Rate Laws and Temperature

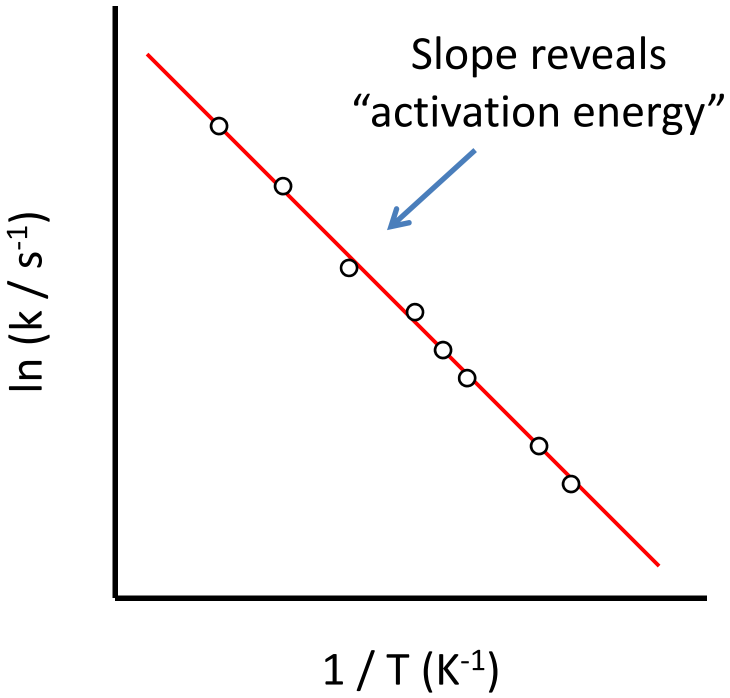
- Suppose we've identified a second-order rate law:

$$v = k[A][B]$$

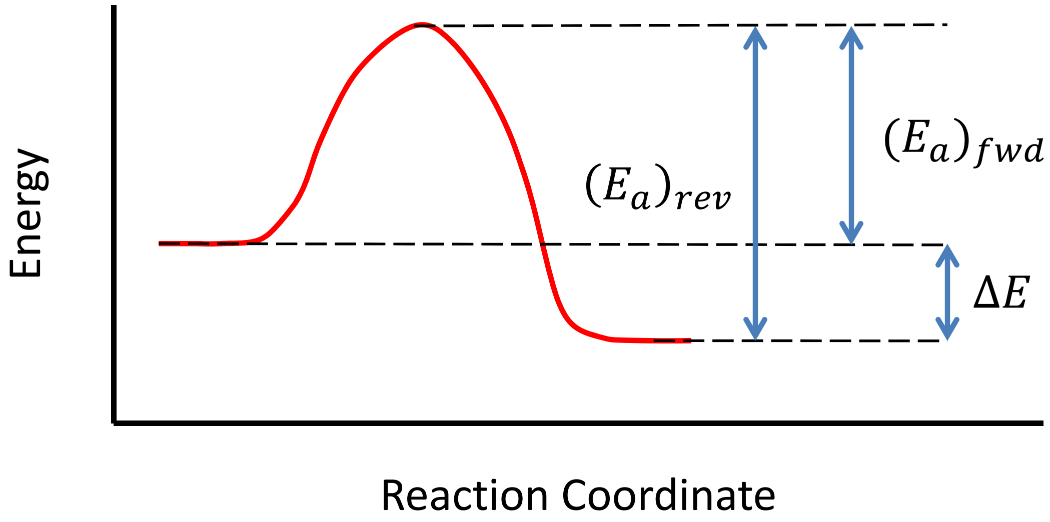
- What changes when we change T?
  - Does rate change?
  - Do concentrations/activities change?

Arrhenius Equation

- Observing rates vs. T
  - Determine *k*
  - Limited temperature range (~25 ^{0}C)
- Result (equivalent):
  - $k = Ae^{-E_a/RT}$
  - $\ln k = -\left(\frac{E_a}{RT}\right) + \ln A$
  - $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$



What is Activation Energy?



