Transition State Theory

$$A \xrightarrow{k_1} P$$

⬇

$$A \underset{k^{\ddagger}}{\overset{k_1}{\rightleftharpoons}} [TS]^{\ddagger} \longrightarrow P$$

reaction coordinate
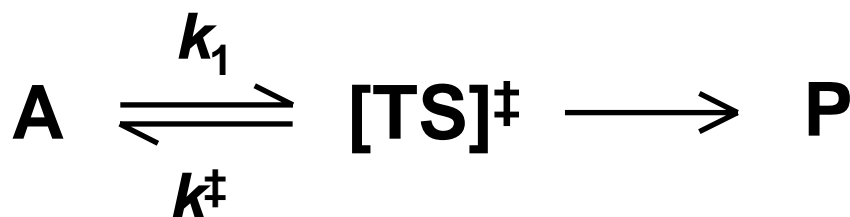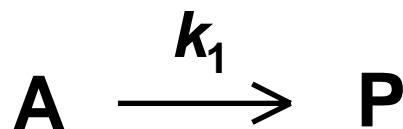
Previously,

$$\frac{n_{TS}}{n_A} = e^{-(E_{TS} - E_A)/k_B T} = e^{-\varepsilon/k_B T}$$

But this is a microscopic equation. For thermodynamic analysis, need functions of whole systems.

Transition State Theory

Analogous expression in the bulk *would* be:

$$\frac{N_{TS}}{N_A} = e^{-(E_{TS} - E_A)/RT} = e^{-\Delta E^{\ddagger}/RT}$$

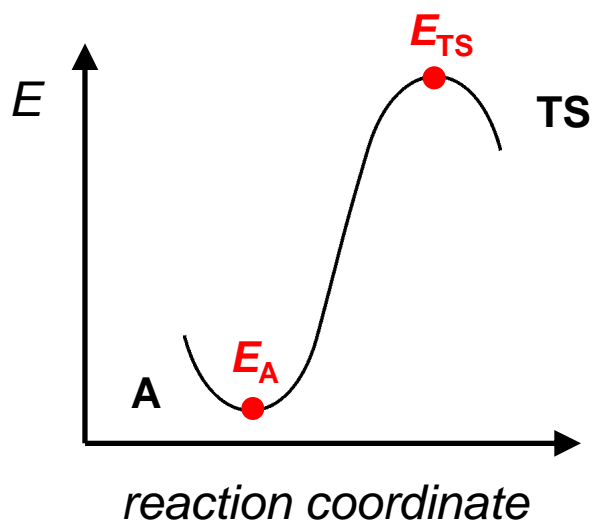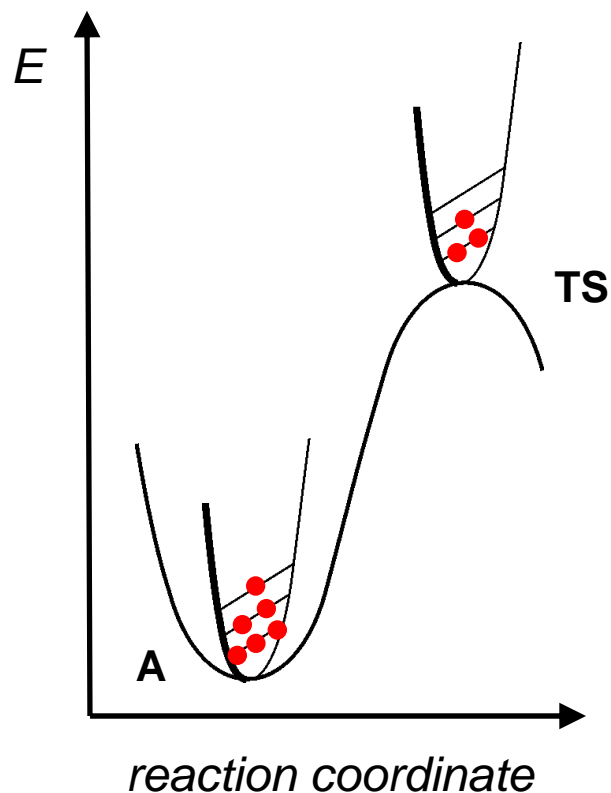But this equation only describes zero-point energy difference. *Not correct.*

Transition State Theory

reaction coordinate

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$$\frac{N_{TS}}{N_A} = e^{-(E_{TS}-E_A)/RT} = e^{-\Delta E^{\ddagger}/RT}$$

But this equation only describes zero-point energy difference. *Only correct at zero K.*

Instead, need to express in terms of distribution of molecules in vibrational modes (that depends on *T*).

