

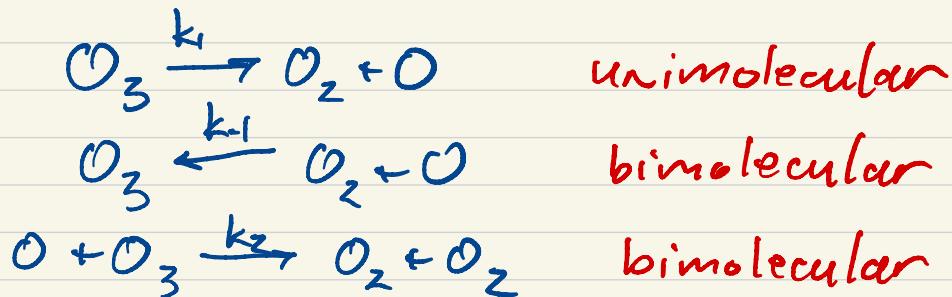
Reaction Rate Theory

Have seen how rate laws can in general have complicated forms.

Postulate that

1. reactions occur through a sequence of elementary steps
2. observed reactions involve a linear combination of elementary steps
3. elementary steps have a distinct molecularity reflective of how they occur physically
4. elementary steps may create intermediates that are produced and consumed through progression through steps

Easiest to think of in gas-phase context:



O is an intermediate - created & destroyed in overall reaction

rate of individual step goes as molecularity

$$r_1 = k_1 C_{\text{O}_3} \quad r_1 = k_{-1} C_{\text{O}_2} C_{\text{O}}$$

$$r_2 = k_2 C_{\text{O}} \cdot C_{\text{O}_3} \quad r_{-2} = k_{-2} C_{\text{O}_2}^2 \approx 0$$

Observed rate convolutes these

$$r_{O_3} = -k_1 C_{O_3} + k_{-1} C_{O_2} C_O - k_2 C_{O_3}$$

$$r_{O_2} = k_1 C_{O_3} - k_{-1} C_{O_2} C_O + 2 k_2 C_{O_3} C_O$$

If $r_2 \ll r_{1,-1}$ $r_1 - r_{-1} \approx 0$ Q.E.D

$$C_O \approx \frac{k_1}{k_{-1}} \frac{C_{O_3}}{C_{O_2}}$$

$$r_{O_2} = 2 k_2 \cdot \frac{k_1}{k_{-1}} C_{O_3} \cdot \left(\frac{C_{O_3}}{C_{O_2}} \right)$$

$$r_{O_2} \propto k_{app} C_{O_3}^2 / C_{O_2}$$

effective
rate

$$r_2 \gg r_{-1} \Rightarrow r_{O_2} = k_1 C_{O_3}$$

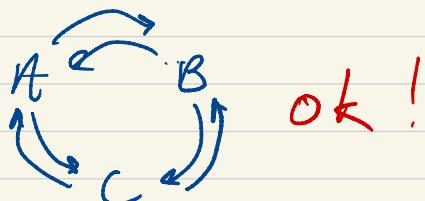
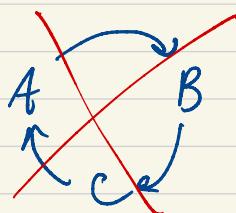
In intermediate case, would have to integrate.

Principle of detailed balance says that at equilibrium, probability to jump from reactant to product or vice versa must be identical.

$$r_f = r_r$$

Implies

Principle of microscopic reversibility



OK !

For an elementary reaction, can write ^{unimolecular}

$$r_f = k_f C_A \quad r_r = k_r C_B$$

$$r_{\text{net}} = r_f - r_r = 0 \quad @ \text{ equilibrium}$$

$$k_f C_A^{\text{eq}} - k_r C_B^{\text{eq}} = 0$$

$$\frac{k_f}{k_r} = \frac{C_B^{\text{eq}}}{C_A^{\text{eq}}} = K_{\text{eq}}$$

Allows us to write in general

$$r_{\text{net}} = r_f - r_r = r_f \left(1 - \frac{r_r}{r_0} \right)$$

$$= r_f \left(1 - \frac{k_r}{k_f} \frac{C_B}{C_A} \right)$$

$$= r_f \left(1 - Q/K_{\text{eq}} \right)$$

where $Q = \frac{C_B}{C_A}$ mass action expression

$$\beta = Q/K_{\text{eq}} = e^{-\Delta G/kT}$$
 "reversibility"

measures distance from equilibrium

$$r_{\text{net}} = \begin{cases} > 0 & \beta < 1 & \Delta G > 0 \\ 0 & \beta = 1 & \Delta G = 0 \\ < 0 & \beta > 1 & \Delta G < 0 \end{cases}$$

$$\beta \rightarrow 0 \quad \text{"irreversible"} \quad r_r \rightarrow 0$$
$$\Delta G \gg \Delta G^\circ$$

