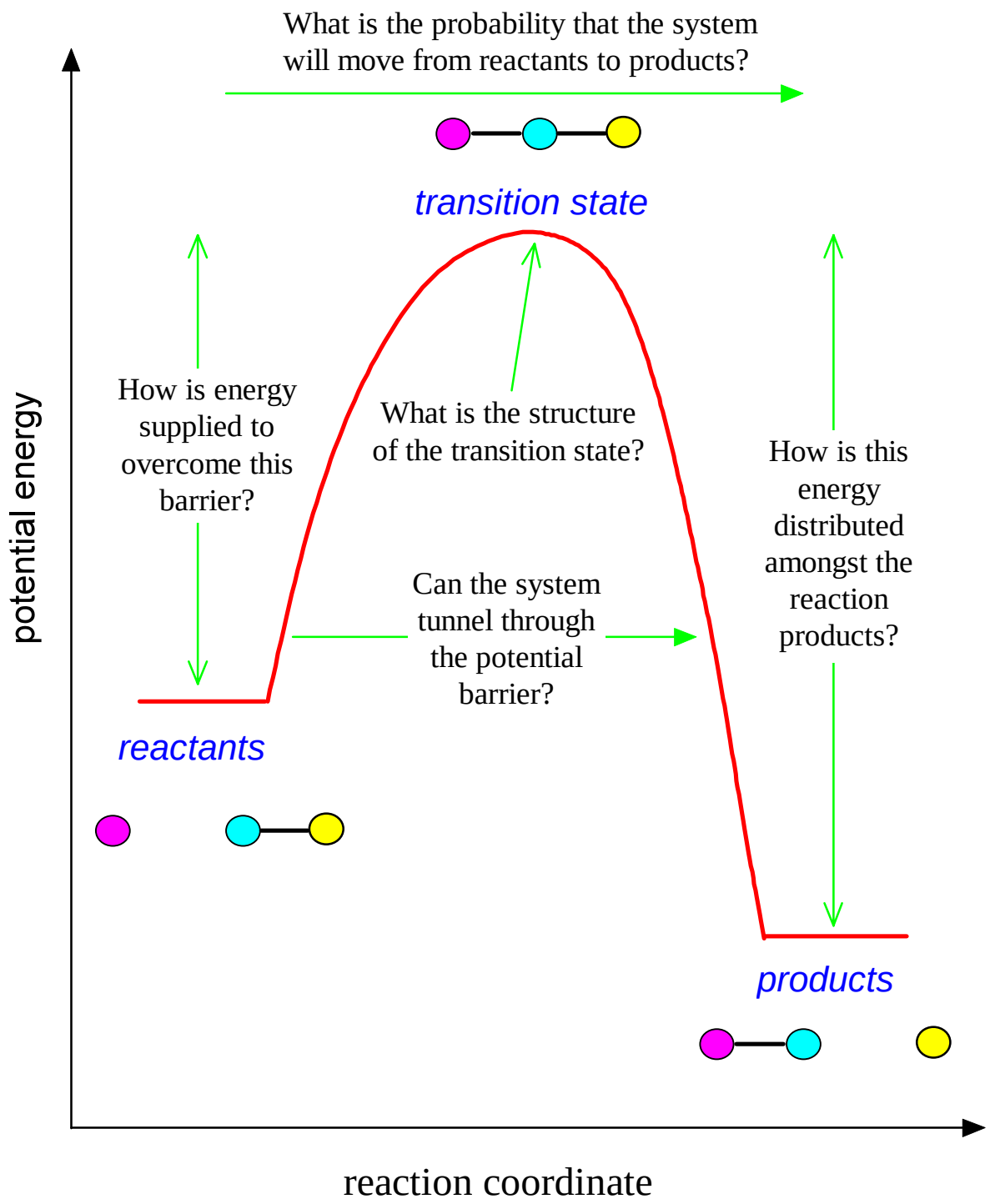
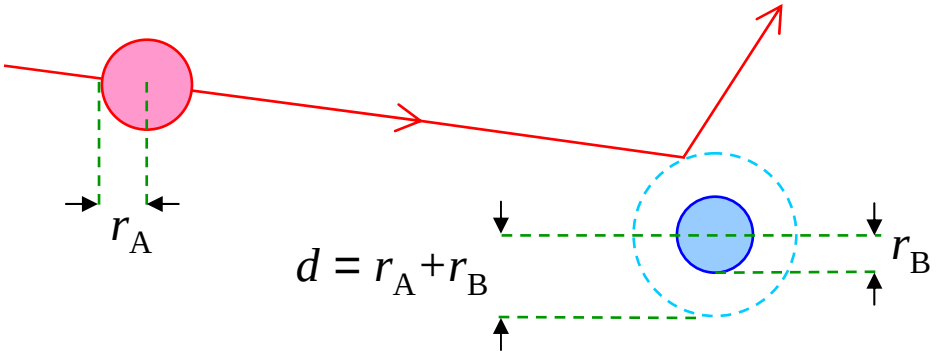
Reaction Dynamics

