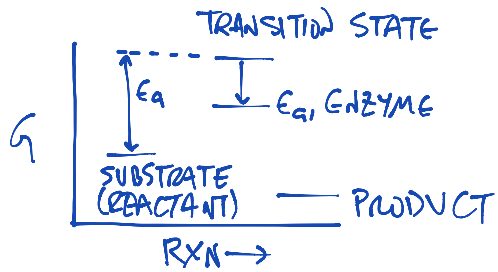
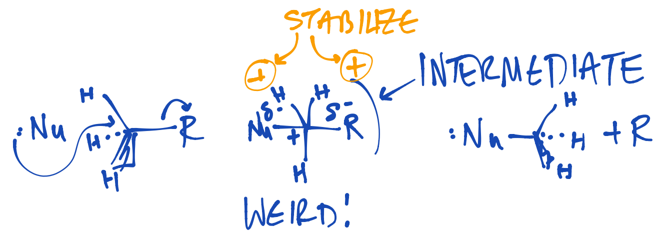




HOW MUCH DO YOU NEED TO STABILIZE TO GET RATE INCREASE?

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

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

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

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

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

THIS GIVES PROBABILITY. WHAT ABOUT RATE?

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

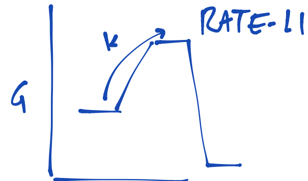
FOR T.S.:

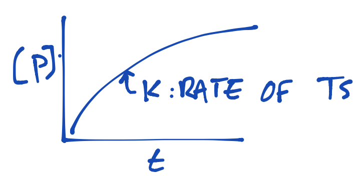
PREFACTOR: TRIES PER UNIT TIME. DIFFUSION (USUALLY) IN BIOLOGY, s^{-1}!

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

$K = \exp(-E_a/RT)$: HOW OFTEN SYSTEM SAMPLES T

RATE-LIMITING STEP. ONLY THING YOU SEE IF YOU WATCH REACTION.





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

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

$$K_{H2O} = A\exp(-E_{a,H2O}/RT) \leftarrow \text{UNCAT RATE}$$

$$\frac{K_{ENZ}}{K_{H2O}} = 1E11 = \frac{\cancel{A}\exp(-E_{a,ENZ}/RT)}{\cancel{A}\exp(-E_{a,H2O}/RT)}$$

$$= \exp(-E_{a,ENZ}/RT) \cdot \exp(E_{a,H2O}/RT)$$

$$= \exp(-E_{a,ENZ}/RT + E_{a,H2O}/RT)$$

$$= \exp((E_{a,H2O} - E_{a,ENZ})/RT) \qquad \Delta E_a = E_{a,ENZ} - E_{a,H2O}$$

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

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

<u>SMALL</u> ΔE_a LEADS TO HUGE RATE INCREASE