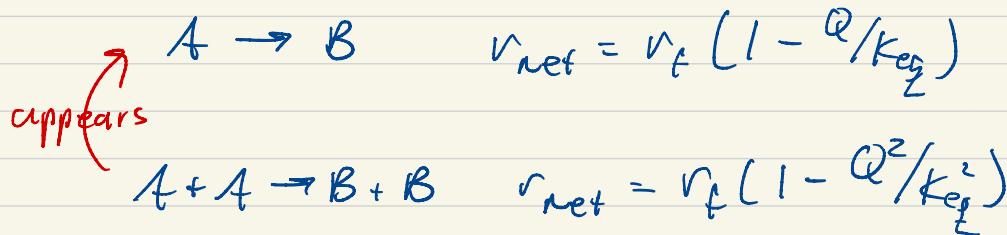
$$\beta \rightarrow 1 \quad \Delta G \rightarrow \Delta G^\circ \quad \text{equilibrated}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = -RT \ln K + RT \ln Q$$

Same idea for bimolecular,
...

CAUTION Form is correct
for elementary reactions.

For non-elementary reactions,
say form must hold, EXCEPT
ambiguity arises because
molecularity is unknown



At equilibrium, must have

$$\frac{C_B}{C_A} = K_c \quad \text{and} \quad r_A - r_B = 0$$

$$k_1 C_A = k_{-1} C_B$$

$$\Rightarrow K_c = \frac{k_1}{k_{-1}}$$

Arrhenius form

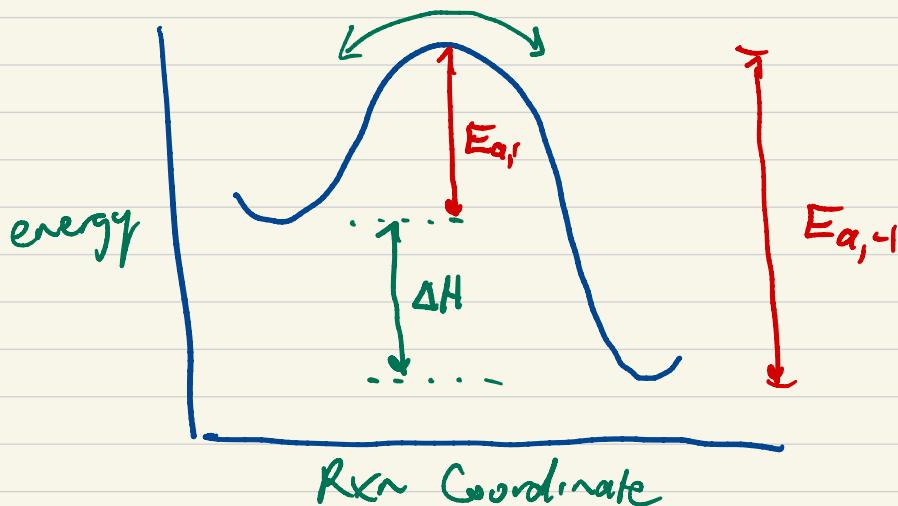
$$\ln K = \ln k_1 - \ln k_{-1}$$

$$-R \frac{\partial \ln K}{\partial T} = -R \frac{\partial \ln k_1}{\partial T} + R \frac{\partial \ln k_{-1}}{\partial T}$$

$$\Delta H$$

$$E_{a,1}$$

$$E_{a,-1}$$



Suggests "collision theory"

- Reactions occur when molecules collide
- Successful events are when collision energy $> E_a$

We can model this!



How often do molecules collide?