- **Reaction coordinate** (x-axis)**:** The degree to which a reaction has completed (recall $d\alpha$ from equilibrium)
- **Reaction energy** (y-axis): The energy state of products vs. reactants

Very High Temperatures

- According to Arrhenius Equation:

$$v = A[x_1]^{n_1}[x_2]^{n_2} \dots e^{-\frac{E_a}{RT}}$$

- At high temperatures, $e^{-\frac{E_a}{RT}} \rightarrow 1$, so

$$v = A[x_1]^{n_1}[x_2]^{n_2} \dots$$

- This factor (A) must tell us something about frequency of collisions, collision efficiency, etc. (more later)

Problems with Arrhenius Approach

- Collision rates can be calculated, and do not always correspond to observed value of A
- Some reactions have higher values of A than are theoretically possible
- Collisions don’t account for chemical structure and rearrangement

Transition State Theory (A New Hope)

- Observations:
  - Collisions don’t account for *molecular structure* during a reaction
  - *Activation energy* seems to work well

- A New Theory:
  - Transition state accounts for structure
  - “Energetically activated” complex

Transition State

- Simple Reaction:

$$M + N \xrightarrow{k_{obs}} P$$

- Written with transition state:

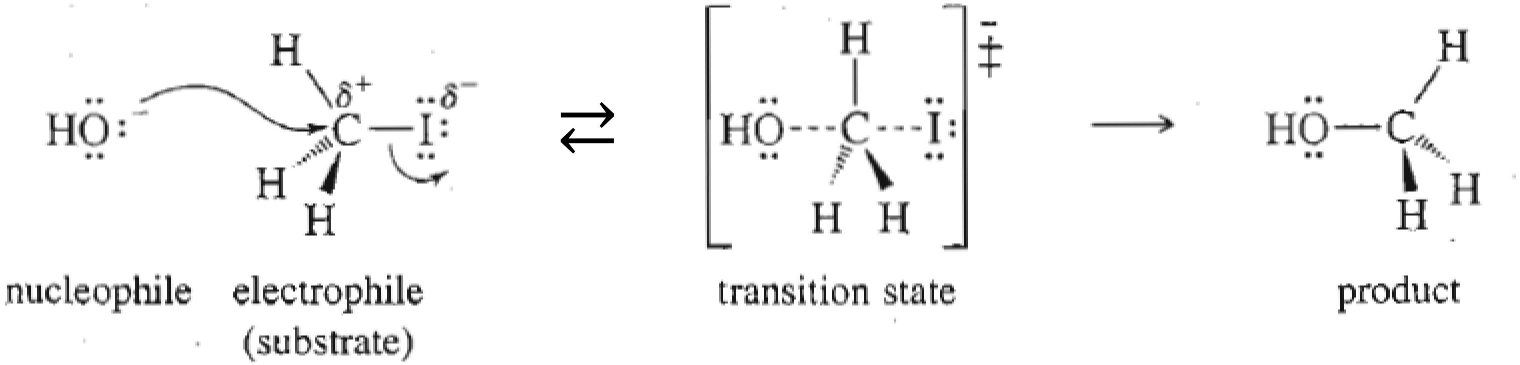
$$M + N \overset{K^{\ddagger}}{\rightleftarrows} [MN]^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

Transition State Example

- Transition state reaction:

$$M + N \overset{K^{\ddagger}}{\rightleftarrows} [MN]^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

- SN_2 Reaction (where OH = SCN):



Transition State Concepts

- Transition state reaction:

$$M + N \overset{K^{\ddagger}}{\rightleftarrows} [MN]^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

- What is $K^{\ddagger}$?
  - – Fast equilibrium between $M + N$ and $[MN]^{\ddagger}$
  - – Establishes a *transition state energy*

$$\Delta\bar{G}^{\ddagger} = -RT\ln K^{\ddagger}$$

Transition State Concepts

- Transition state reaction:

$$M + N \overset{K^{\ddagger}}{\rightleftarrows} [MN]^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