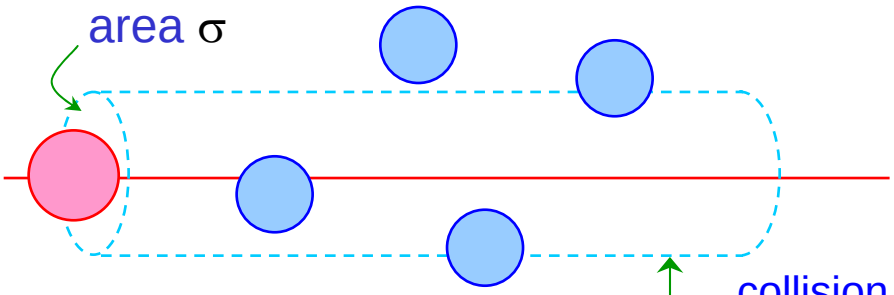


Collision Theory 1

In the simple hard sphere model of molecular collisions, the impact parameter (distance of closest approach) is the sum of the radii of the collision pair.



Collision cross-section $\sigma = \pi d^2$



collision volume swept by A per sec.

Collision frequency $Z_{AB} = \bar{N}_A \bar{N}_B \sigma v_{rel}$

collision frequency per A molecule

number of collisions per unit time per unit volume

= (m^{-3}) (m^{-3}) (m^2) ($m\ s^{-1}$) $\Rightarrow$ $m^{-3}\ s^{-1}$

Collision Theory 2

Maxwell $$\bar{v}_{\text{rel}} = \left[\frac{8RT}{\pi M_{\text{A}}} + \frac{8RT}{\pi M_{\text{B}}} \right]^{1/2} = \left(\frac{8RT}{\pi \mu} \right)^{1/2}$$

where $\mu = \dfrac{M_{\text{A}} M_{\text{B}}}{M_{\text{A}} + M_{\text{B}}}$ is the reduced mass.

Activation Energy: Only a fraction of collisions have sufficient kinetic energy to overcome the activation barrier.

$$\text{reaction rate} = Z_{\text{AB}}\, \text{e}^{-E_{\text{a}}/RT}$$ molecules m^{-3} s^{-1}

Bimolecular Rate Constant

$$-\frac{d[\text{A}]}{dt} = \frac{Z_{\text{AB}}}{L} \text{e}^{-E_{\text{a}}/RT}$$ mol m^{-3} s^{-1}

L = Avogadro's no.

$$= \frac{N_{\text{A}} N_{\text{B}}}{L} \sigma v_{\text{rel}}\, \text{e}^{-E_{\text{a}}/RT}$$ mol m^{-3} s^{-1}

$$= 10^6\, L[\text{A}][\text{B}] \sigma v_{\text{rel}}\, \text{e}^{-E_{\text{a}}/RT}$$ mol m^{-3} s^{-1}

$$= 10^3\, L[\text{A}][\text{B}] \sigma v_{\text{rel}}\, \text{e}^{-E_{\text{a}}/RT}$$ mol dm^{-3} s^{-1}

$$k_{\text{AB}} = 10^3\, L \sigma v_{\text{rel}}\, \text{e}^{-E_{\text{a}}/RT}$$ mol^{-1} dm^3 s^{-1}

$$k_{\text{AB}} = 10^3\, L d^2 \left(8\pi RT \frac{(M_A + M_B)}{M_A M_B} \right)^{1/2} \text{e}^{-E_{\text{a}}/RT}$$ M^{-1} s^{-1}

Collision Theory 3

Basic collision theory has several deficiencies, which can be partially overcome by making more sophisticated models.