Statistical Q:

$$Z = \langle v \rangle \sigma_{AB} \cdot \frac{N_B}{V} \quad \text{collisions / A. time}$$

$$\langle v \rangle = \left(\frac{8 k_B T}{\pi m} \right)^{1/2} \quad \text{mean speed}$$

$$\sigma_{AB} = \pi d_{AB}^2 \quad \text{collision cross-section (area)}$$

$$d_{AB} = \frac{1}{2}(d_A + d_B)$$

Total collisions

$$Z_{\text{tot}} = Z \cdot \frac{N_A}{V} = \sigma_{AB} \cdot \langle v \rangle \cdot C_A \cdot C_B \cdot N_A^2$$

Energy E :

Collisions more energetic than E_a ?

$$P(E > E_a) = e^{-E_a/kT} \quad \text{Boltzmann}$$

$$\text{rate} = \overline{\sigma_{AB}} \langle v \rangle N_{AV} e^{-E_a/kT} C_A C_B$$

collisions
vol. time

$$r = \overline{\sigma_{AB}} \langle v \rangle N_{AV} e^{-E_a/kT} C_A C_B$$

molec
vol. time

A $e^{-E_a/kT}$

Success!! Correct form. (ish.)

$$-k_B \frac{d ln k}{dT} = E_A^* = E_a + \frac{1}{2}RT$$

predicts weak
T-dependence
from it



$$k_{\text{pred}} \sim 10^{12} \text{ M}^{-1}\text{s}^{-1}$$

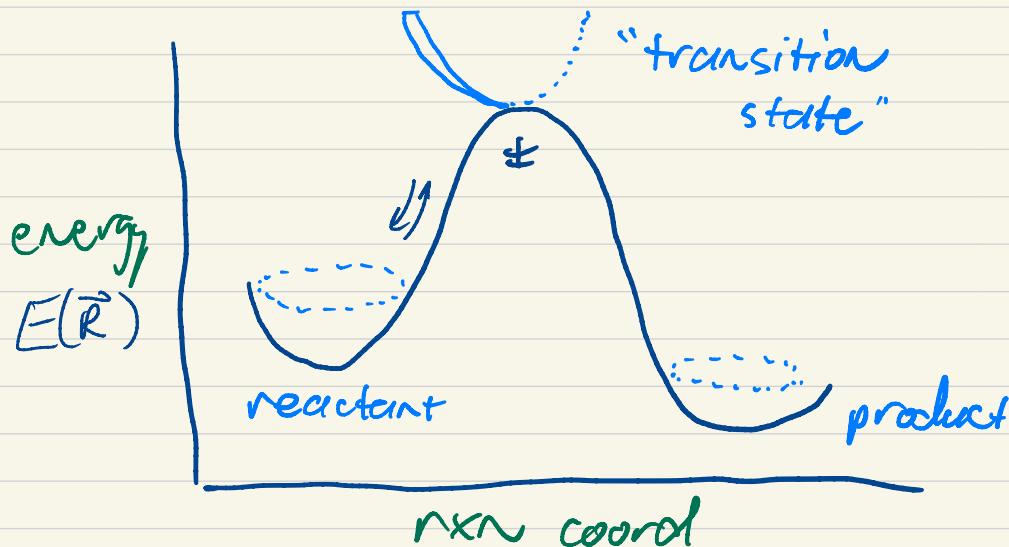
$$k_{\text{obs}} \sim 10^6 \text{ M}^{-1}\text{s}^{-1}$$

ouch

not great

Assumption that all collisions are successful
is too generous.

Molecular view



Molecules "live" on a "potential energy surface" (PES) that is a function of atom positions, $E(\vec{R})$

Reaction proceeds by molecule traveling along that landscape from reactants to products

That landscape is given by QM and manifested in kinetics + thermo

$$\hat{H}\Psi = (KE + V_{ee} + V_{ne})\Psi = E_e\Psi$$

"Born-Oppenheimer" approximation

$$E(\vec{R}) = E_e + V_{nn}$$

$$\Delta E_{rxN} = E(\vec{R}_{\text{prob}}) - E(\vec{R}_{\text{react}})$$

$$\text{Where } \nabla_R E(\vec{R}_j) = 0$$

If we knew $E(\vec{R})$, we could use Newton's law to "propagate" molecules over landscape. Called Molecular Dynamics. Possible, very difficult computationally expensive, not useful for organizing / explaining.

Eyring, Laidler

Thermodynamic / statistical mechanic
view

Molecules "wiggle" within those wells, captured in partition function

$$Q_j(T) = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}}$$

$$\text{eg } Q_{\text{vib}}(T) = \sum_n e^{-nh\nu/kT} = \frac{1}{1 - e^{-h\nu/kT}}$$

ν : freq of vibration

$$A(T) = E - RT \ln Q(T)$$

$$G(T) = A(T) + PV$$

$$K(T) = \frac{Q_{\text{prod}}^{\circ}}{Q_{\text{react}}^{\circ}} e^{-\Delta E_{\text{act}}/kT}$$

Rationalizes thermodynamics...

Eyring (1930's) had the epiphany to apply these same concepts to kinetics.

Activated-complex theory Transition State Theory

Postulates existence of an "activated state" between reactants and products.