- What is $k^{\ddagger}$?
  - *Universal* rate constant: $k^{\ddagger} = \frac{k_B T}{h} = 6.21 \times 10^{12}\ s^{-1}$ (at 298 K)
  - Approximate frequency of one bond vibration

Relating k_{obs} to Transition State Parameters

- Simple Reaction:

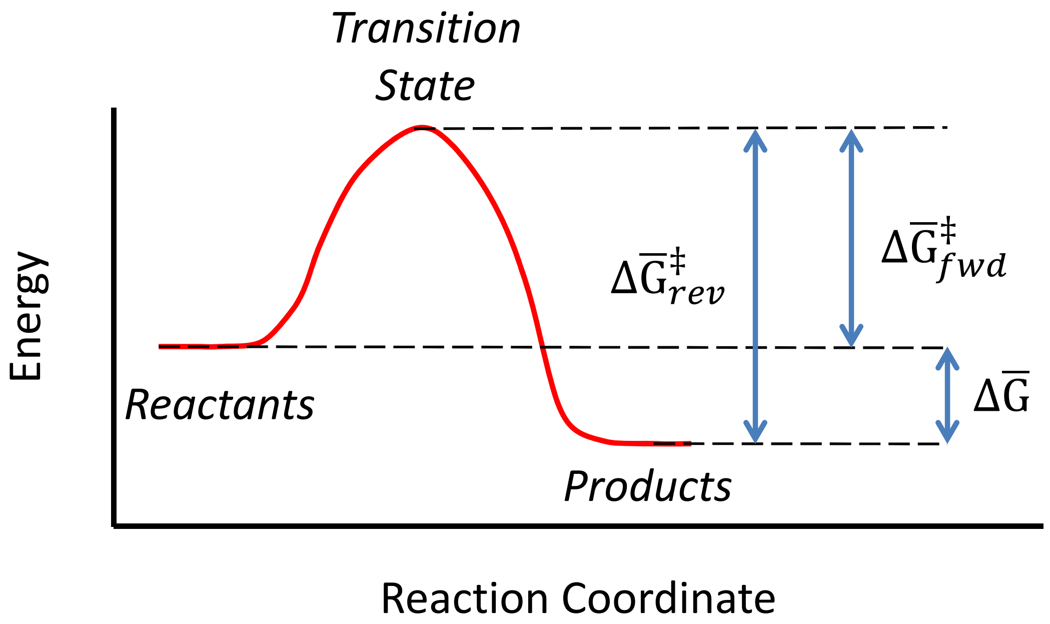
$$M + N \xrightarrow{k_{obs}} P$$

- Written with transition state:

$$M + N \overset{K^{\ddagger}}{\rightleftarrows} [MN]^{\ddagger} \overset{k^{\ddagger}}{\rightarrow} P$$

- How do we relate these two models?

A Slightly New Paradigm



- Therefore:

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

- **Question:** Is this reaction at equilibrium?

Enthalpies and Entropies

- We know that:

$$\Delta\bar{G}^{\ddagger} = \Delta\overline{H}^{\ddagger} - T\Delta\bar{S}^{\ddagger}$$

- It must be true that:

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

- Hold it! What about Arrhenius?

Temperature Dependence

- Slope of $\ln k$ vs. 1/T:

$$\frac{\partial \ln k}{\partial(1/T)} = -\frac{(RT + \Delta\overline{H}^{\ddagger})}{R}$$

- Compare to Arrhenius:

$$\frac{\partial \ln k}{\partial(1/T)} = -\frac{(E_a)}{R}$$

Comparing TS Theory to Arrhenius

- Transition state theory predicts a not-so-linear dependence of $\ln k$ vs. 1/T

$$E_{a,obs} = RT + \Delta \overline{H}^{\ddagger}$$

- **But:** RT doesn't change much from 250 K (2.1 kJ mol^{-1}) to 350 K (2.9 kJ)
  - Deviation from linearity hard to detect

