) - \frac{1}{2} C_2 s^2 + E_0 \]

Motion on the potential surface

TST is based on the postulate that the rate of transformation of systems from reactants to products is given solely by passage in the forward direction from coordinates \( r_1 > r_2 \ (s < 0) \) to \( r_1 < r_2 \ (s > 0) \).
Derivation of transition state theory

Eyring, Evans, and Polanyi introduced it in 1935
Based essentially on classical mechanics

Two basic assumptions:
1) Separation of electronic and nuclear motions
   (equivalent to Born-Oppenheimer approximation)
2) Maxwell-Boltzmann distribution of molecules among their states

Additional assumptions:
1) Molecular systems that cross the transition state in the direction
   of the products cannot turn back and reform the reactants
2) In the transition state, motion along the reaction coordinate may
   be separated from other motions and treated classically
3) Even in the absence of equilibrium, the transition states that are
   becoming products are distributed according to Maxwell-Boltzmann

Suppose the bimolecular reaction:

\[ A + B \rightarrow X^1 \rightarrow C \]
Derivation of transition state theory

Suppose the bimolecular reaction:
\[ A + B \rightarrow X^1 \rightarrow C \]
At equilibrium:
\[ N_f^0 + N_b^0 = N^\ddagger = K^\ddagger[A][B] \]

We move the system out of equilibrium by doing,
\[ N_f^0 = 0 \]
Therefore (since backward reaction should not change):
\[ N_f^0 = K^\ddagger[A][B]/2 \]
Derivation of transition state theory

Suppose the bimolecular reaction:

\[ A + B \rightarrow X^1 \rightarrow C \]

At equilibrium:

\[ N_{\frac{1}{2}}^T + N_{p}^T = N^\ddagger = K^\ddagger[A][B] \]

We move the system out of equilibrium by doing,

\[ N_{\frac{1}{2}}^T = 0 \]

Therefore:

\[ N_{p}^T = K^\ddagger[A][B]/2 \]

The average velocity at which transition states pass over the barrier to products, we derive:

\[ \frac{dN}{dt} (\text{reactants} \rightarrow \text{products}) = \frac{\delta N^\ddagger}{\delta t} \]
Derivation of transition state theory

Suppose the bimolecular reaction:

\[ A + B \rightarrow X^1 \rightarrow C \]

At equilibrium:

\[ N_p^1 + N_p^0 = N^1 = K^t[A][B] \]

We move the system out of equilibrium by doing,

\[ N_p^1 = 0 \]

Therefore:

\[ N_p^1 = K^t[A][B] / 2 \]

The average velocity at which transition states pass over the barrier to products, we derive:

\[ \frac{dN}{dt} \text{ (reactants } \rightarrow \text{ products)} = \frac{\Delta N^1}{\delta t} \]

Average time to cross the barrier

\[ \delta t = \frac{\delta}{V_k} \]

Number of transition states per unit volume having velocity between \( v \) and \( v + dv \) in one direction.
Derivation of transition state theory

Suppose the bimolecular reaction:

\[ A + B \rightarrow X^1 \rightarrow C \]

At equilibrium:

\[ N_{A}^0 + N_{B}^0 = N^1 = K'[A][B] \]

We move the system out of equilibrium by doing,

\[ N_{A}^0 = 0 \]

Therefore:

\[ N_{A}^0 = K'[A][B]/2 \]

The average velocity at which transition states pass over the barrier to products, we derive:

\[
\delta \frac{dN}{dt} \text{ (reactants } \rightarrow \text{ products)} = \frac{\delta N^1}{\delta} \delta t = \frac{dN}{dt} = \delta N^1 \frac{\bar{v}_1}{\delta} = \frac{dN}{dt} = \frac{N^1}{2} \frac{\bar{v}_1}{\delta} \]

Number of transition states per unit volume having velocity between \( v \) and \( v + dv \) in one direction.
Derivation of transition state theory

Suppose the bimolecular reaction:

\[ A + B \rightarrow X^1 \rightarrow C \]

