

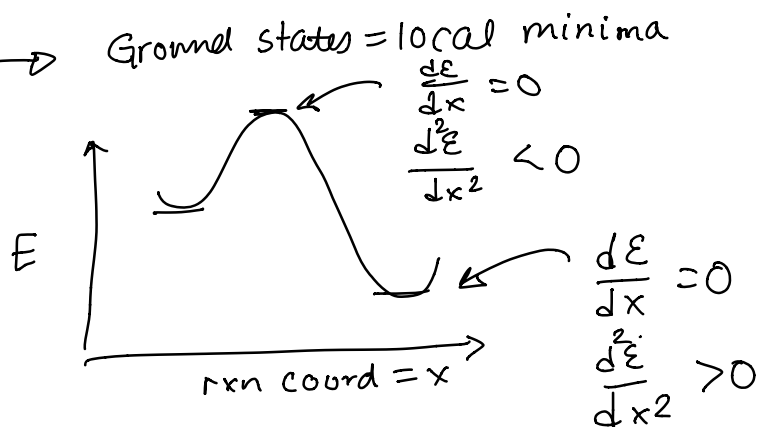
Lecture 13: Kinetics (continued)

Announcements:

- Midterm 1 is still not graded (in progress, though!)
- Problem Set 3 will be posted tomorrow. Due next Thurs.

Today:

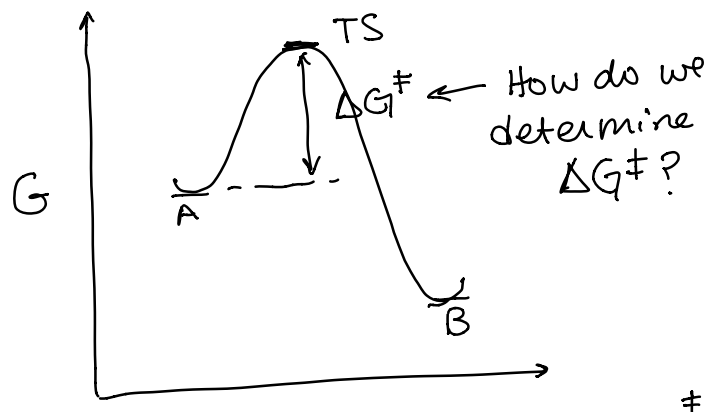
- 1 correction from last time →
- Transition State Theory
- Hammond Postulate
- Kinetic rate laws



Transition State Theory

How do we get information about TS's (intermediates) that not observable?

Simplest Case:
A → B



Recall: $\text{rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A] = k^\ddagger [TS]$

$k^\ddagger \approx \frac{k_B}{h} T \kappa$

k_B Boltzman constant
h Planck's constant
T rate for fastest possible reaction (no barrier) = 1 vibration
κ "kappa" ≈ inefficiency in going over TS. ≈ 1

$\frac{k_B}{h} = 2.083 \times 10^{10} \text{ s}^{-1} \text{ K}^{-1}$
 ↑
 ° Kelvin

@ rt (298 K) $k^\ddagger = 6 \times 10^{12} \text{ s}^{-1} \approx 10^{13} \text{ s}^{-1}$

↑ rate of molecular vibration.

"equilibrium" between A & TS.

$K^\ddagger = \frac{[TS]}{[A]}$

$[TS] = K^\ddagger [A]$

$[TS] = e^{-\Delta G^\ddagger / RT} [A]$

↑ $[TS] = \frac{k[A]}{k^\ddagger}$

Recall:
 $\Delta G = -RT \ln K_{eq}$
 $K_{eq} = e^{-\Delta G / RT}$

$$\cancel{k} \cdot \frac{k[A]}{\cancel{k}^\ddagger} = e^{-\Delta G^\ddagger/RT} [A] \cdot \cancel{k}^\ddagger$$

$$k^\ddagger = \frac{k_B T \bar{h}}{h}$$

$$k = \frac{k_B T \bar{h}}{h} e^{-\Delta G^\ddagger/RT}$$

Relationship between rate (k) & ΔG^\ddagger
 measure rate \Rightarrow Learn ΔG^\ddagger