Transition State Theory

E

no vibrational states in RC "mode"

TS

A

reaction coordinate

Analogous expression in the bulk *would* be:

$$\frac{N_{TS}}{N_A} = e^{-(E_{TS} - E_A)/RT} = e^{-\Delta E^{\ddagger}/RT}$$

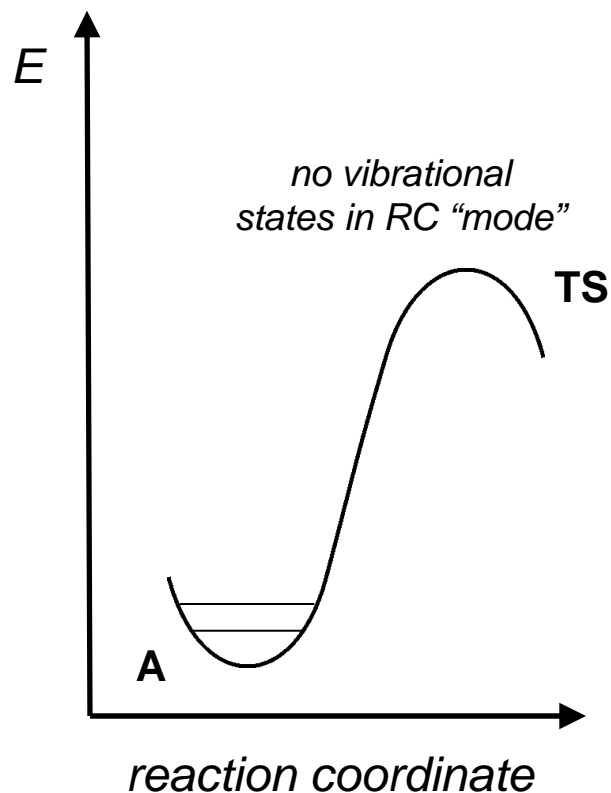But this equation only describes zero-point energy difference. *Only correct at zero K.*

Instead, need to express in terms of distribution of molecules in vibrational modes (that depends on *T*).

Challenge: How to deal with that funny reaction-coordinate vibrational mode? Can't describe energetics until we do.

Transition State Theory:
Zero-Point Energies and Partition Functions

E

$E_{TS,0K}$

TS

$E_{A,0K}$

A

reaction coordinate
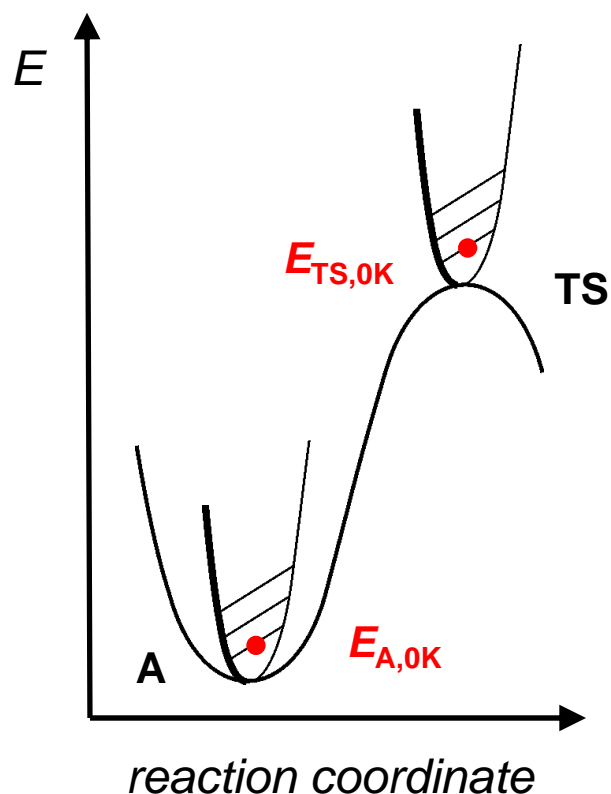
Define "partition function" **Q** as distribution of energy states for each degree of freedom

Q defines how these states are filled at temperature *T*.

$$\mathbf{Q} = q_{vib}\,q_{rot}\,q_{trans} = (q_{vib1}\,q_{vib2}\cdots)\cdots$$

$$Q_A = \frac{N_A}{N_{A,0K}} \qquad Q_{TS}\,\boxed{q_{vibRC}} = \frac{N_{TS}}{N_{TS,0K}}$$

Reaction coordinate mode can't be represented by partition function. So we include extra factor q_{vibRC}.

