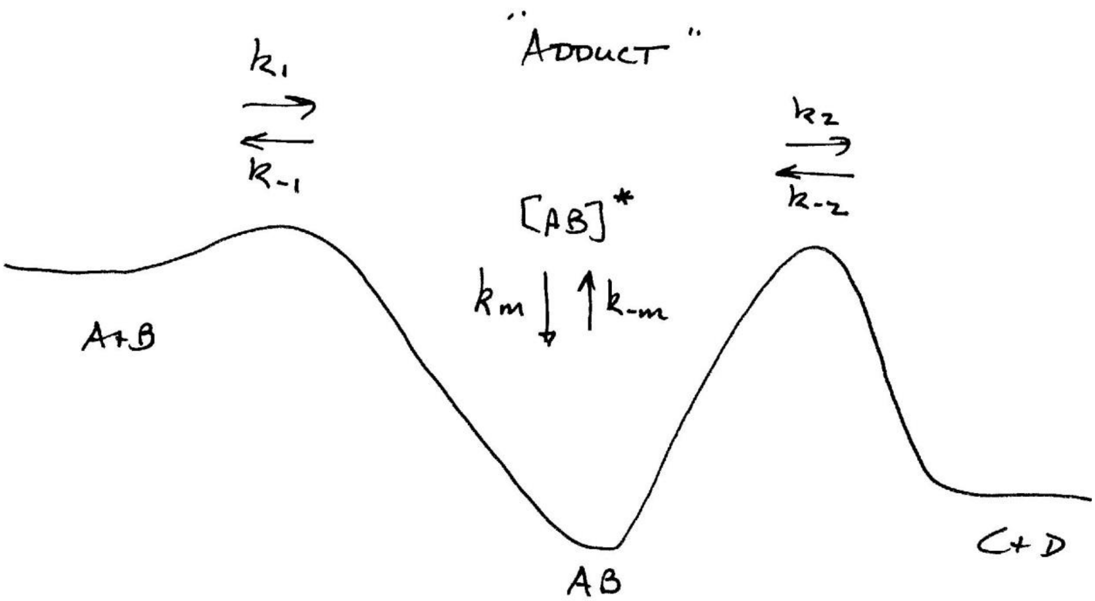
①



$$① \quad \boxed{\frac{d[A]}{dt} = -k_1[A][B] + k_{-1}[AB^*]}$$

$$② \quad \frac{d[AB^*]}{dt} = k_1[A][B] - k_{-1}[AB^*] + k_{-2}[C][D] - k_2[AB^*] - k_m[M][AB^*] + k_{-m}[AB][M]$$

Assume steady-state $[AB^*]$

Assume small

$$k_1[A][B] - k_{-1}[AB^*] + \cancel{k_{-2}[C][D]} - k_2[AB^*] - k_m[M][AB^*] + k_{-m}[M][AB] = 0$$

OR, rearranging

$$\boxed{[AB^*] = \frac{+k_1[A][B] + k_{-m}[M][AB]}{k_{-1} + k_2 + k_m[M]}}$$

②

So,
$$\frac{d[A]}{dt} = -k^{II}[A][B] = -k_1[A][B] + k_{-1}[AB^*]$$

Apparant 2nd order Rate Constant.

$$\frac{d[A]}{dt} = -k_1[A][B] + k_{-1}\left\{\frac{k_1[A][B] + k_{-m}[M][AB]}{k_{-1}+k_2+k_m[M]}\right\}$$

$$= -[A][B]\left\{\frac{\cancel{k_1k_{-1}} + k_1k_2 + k_1k_m[M] - \cancel{k_1k_{-1}} - \dfrac{k_{-1}k_{-m}[M][AB]}{[A][B]}}{k_{-1}+k_2+k_m[M]}\right\}$$

OR,
$$k^{II} = \left\{\frac{k_1k_2 + k_1k_m[M] - \dfrac{k_{-1}k_{-m}[M][AB]}{[A][B]}}{k_{-1}+k_2+k_m[M]}\right\}$$

$$\boxed{k^{II} = k_1\left\{\frac{k_2 + k_m[M] - \dfrac{k_{-1}k_{-m}}{k_1}\left[\dfrac{[M][AB]}{[A][B]}\right]}{k_{-1}+k_2+k_m[M]}\right\}}$$

NOTE:

IF $[AB] \ll [AB]_{eq}$

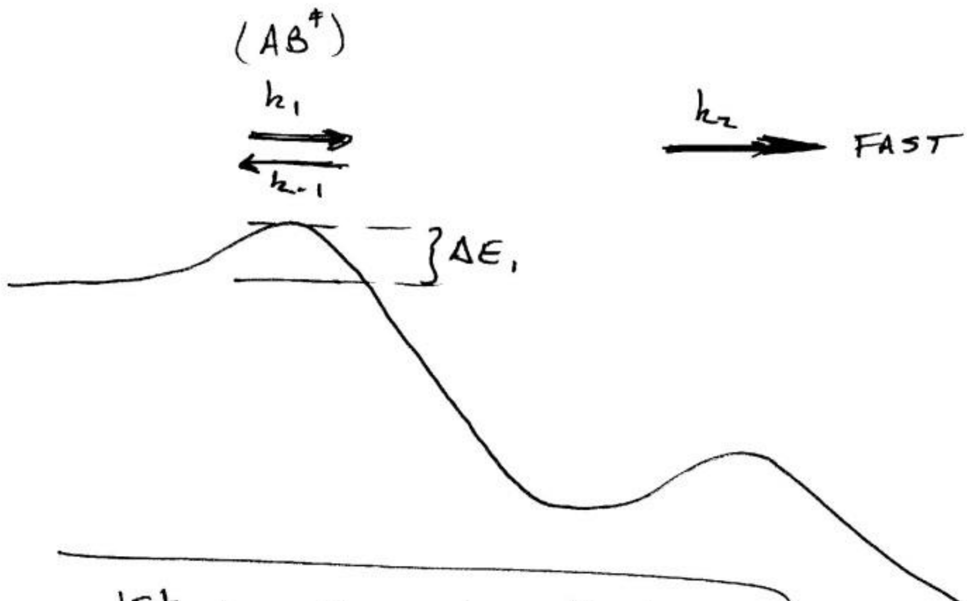
$$k^{II} = k_1 \left\{ \frac{k_2 + k_m[M]}{k_{-1} + k_2 + k_m[M]} \right\}$$

- Then, if k_2 is large,

$$k_2 + k_m[M] \sim k_2$$
$$k_2 + k_{-1} + k_m[M] \sim k_2$$

$$\boxed{k^{II} = k_1 \cdot k_2 / k_2 = k_1 = A_1 e^{-\Delta E_1/RT}}$$

k_2 large means what ?? Low barrier,



1st transition State limiting

(A) If 1st transition state is limiting, then we refer to the reaction as "Simple bimolecular"

- IF $k_m[M] \gg k_{-1} + k_2$

$$k^{II} = k_1 \left(\frac{k_m[m]}{k_m[m]} \right) = k_1$$ SAME result.

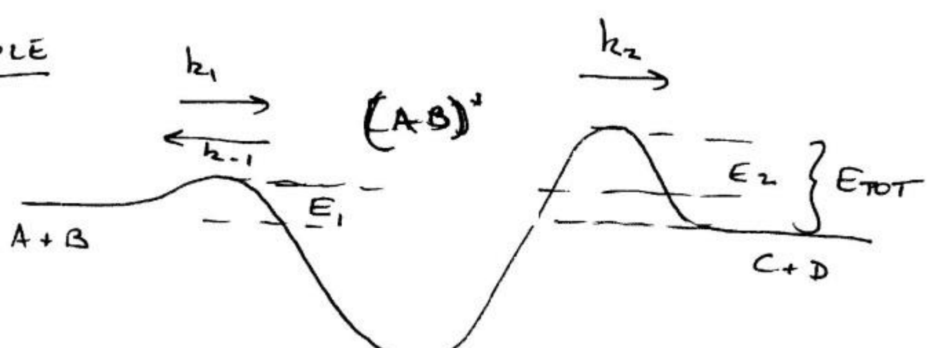
- IF $k_{-1} \gg k_2 + k_m[M]$

$$k^{II} = \frac{k_1 (k_2 + k_m[m])}{k_{-1}} = \frac{k_1 k_2}{k_{-1}}$$

NOTE, $k_1/k_{-1} = \frac{[AB^*]}{[A][B]}$ OR, "K_{eq}"

This means $[AB^*]$ is in equilibrium with $[A][B]$.