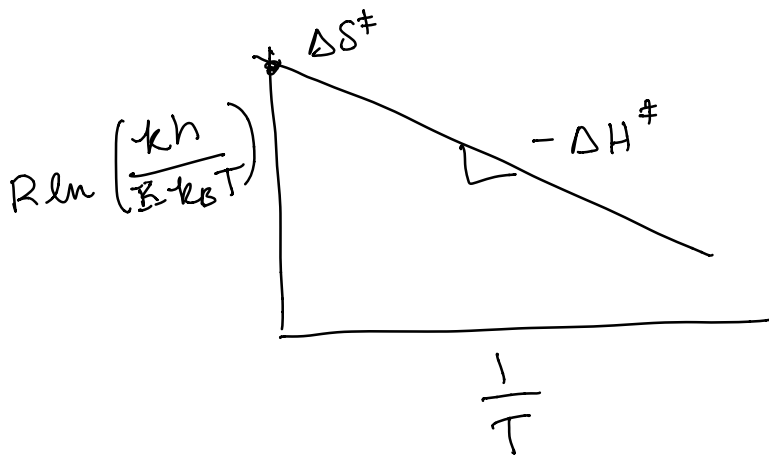
Recall: $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

$$k = \frac{k_B T \bar{h}}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

$$\ln\left(\frac{k h}{\bar{h} k_B T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

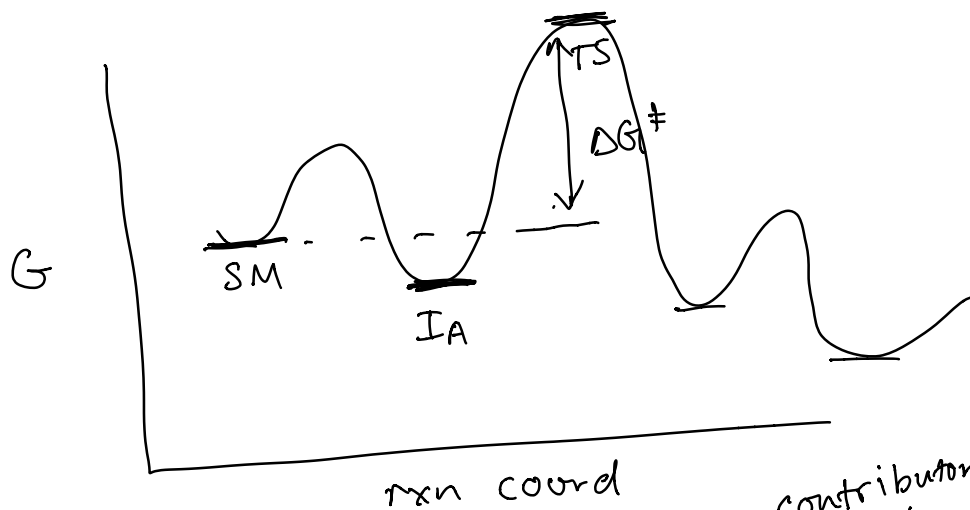
$$y = mx + b$$

\uparrow \uparrow
 $\ln\left(\frac{k h}{\bar{h} k_B T}\right)$ $\frac{1}{T}$



Eyring Equation

Warning: For multistep reactions, you are measuring composites of ΔH^\ddagger & ΔS^\ddagger .



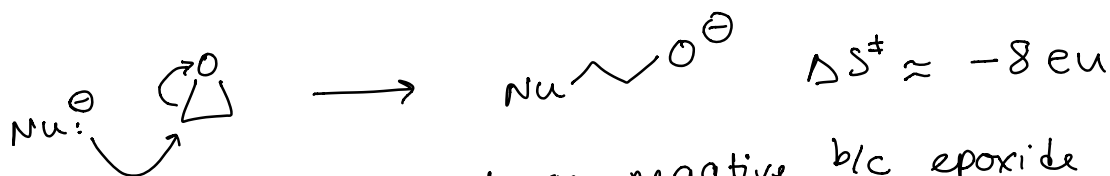
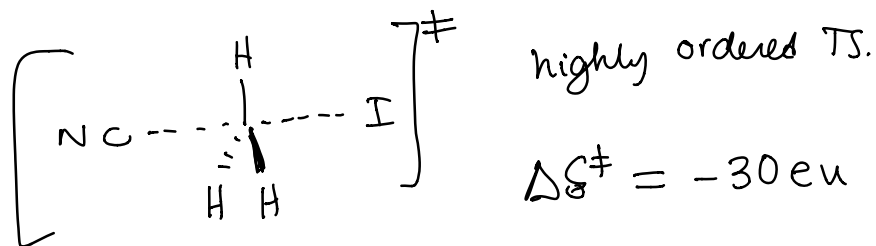
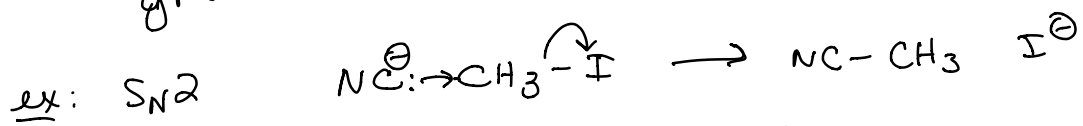
Enthalpy Control: ΔH^\ddagger is major contributor to ΔG^\ddagger .