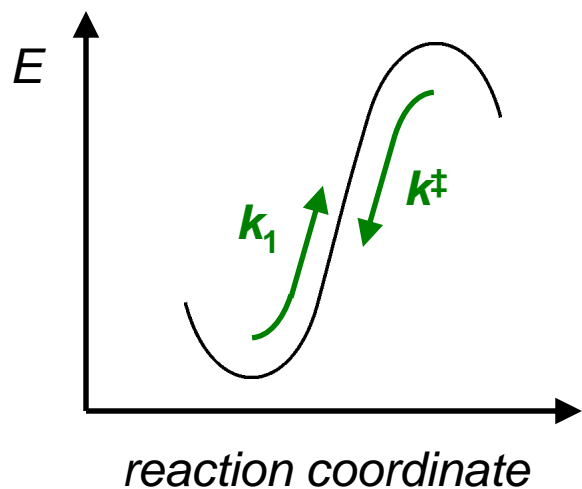# Transition State Theory: Zero-Point Energies and Partition Functions

reaction coordinate
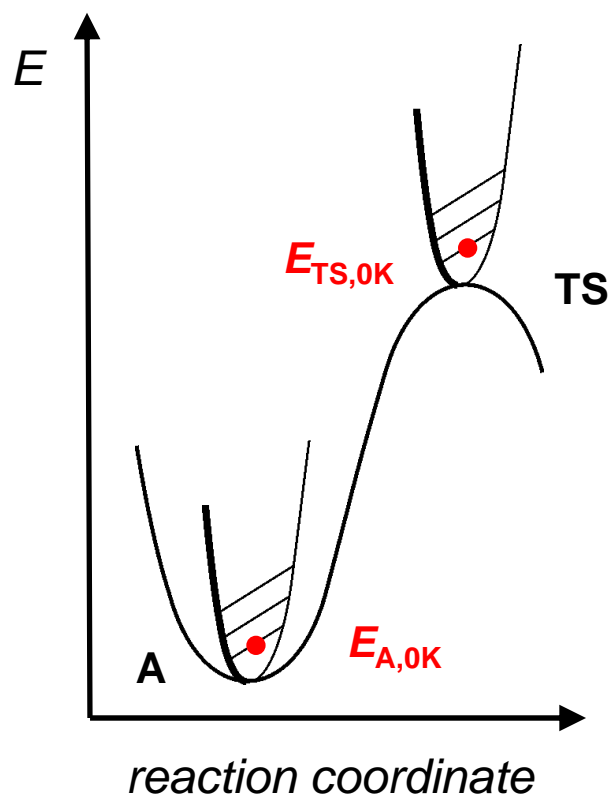
$$K^{\ddagger} = \frac{k_1}{k^{\ddagger}} = \frac{N_{TS}}{N_A} = \frac{q_{vibRC} Q_{TS} N_{TS,0K}}{Q_A N_{A,0K}}$$

$$= q_{vibRC} \frac{Q_{TS}}{Q_A} e^{-\Delta E_{0K}^{\ddagger} / RT}$$

$$= q_{vibRC} e^{-\Delta G^{\ddagger} / RT}$$

(with $\Delta G^{\ddagger}$ representing free energy of activation for any temperature)

Transition State Theory:
Zero-Point Energies and Partition Functions

$$\frac{k_1}{k^{\ddagger}} = q_{vibRC}\, e^{-\Delta G^{\ddagger}/RT}$$

reaction coordinate

$$k_1 = k^{\ddagger}\left(\frac{k_B T}{h\nu^{\ddagger}}\right) e^{-\Delta G^{\ddagger}/RT}$$

standard vibrational partition function

We assume $k^{\ddagger} = \nu^{\ddagger}$.

$$k_1 = \frac{k_B T}{h}\, e^{-\Delta G^{\ddagger}/RT}$$

Transition State Theory: The Eyring Equation

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

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}, \text{ so}$$

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

Eyring equation.

Relates rate constant to T in a physical way.

$\Delta H^{\ddagger}$: Enthalpy required to reach transition state (like E_a)

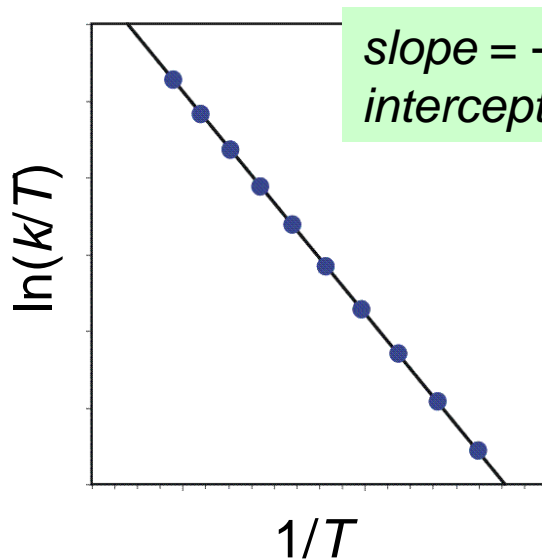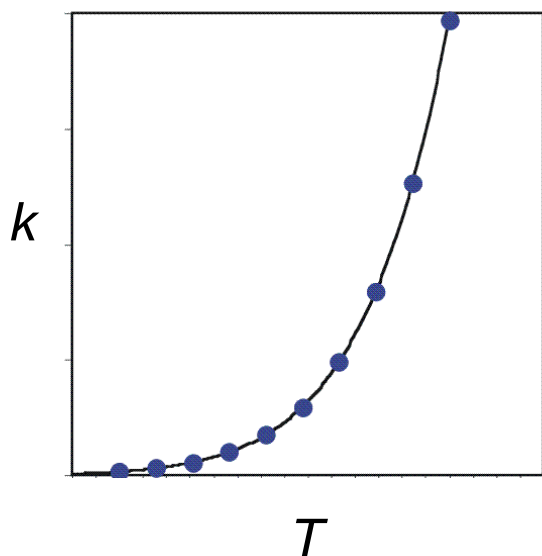$\Delta S^{\ddagger}$: Entropy lost/gained getting to transition state