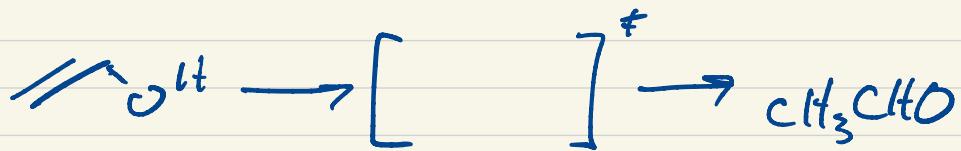
"Point of no return" - every visit to that point leads irreversibly to product

Called the "transition state".
Lowest free energy passage from reactants to products.

$$\nabla_r E(TS) = 0$$

$$\frac{\partial^2 E}{\partial r_{\text{rea}}^2} < 0 \quad \text{"imaginary" mode}$$

Example



- illustrate on WebMO
- key observation is that curvature along rxn coord is < 0 @ TS.

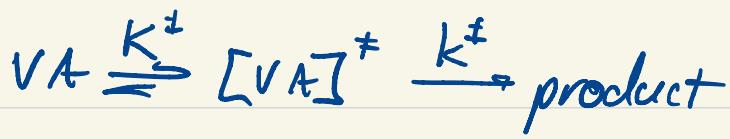
"imaginary mode"

$$\gamma^{\ddagger} \propto \sqrt{k} = \text{imaginary}$$

$$\Delta E^{\ddagger}(0) \sim 216 \text{ kJ/mol}$$

Quantitative model:

- rxn coord exists
- dividing surface b/w reactants + products
- special region on dividing surface called "transition state"
- equilibrium between reactants + TS



- harmonic form of rxn coord near TS

rate = $k^\pm C_\pm$

k^\pm 1st order
/time

$$\begin{aligned} C_\pm &= K^\pm C_{VA} \\ &= k^\pm k^\pm C_{VA} \end{aligned}$$

If we assume motion along rxn coord is harmonic:

prefactor

$$\text{rate} = \underbrace{\frac{k_B T}{h}}_{\text{s}^{-1}} \cdot K^\pm C_{VA}$$

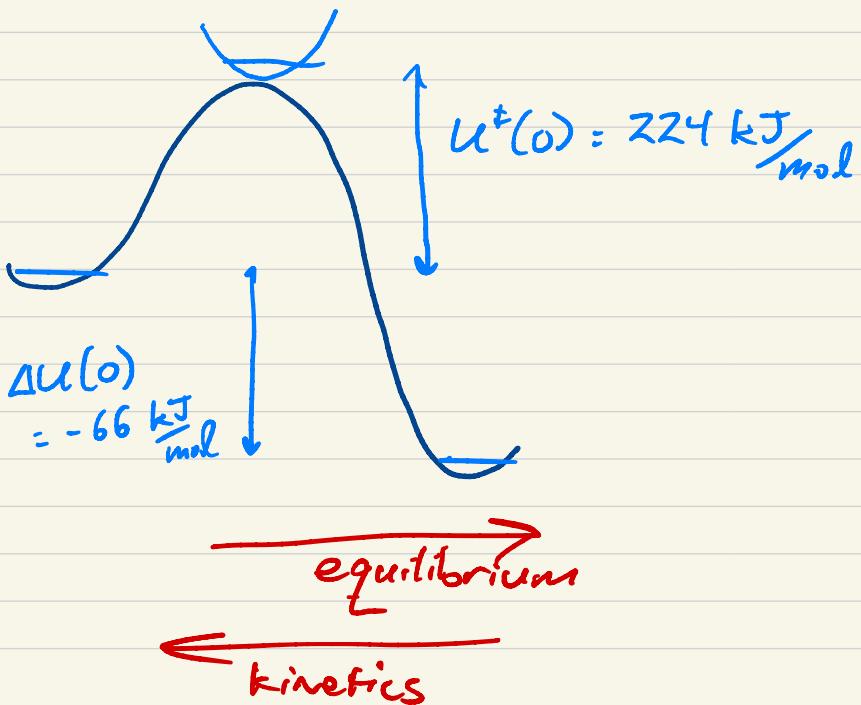
From statistical mechanics we know how to get an equilibrium const:

$$K^\pm = \frac{g_\pm^\circ(T)}{g_{VA}^\circ(T)} e^{-\Delta U(0)/k_B T}$$

$$k(T) = \frac{k_B T}{h} \frac{\mathcal{E}^\circ(T)}{\mathcal{E}_{\text{vib}}^\circ(T)} e^{-\Delta U^\circ(T)/k_B T}$$

$$\mathcal{E}^\circ(T) = \mathcal{E}_{\text{trans}}^\circ \mathcal{E}_{\text{vib}}^\circ \mathcal{E}_{\text{rot}}$$