1. Orientation Dependence

   The reactions of polyatomic molecules typically depend on their mutual orientation.

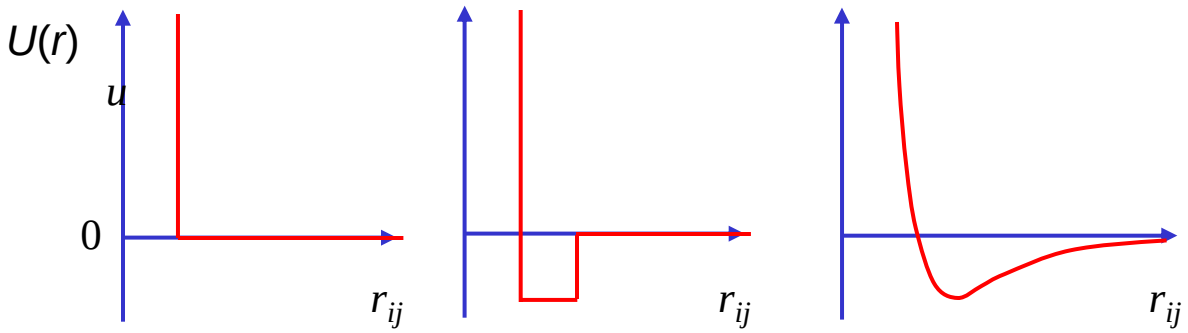
   Solution: Replace σ with σ^*, the reactive cross-section:

$$\sigma^* = P\,\sigma$$

   P: steric factor

2. Intermolecular Interactions

   Molecules are not incompressible hard spheres!



Hard sphere Square well Lennard-Jones

3. The collision energy depends on the impact parameter, which is angular dependent.

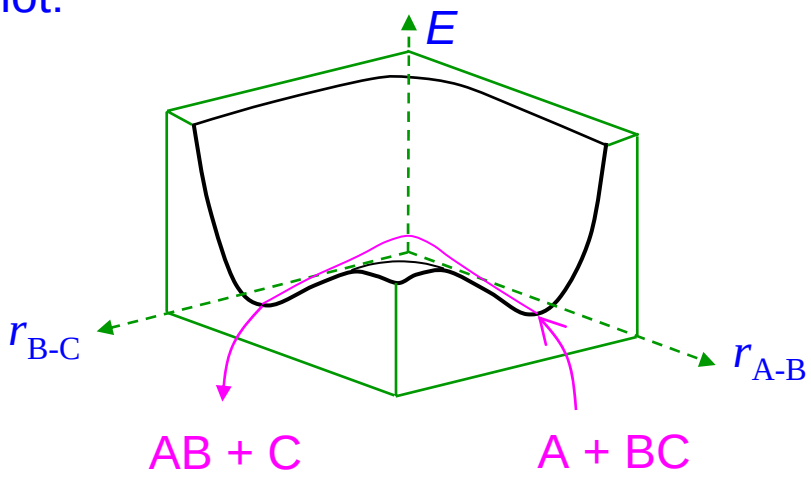
4. There is no way to predict the activation energy.

Potential Energy Surfaces 1

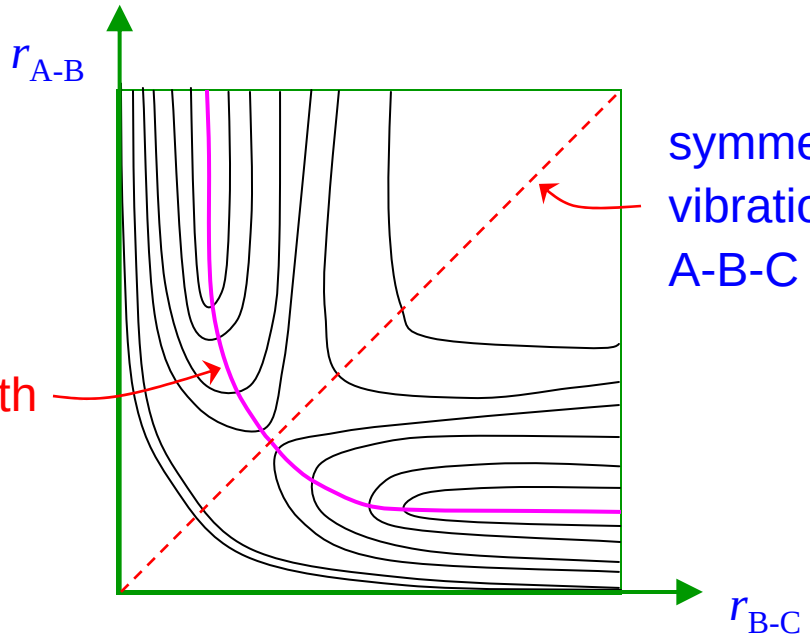
A reaction surface is a plot of the energy of a reaction system as a function of all the independent variables (bond lengths and bond angles). Even a collinear triatomic reaction such as