<u>EXAMPLE</u>



5

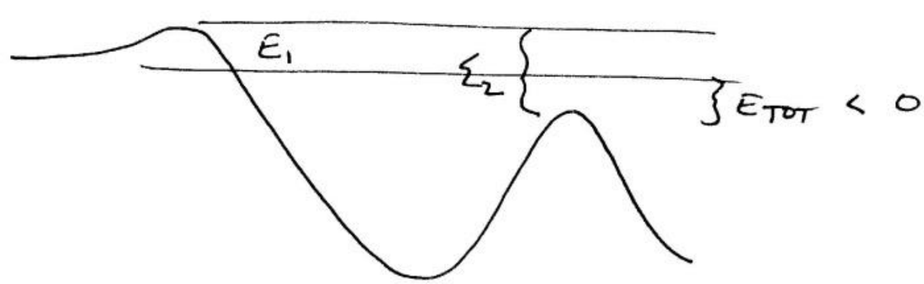
Typically,
k_{-1} has a very small T-dependence,

$$k^{II} = \frac{A_1 e^{-E_1/RT} \cdot A_2 e^{-E_2/RT}}{A_{-1} \cancel{e^{-E_{-1}/RT}}} \sim \frac{A_1 \cdot A_2 e^{-(E_1+E_2)/RT}}{A_{-1}}$$

or, $k^{II} \propto e^{-(E_{TOT})/RT}$

OR, "BARRIER" TO REACTION IS THE SUM OF TWO STEPS.

What if E_2 is negative?



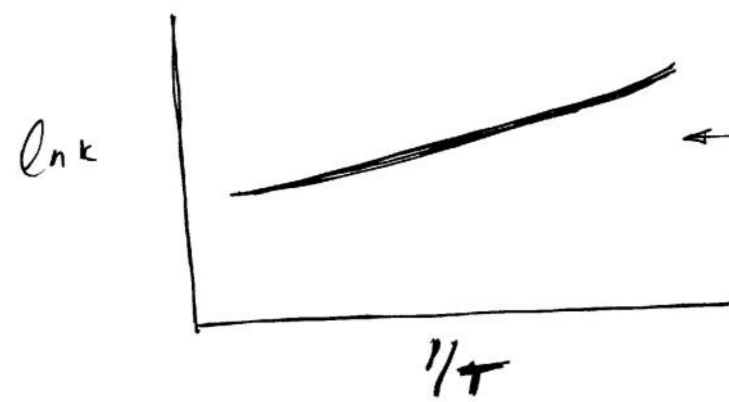
$E_{TOT} = E_1 + E_2 < 0$!!

⑥

$$k^{II} = \frac{A_1 \cdot A_2}{A_{-1}} e^{-(E_{TOT})/RT}$$

This is an exponential term that is positive!

"NEGATIVE T-dependence"



RATE const. for reaction increases with decreasing Temp!

IN order for this to occur, $k_{-1} > k_2$,

So

$$A_1 e^{-\varepsilon_{-1}/RT} > A_2 e^{-\varepsilon_2/RT}$$

or,

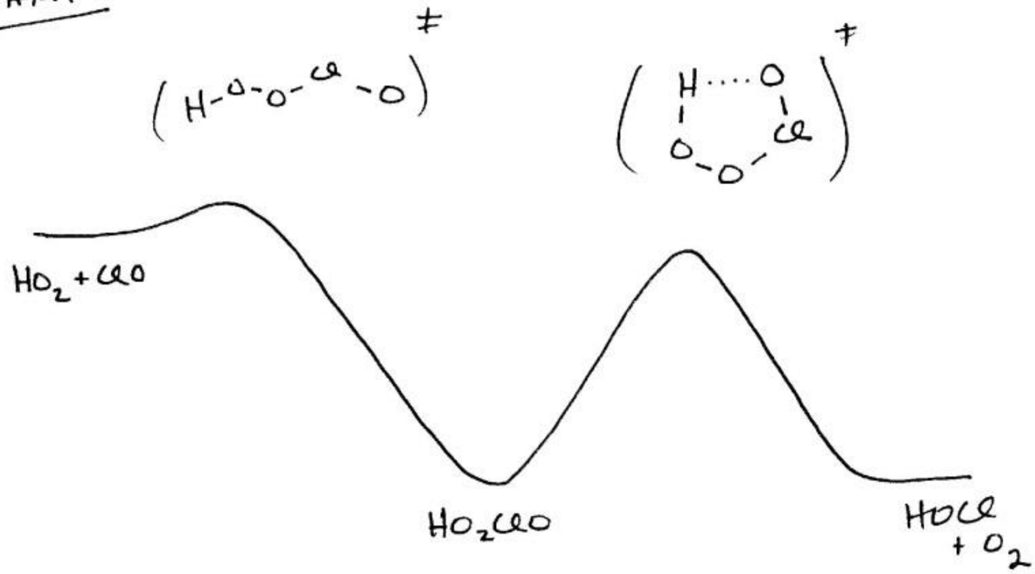
$$A_{-1} > A_2 e^{-\varepsilon_2/RT}$$

larger than 1

$$\boxed{A_2 < A_{-1} e^{\varepsilon_2/RT}}$$

That is, the A-factor for decomposition of AB^* into $C+D$ must be much smaller than the A-factor for decomposition of AB^* into $A+B$.