At equilibrium:

\[ N_f^1 + N_f^2 = N_f^\dagger = K_f^\dagger [A][B] \]

\[
\frac{dN}{dt} = \frac{\delta N}{\delta} \delta = \frac{N_f^1}{2} \frac{\ddot{\nu}}{\delta}
\]

\[
\bar{v}_f = \int_0^\infty v_c e^{-\frac{v_c^2}{8k_BT}} dv_c = \left( \frac{2k_BT}{\pi \mu_r} \right)^{1/2}
\]

\[
\frac{dN}{dt} = \frac{N_f^1}{2} \left( \frac{2k_BT}{\pi \mu_r} \right)^{1/2} \frac{1}{\delta} e^{-E_0/k_BT} [A][B]
\]

\[
K_f^\dagger = \frac{N_f^1}{[A][B]} \quad \rightarrow \quad K_f^\dagger = \frac{N_f^1}{[A][B]} = \frac{Q_{\text{tot}}^1}{Q_A Q_B} e^{-E_0/k_BT} [A][B]
\]

Translations:

\[
Q_{\text{tot}}^1 = Q_f^1 \quad Q_i = (2\pi \mu_r k_BT)^{1/2} \delta/h
\]

\[
\frac{dN}{dt} = \frac{k_BT}{h} Q_f^1 e^{-E_0/k_BT} [A][B]
\]

\[
\frac{dN}{dt} = k[A][B]
\]

\[
k = k_{\text{abs}} = \frac{k_BT}{h} \frac{Q_f^1}{Q_A Q_B} e^{-E_0/k_BT}
\]
Derivation of transition state theory

At equilibrium:

\[ k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q_A^f Q_B^f}{Q_A Q_B} e^{-E_a/k_B T} \]

Remember the TPD pre-exponential factor for the 1st order process?

\[ f = \frac{k_i T}{h} \]

\[ k = f \cdot \frac{q^{TS}}{q^{\text{react}}} = f \cdot \frac{k_i T}{h} = \frac{1.3806505 \times 10^{-21} J}{K} \times \frac{298.15 K}{6.6260693 \times 10^{-34} J s} = 6.212 \times 10^{12} s^{-1} \]

Derivation of transition state theory

Suppose the bimolecular reaction:

\[ A + B \rightarrow X \rightarrow C \]

At equilibrium:

\[ k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q_A^f Q_B^f}{Q_A Q_B} e^{-E_a/k_B T} \]

\[ k = \frac{k_B T}{h} K_c^f \]

\[ K_c^f = \frac{Q_A^f Q_B^f}{Q_A Q_B} e^{-E_a/k_B T} \]

\[ \Delta G^{10} = -RT \ln K_c^f \]

\[ k = \frac{k_B T}{h} e^{-\Delta G^{10}/RT} \]

\[ \Delta G^{10} = \Delta H^{10} - T \Delta S^{10} \]

\[ k = \frac{k_B T}{h} [\Delta S^{10}/R] e^{-\Delta H^{10}/RT} \]
Transition state theory

- Molecular systems that have crossed the transition state in the direction of products cannot turn around and reform reactants.
- In the transition state, motion along the reaction coordinate may be separated from the other motions and treated classically as a translation.
- Even in the absence of an equilibrium between reactant and product molecules, the transition state that are becoming products are distributed among their states according to the Maxwell-Boltzmann laws.

Transition state theory: Some Issues

- Uses classical mechanics to evaluate partition functions and canonical averages. Does not describe tunneling (important for light species, such as H and D)
- Simplifies motion on the potential surface to 1D along reaction coordinate, the actual motion may include a normal component
- Uses harmonic potentials, which may be an issue at high temperatures
- Experimental evidence suggests that there may be multiple crossings of the TS, meaning that the forward motion is not representative of half of the TS
- If recrossing of the TS does occur, then the local equilibrium is not maintained
- The may be non-Boltzmann distributions (can be selective energy consumption by the reactants and specific energy release by the products), however, that may be fine if relaxation of reactants and products is rapid compared with the reaction rate
- Solvent effects often lead to significant deviations from the TS theory (diffusion limit)