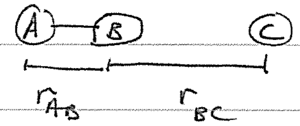
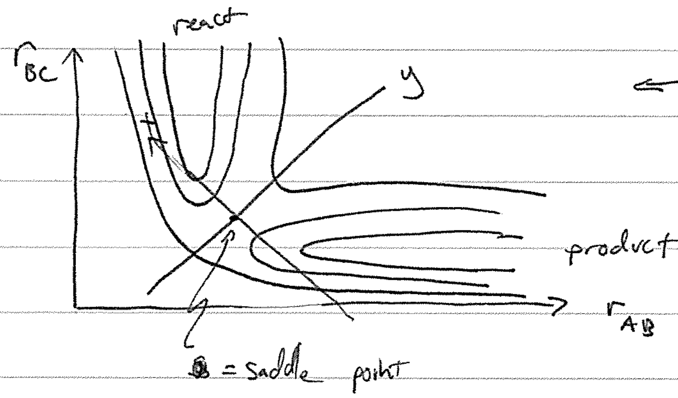
Transition state theory:

Consider a reaction:

$$AB + C \longrightarrow A + BC$$

(living in a line:



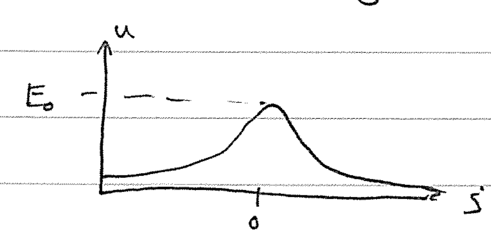


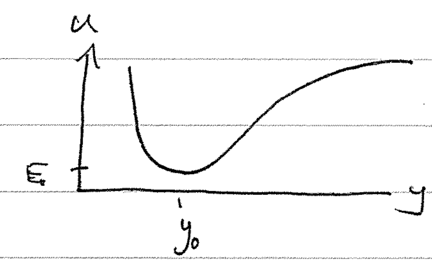
contour plot of $U(r_{AB}, r_{BC})$

$$\left.\begin{aligned} s &= r_{BC} - r_{AB} \\ y &= r_{BC} + r_{AB} \end{aligned}\right\} \text{ new coordinates at saddle point.}$$

s = reaction path

Consider potential along these 2 curves





At the saddle point,

$$\frac{\partial U}{\partial s} = 0 \quad , \quad \frac{\partial^2 U}{\partial s^2} < 0 \quad \leftarrow \text{ imaginary frequency at saddle}$$

$$\frac{\partial U}{\partial y} = 0, \quad \frac{\partial^2 U}{\partial y^2} > 0 \quad \leftarrow \text{ \underline{real} frequency at saddle}$$

Approximate surface near saddle:

$$U(s,y) = \frac{1}{2} C_y (y - y_0)^2 - \frac{1}{2} C_s s^2 + E_0$$

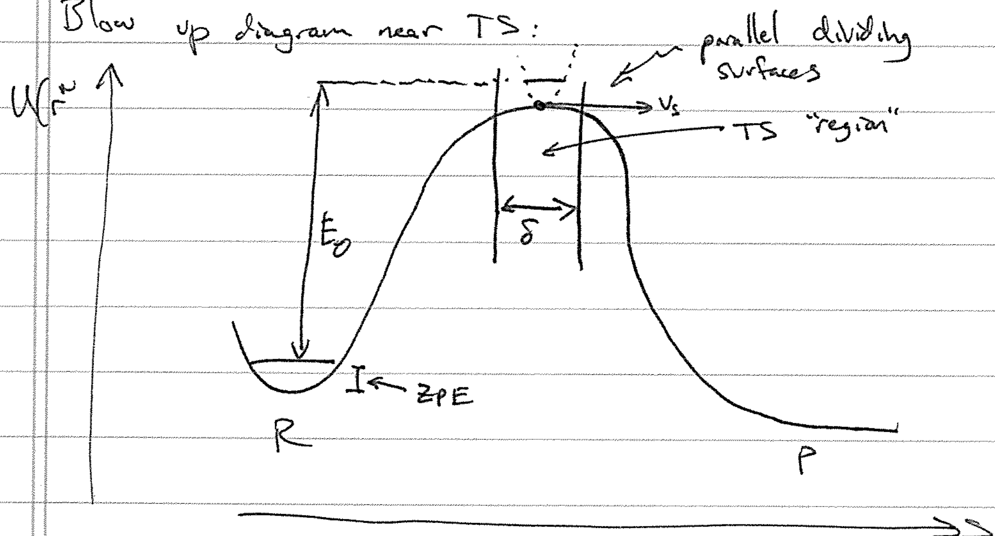
Basic tenets of TST

1) molecules that have crossed the TS in the direction of products can't turn around & form reactants

2) Aft the TS, motion along reaction coordinate is seperable from other motions and is treated as a translation.