Transition State Theory: Eyring Plots

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

can also be written:

$$\ln\left(\frac{k_{rxn}}{T}\right) = \left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) - \frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right)$$

(Has form y = mx + b.)

slope = $-\Delta H^{\ddagger}/R$
intercept = $\ln(k_B/h) + \Delta S^{\ddagger}/R$

Different from Arrhenius plot—vertical axis $\ln(k/T)$.

Transition State Theory: Eyring and Arrhenius

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

Has Arrhenius form!

But, E_a and ΔH vary (slightly) differently w/ T.

Fix this by re-writing as

$$k_{rxn} = \underbrace{\frac{e k_B T}{h} e^{\Delta S^{\ddagger}/R}}_{A} e^{\overbrace{-(\Delta H^{\ddagger}+RT)/RT}^{E_a}}$$

$$A = \frac{e k_B T}{h} e^{\Delta S^{\ddagger}/R}; \quad E_a = \Delta H^{\ddagger} + RT$$

Makes intuitive sense.

Better to graph than transform.

Transition State Theory: Activation Parameters

What does $\Delta H^{\ddagger}$ tell us about a reaction?
$\Delta H^{\ddagger}$ dominates $\Delta G^{\ddagger}$.

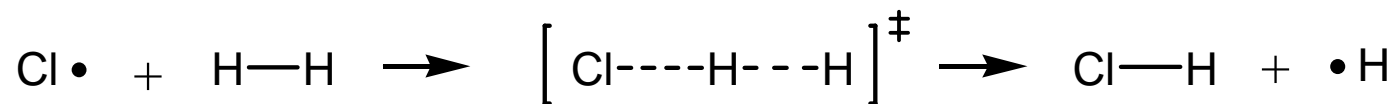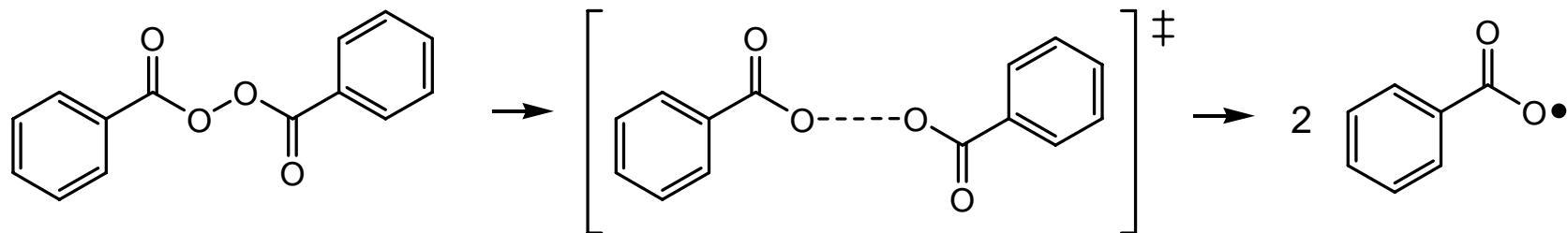| $\Delta H^{\ddagger}$ (kcal/mol) (for $\Delta S^{\ddagger} = 0$)	$t_{1/2}$	
5	30 ns	
10	2.6 μs	
15	12 ms	
20	57 s	*chemists work here.*
25	3.2 days	
30	41 years	

Transition State Theory: Activation Parameters

What does $\Delta S^{\ddagger}$ tell us about a reaction?
Illustrates structure of transition state.

Obvious examples:

$$Cl \bullet \; + \; H\text{—}H \quad \longrightarrow \quad \left[Cl\text{----}H\text{--}\text{-}H \right]^{\ddagger} \quad \longrightarrow \quad Cl\text{—}H \; + \; \bullet H$$

$$\Delta S^{\ddagger} = \text{-12 cal/mol·K} \quad \text{(e.u., entropy units)}$$

$$\Delta S^{\ddagger} = \text{+10 cal/mol·K}$$