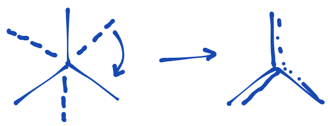
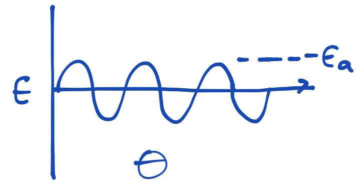
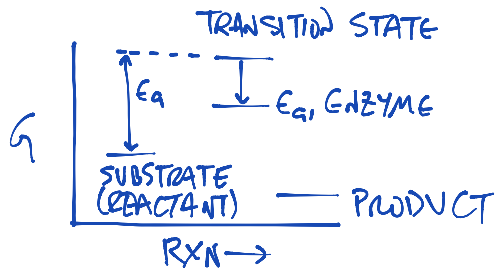




$K = A \cdot \exp(-E_a/RT)$



HOW MUCH DO YOU NEED TO STABILIZE TO GET RATE INCREASE?

$S \underset{}{\overset{K}{\rightleftharpoons}} T.S.$

$P_{T.S} = \dfrac{[TS]}{[S]+\cancel{[TS]}}$ IF $\Delta G >> 0$, $[TS] << [S]$

$P_{T.S.} = \dfrac{[TS]}{[S]} = K$

$\Delta G = -RT\ln(K)$

$\therefore P_{T.S.} = \exp(-\Delta G/RT)$

THIS GIVES PROBABILITY. WHAT ABOUT RATE?

DIE: $P_6 = \frac{1}{6}$ HOW OFTEN I GET 6: $\underbrace{\text{HOW OFTEN I ROLL}}_{A} \times P_6$

FOR T.S.: PREFACTOR: TRIES PER UNIT TIME. DIFFUSION (USUALLY) IN BIOLOGY, s^{-1}!

$$\underset{\substack{\uparrow \\ \text{RATE CONSTANT}}}{k} = A \cdot \exp(-\underset{\substack{\uparrow \\ E_a}}{\Delta G}/RT)$$

IN BIOLOGY, ENZYMES INCREASE RATES <u>DRAMATICALLY</u>. TRYPSIN GIVES 10^{11} SPEEDUP!

OK, SO WHAT CHANGE IN E_a WOULD LEAD TO 10^{11} SPEED UP FOR TRYPSIN?

$$K_{Enz} = A\exp(-E_{a,enz}/RT) \leftarrow \text{CAT RATE}$$

$$K_{H_2O} = A\exp(-E_{a,H_2O}/RT) \leftarrow \text{UNCAT RATE}$$

$$\frac{K_{Enz}}{K_{H_2O}} = 1E11 = \frac{\cancel{A}\exp(-E_{a,Enz}/RT)}{\cancel{A}\exp(-E_{a,H_2O}/RT)}$$

$$= \exp(-E_{a,Enz}/RT)\cdot\exp(E_{a,H_2O}/RT)$$

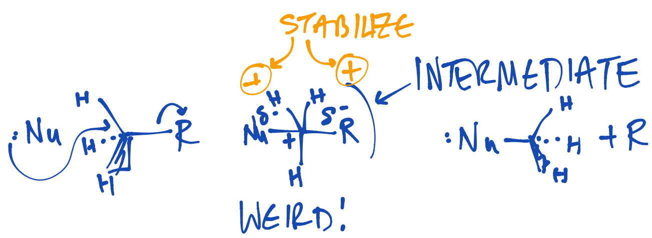
$$= \exp(-E_{a,Enz}/RT + E_{a,H_2O}/RT)$$

$$= \exp((E_{a,H_2O} - E_{a,Enz})/RT) \qquad \Delta E_a = E_{a,Enz} - E_{a,H_2O}$$

$$= \exp(-\Delta E_a/RT)$$

$$-RT\ln(1E11) = \Delta E_a = -300\cdot 0.0083\cdot\ln(1E11) = {}^{-}63\ \text{kJ/mol}$$

SMALL ΔE_a LEADS TO HUGE RATE INCREASE

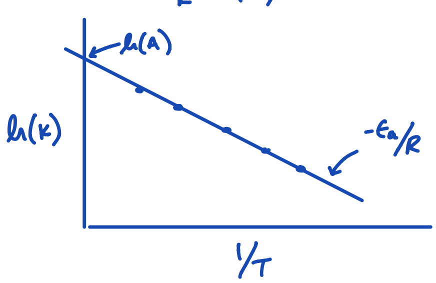


ENZYMES PREPAY TO STABILIZE T.S. BY HAVING UNFULFILLED INTERACTIONS THAT CAN ONLY BE FULFILLED BY INTERMEDIATE.

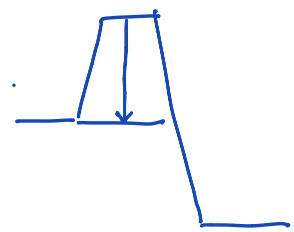
HOW CAN WE MEASURE THIS?

$$\ln(k) = \ln(A) - E_a/RT$$

$$\ln(k) = \frac{-E_a}{R}\cdot\left(\frac{1}{T}\right) + \ln(A)$$



WHAT IF E_a GETS REALLY SMALL?



$E_a = \emptyset$: $k = Ae^{-0/RT}$

$k = A$

SUMMARY:

(1) RATE IS DETERMINED BY HOW OFTEN WE "TRY" REACTION TIMES PROBABILITY OF SUCCESS

$$\left(k = Ae^{-E_a/RT}\right)$$

(2) SMALL CHANGE IN ENERGY BARRIER, HUGE CHANGE IN RATE

(3) CAN BE MEASURED BY PLOTTING $\ln(k)$ AGAINST $1/T$

(4) FOR "BARRIERLESS" TRANSITIONS, LIMIT IS PREFACTOR (DIFFUSION).