$$A + BC \rightarrow AB + C$$

needs a 3-D plot:



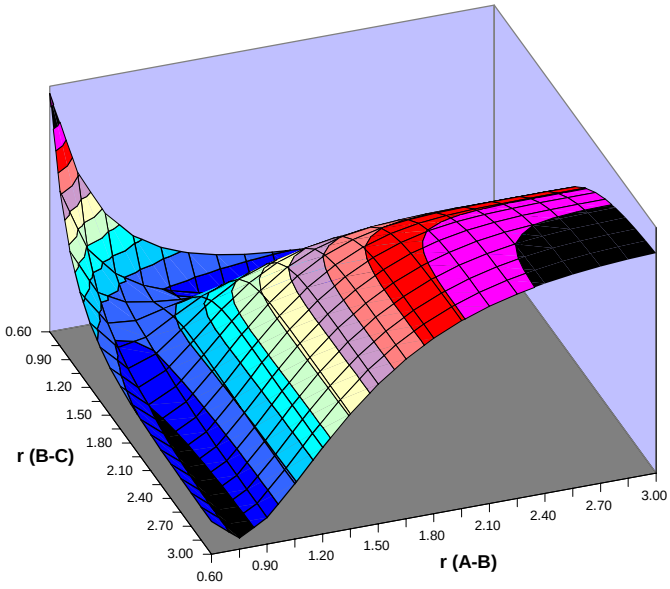
or a contour plot:

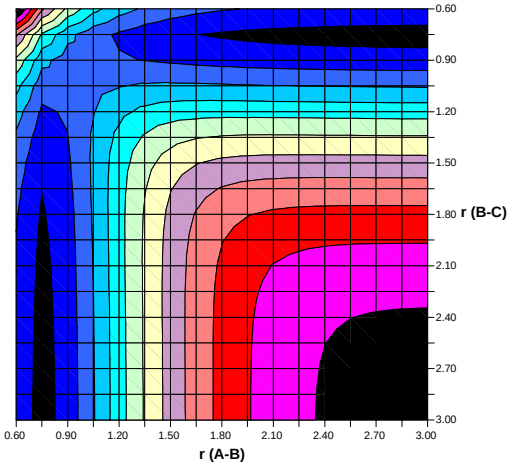


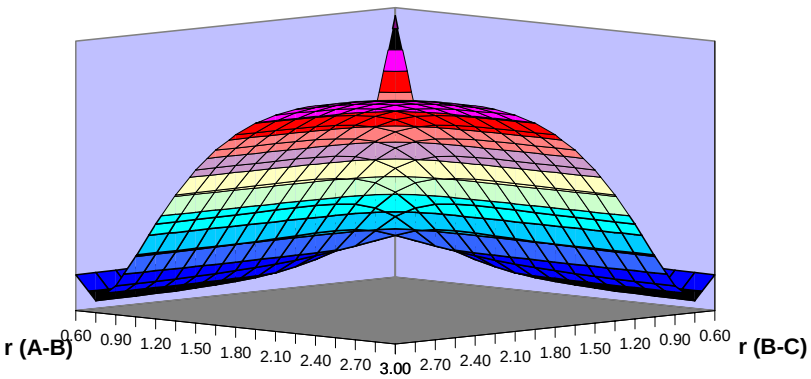
symmetric vibration of A-B-C

minimum energy path

Potential Energy Surfaces 2

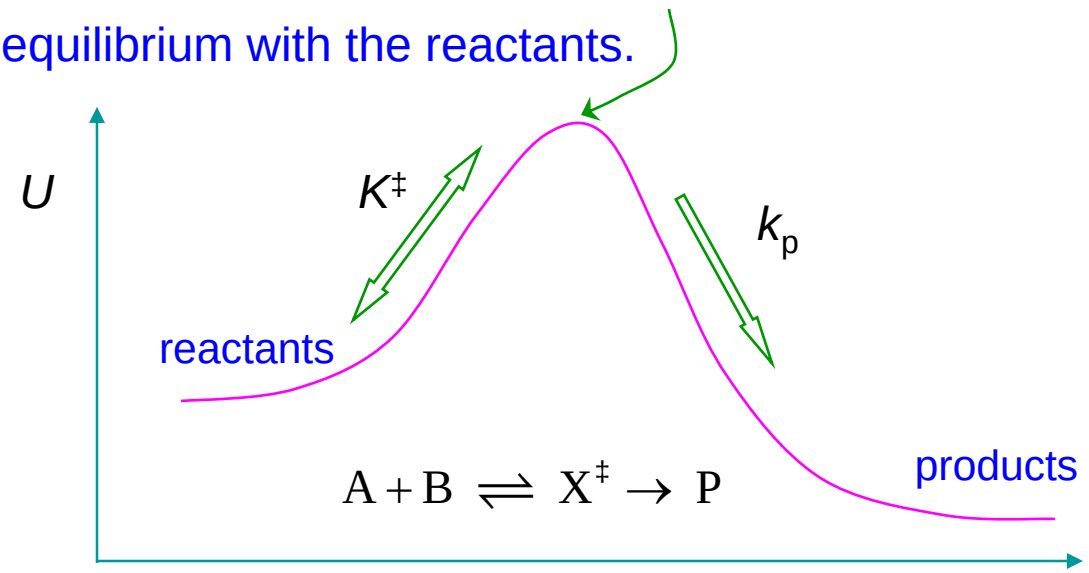






Transition State Theory

1. Assume that in the course of a reaction there is some dividing surface (point on a one-dimensional reaction path) past which reaction to products is inevitable.
2. Assume that this transition state is in effective equilibrium with the reactants.



$$\frac{d[\mathrm{P}]}{dt} = k_p[\mathrm{X}^{\ddagger}] = k_p K^{\ddagger}[\mathrm{A}][\mathrm{B}]$$

$$k_2 = k_p K^{\ddagger}$$

A full discussion of k_p and $K^{\ddagger}$ requires quantum chemistry and statistical mechanics, and leads to the

Eyring Equation $$k_2 = \kappa\left(\frac{RT}{hL}\right)K^{\ddagger}$$

κ: transmission coefficient or tunneling factor

Thermodynamic Formulation of TST

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}$$

For gases, $\Delta G^\circ = -RT \ln K^\circ$

where $K^\circ = \dfrac{(p_\mathrm{X}/p^\circ)}{(p_\mathrm{A}/p^\circ)(p_\mathrm{B}/p^\circ)} = K_\mathrm{c}\left(\dfrac{p^\circ}{RT}\right)$ $\quad \dfrac{p}{p^\circ} = \dfrac{nRT}{Vp^\circ} = c\left(\dfrac{RT}{p^\circ}\right)$

Substitute into the Eyring Equation:

$$k_2 = \kappa\left(\frac{RT}{hL}\right)K_\mathrm{c}^\ddagger$$

$$= \kappa\left(\frac{RT}{hL}\right)\left(\frac{RT}{p^\circ}\right)K^\ddagger$$

$$= \kappa\left(\frac{RT}{hL}\right)\left(\frac{RT}{p^\circ}\right)\mathrm{e}^{-\Delta G^\ddagger/RT}$$

$$= \left(\frac{RT}{hL}\right)\left(\frac{RT}{p^\circ}\right)\mathrm{e}^{\Delta S^\ddagger/R}\,\mathrm{e}^{-\Delta H^\ddagger/RT}$$

"hide" κ in the ΔS factor

Since $E_\mathrm{act} = \Delta U^\ddagger + RT = \Delta H^\ddagger + 2RT$ (for gases only)

$$k_2 = \left\{\mathrm{e}^2\left(\frac{RT}{hL}\right)\left(\frac{RT}{p^\circ}\right)\mathrm{e}^{\Delta S^\ddagger/R}\right\}\mathrm{e}^{-E_\mathrm{act}/RT}$$