3) TS is in a state of quasi-equilibrium and equilibrium distributions apply. (actually follows from point 1)

Blow up diagram near TS:



Molecules moving forward out of TS region: $N_f^{\ddagger}$

Molecules moving backwards out of TS region: $N_b^{\ddagger}$

$N^{\ddagger} = N_f^{\ddagger} + N_b^{\ddagger}$ $\quad$ $K^{\ddagger} = \frac{N^{\ddagger}}{[AB][C]}$

or

$$N^{\ddagger} = K^{\ddagger}[AB][C]$$

Now, let's consider only those forward moving states while we're still at eqm with reactants:

eqm.. $N_f^{\ddagger} = N_b^{\ddagger} = N^{\ddagger}/2$

so: $N_f^{\ddagger} = K^{\ddagger}[AB][C]/2$ $\leftarrow$ quasi-equilibrium hypothesis

Net rate of reaction in forward direction

$$\frac{dN}{dt}(r \to p) = \frac{\delta N^{\ddagger}}{\delta t}$$

Now if we know the average <u>velocity</u> $\bar{V}_s$ along RC,

gap between dividing surfaces

$$\bar{V}_s = \frac{\delta}{\delta t}$$

$$\delta t = \delta / \bar{V}_s$$

So:

but this is just <u>half</u> the total population in the TS region

$$\frac{dN}{dt} = \delta N^{\ddagger} \frac{\bar{V}_s}{\delta}$$

$$\delta N^{\ddagger} = \frac{N^{\ddagger}}{2}$$

$$\therefore \quad \frac{dN}{dt} = \frac{N^{\ddagger}}{2} \frac{\bar{V}_s}{\delta}$$

all we need is this!

$$\bar{V}_s = \frac{\int_0^{\infty} V_s \, e^{-(\mu_s V_s^2 / k_B T)} \, dV_s}{\int_0^{\infty} e^{-\mu_s V_s^2 / k_B T} \, dV_s}$$

equilibrium distribution of velocities at TS

μ_s = reduced mass of reaction coord $= \frac{m_{AB} m_c}{m_{AB} + m_c}$

we only consider forward <u>moving</u> TS

$$\bar{V}_s = \sqrt{\frac{2 k_B T}{\pi \mu_s}}$$

$$\therefore \quad \frac{dN}{dt} = \frac{N^{\ddagger}}{2} \left(\frac{2 k_B T}{\pi \mu_s} \right)^{1/2} \frac{1}{\delta}$$

tot PF at TS

Now remember that:

$$K_c^{\ddagger} = \frac{N^{\ddagger}}{[AB][C]} = \frac{Q_{tot}^{\ddagger}}{Q_{AB} Q_C} e^{-E_0 / k_B T}$$

$$\frac{dN}{dt} = \sqrt{\frac{2kT}{\pi \mu_s}} \frac{1}{2\delta} \frac{Q^{\ddagger}_{tot}}{Q_{AB} Q_C} e^{-E_0/k_BT} [AB][C]$$

$$Q^{\ddagger}_{tot} = Q_s Q^{\ddagger} = Q^{\ddagger} \underbrace{\sqrt{2\pi\mu k_B T}\, \delta/h}$$

1-D box size

↑ 1-D translational PF along s

$$\frac{dN}{dt} = \frac{k_BT}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_BT} [AB][C]$$

Consider 1st order rate law

$$\frac{dN}{dt} = k[AB][C]$$

rate const

$$k = \frac{k_BT}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_BT}$$

Everything artificial δ, μ_s, v_s, factors of $\frac{1}{2}$ have cancelled!

$Q^{\ddagger}$ is the PF for the activated complex with relative motion (s) frozen.

A···B···C ⟶ still has 3 translations
still has 3 rotations (but geometry is different)

has $3N-6-1$ vibrations

↑ asymmetric stretch is now s! and has imaginary frequency