- **Also:** Typical $\Delta \overline{H}^{\ddagger}$ is ~40 kJ mol^{-1}. Therefore:

$$E_a \approx \Delta \overline{\mathrm{H}}^{\ddagger}$$

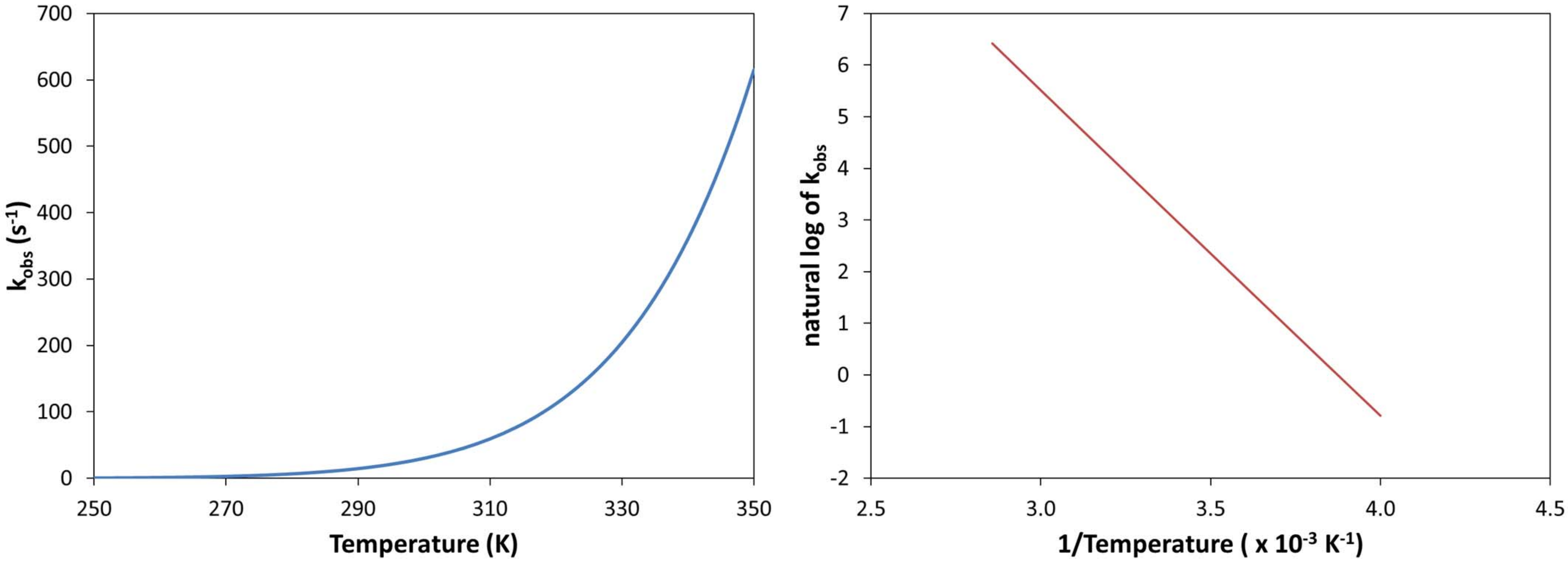
Comparing TS Theory to Arrhenius

- What about the collision term A?

$$\Delta\bar{S}^{\ddagger} \approx R\ln\left(\frac{Ah}{k_B T_{avg}}\right) = R\left(\ln A - \ln\frac{k_B T_{avg}}{h}\right)$$