EXAMPLE

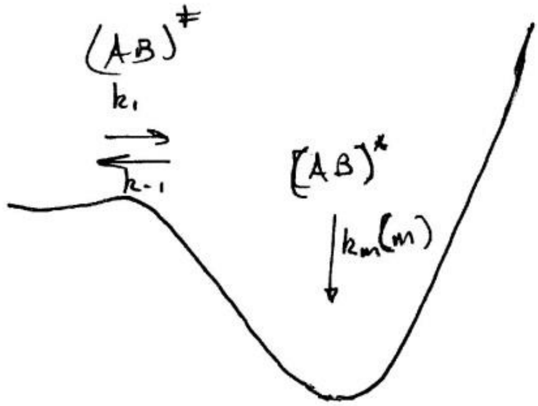


Reaction exhibits a negative T-dependence & 2nd transition state is more constrained than 1st ...

MORE degrees of freedom, larger A,

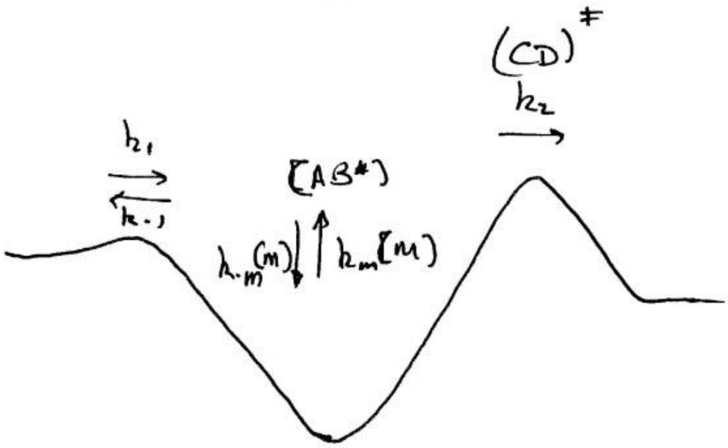
$$A_1 > A_2$$

I



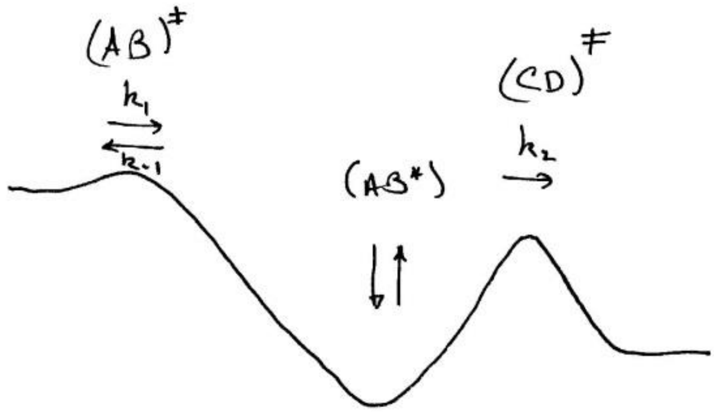
Recombination

II



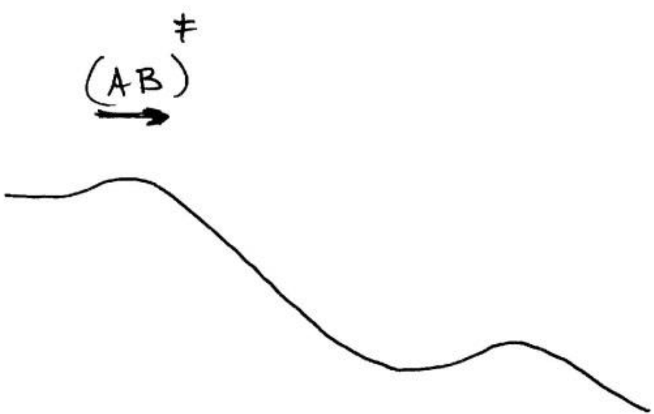
Bimolecular, 2nd transition state limiting

III



Mixed Bimolecular/ termolecular, Transition States in competition

IV



Bimolecular, 1st transition state limiting