Entropy Control: $T\Delta S^\ddagger$ is major contributor to ΔG^\ddagger .

↳ Changes w/ Temperature.

Interpretation of ΔS^\ddagger

If $\Delta S^\ddagger < 0 \rightarrow$ TS is more ordered than ground state.



\rightarrow Entropy not as negative b/c epoxide opening (more degrees of freedom).

If $\Delta S^\ddagger > 0$: TS more disordered than GS



In general:

$$-30 \text{ eu} \leq \Delta S^\ddagger \leq +10 \text{ eu}$$

(exceptions for trimolecular TS)

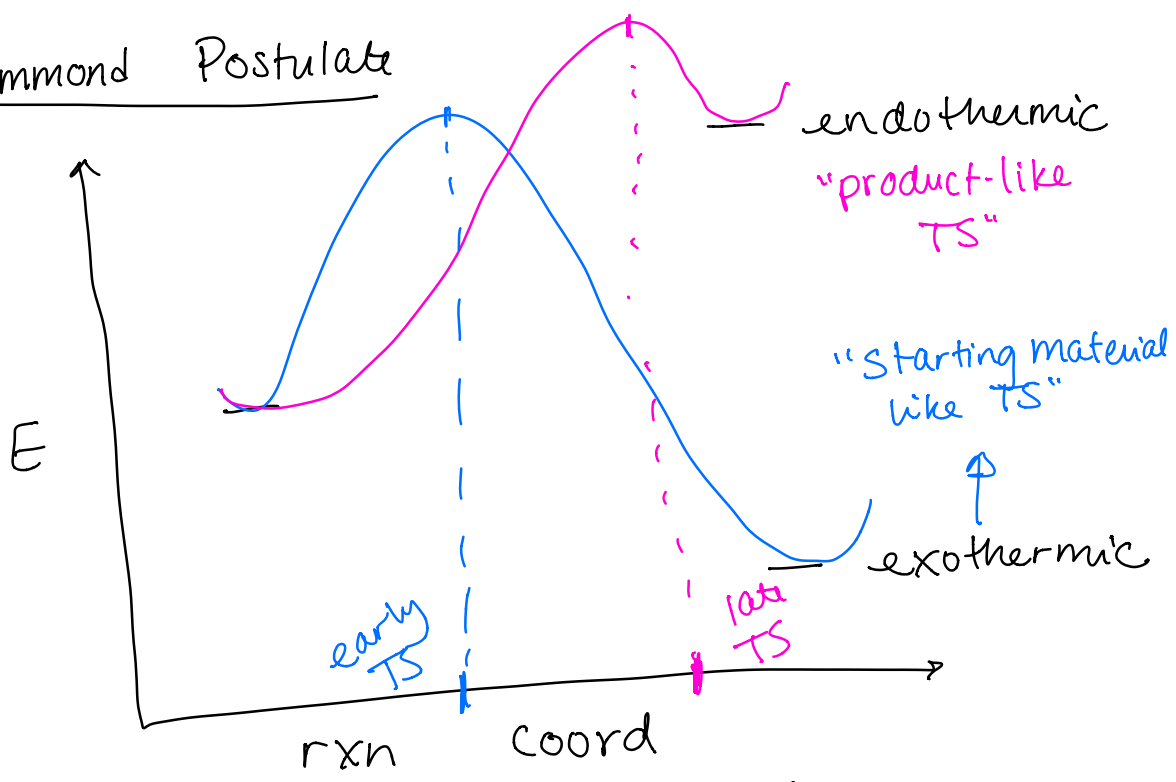
Arrhenius Equation

$$k = A e^{(-E_a/RT)}$$

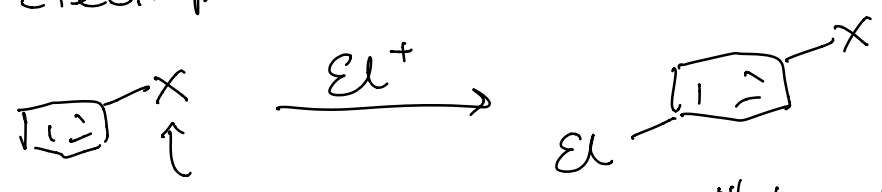
\uparrow related to ΔH^\ddagger
 \uparrow related to ΔS^\ddagger

ΔG^\ddagger ($\frac{\text{kcal}}{\text{mol}}$)	rate (s^{-1})	$t_{1/2}$
3	4.2×10^{10}	1.6×10^{-11}
10	3.6×10^5	2×10^{-6}
20	0.02	33
30	1.2×10^{-9}	6×10^8 (18 years)

Hammond Postulate



ex: Electrophilic Aromatic Substitution



Why do EDG accelerate EAS?