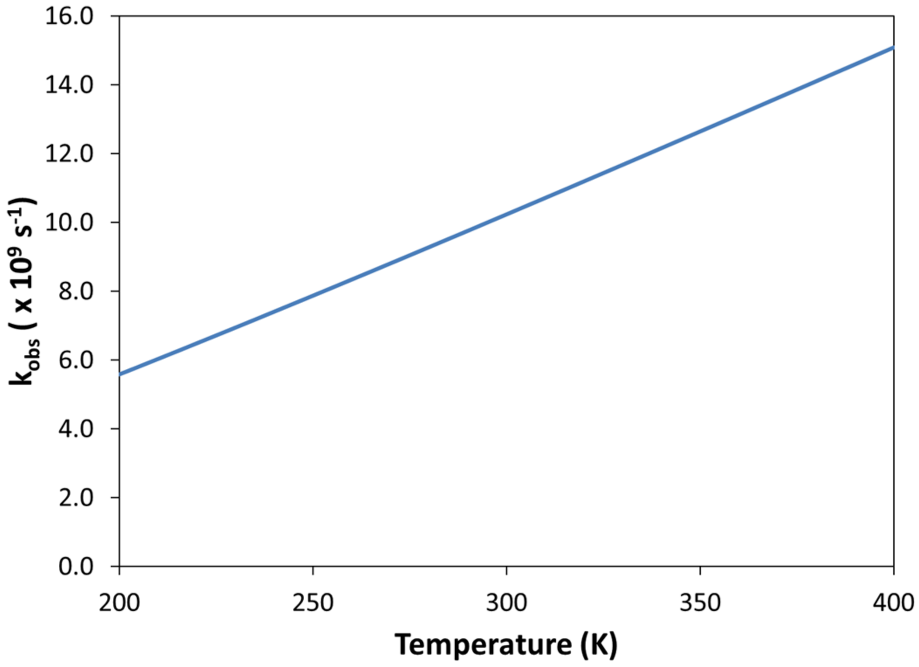
- A is typically less than $\frac{k_B T_{avg}}{h}$, so entropies are usually negative

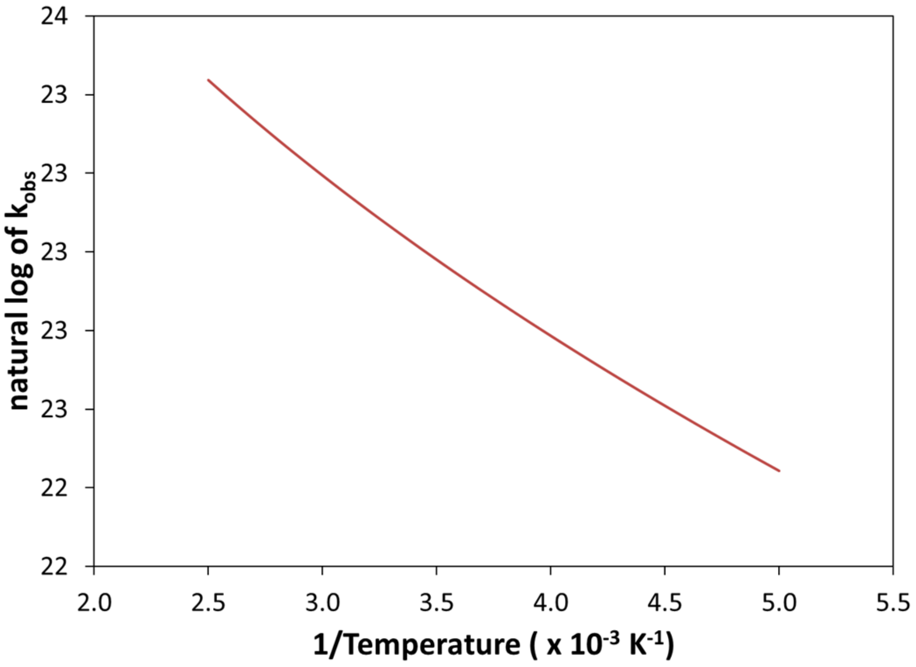
But Is It Linear?



$\Delta\overline{H}^{\ddagger} = 50\ \mathrm{kJ\ mol^{-1}}$ and $\Delta\bar{S}^{\ddagger} = -50\ \mathrm{J\ mol^{-1}\ K^{-1}}$

But Is It Linear?





$$\Delta\overline{H}^{\ddagger} = 0.1\ \mathrm{kJ\ mol^{-1}}\ \text{and}\ \Delta\bar{S}^{\ddagger} = 50\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Problems With Transition States

- What about complex reactions?
  - What's the transition state in binding?
  - What's the transition state in folding?

- Challenges of interpreting entropy and enthalpy