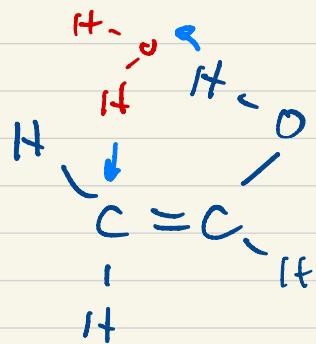
Same sum as before, except, $\mathcal{E}_{\text{vib}}^\circ$ has only $3n-7$ contributions — reaction coord “vibration” excluded.



See graphs. Due to Boltzmann factor, k is tiny, $t^{1/2}$ huge.

Is a container of VA stable forever? Maybe. Maybe not.

Other pathways may exist, involving eg catalyst



Thermodynamic view

Because K^\ddagger is an equilibrium const, can write

$$\text{in isochoric } K^\ddagger(T) = e^{-\Delta U^\ddagger(T)/kT}$$

S.S. $= e^{\Delta S^\ddagger/k} e^{-\Delta U^\ddagger/kT}$

$$k(T) = \frac{k_B T}{h} e^{\Delta S^\ddagger/k} e^{-\Delta U^\ddagger/kT}$$

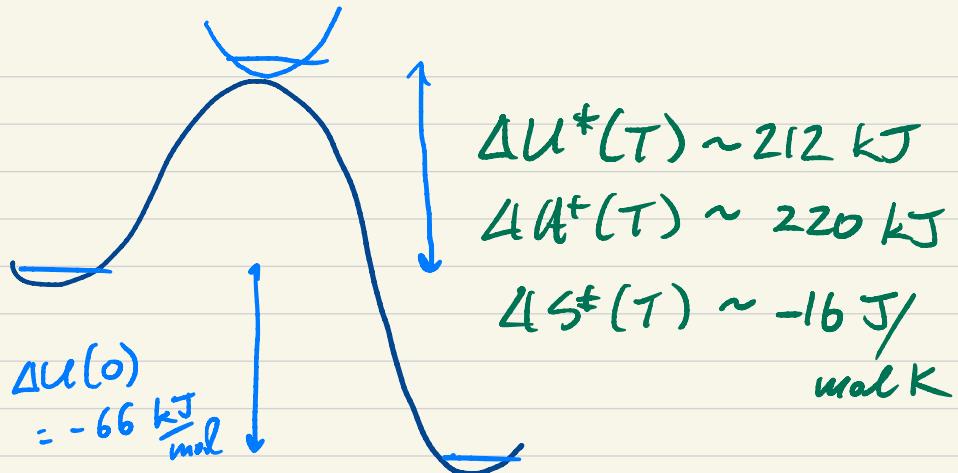
$$\text{Arrhenius eq: } k = A e^{-E_a/RT}$$

$$-\frac{E_a}{R} = \frac{\partial \ln k}{\partial 1/T} = \frac{\partial \ln \left(\frac{k_B T}{h} \right)}{\partial 1/T} + \frac{1}{k_B} \frac{\partial \Delta S^\ddagger}{\partial 1/T} + \frac{1}{k_B} \frac{\partial \Delta U^\ddagger}{\partial 1/T}$$

$$E_a = k_B T + \Delta U^\ddagger$$

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger/k_B} \cdot e^1$$

Prefactor related to entropy loss from reactant to TS



equilibrium
 kinetics

Typically $\Delta S^* < 0$
 $\Delta U^* > 0$

By measuring $k(T)$, can extract
 ΔS^* , ΔU^*

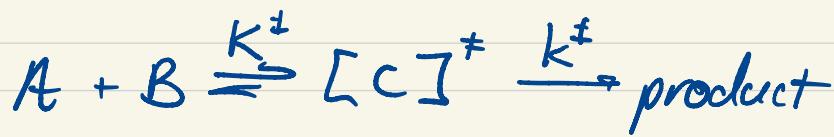
highlights fact that it intimately related to entropy

Typically $\Delta S^\ddagger < 0$

$$\Delta H^\ddagger > 0$$

By measuring $k(T)$, can extract
 $\Delta S^\ddagger, \Delta H^\ddagger$

Same idea for a bimolecular rxn



- harmonic form of rxn coord near TS

$$\text{rate} = k^\pm C_\pm \quad \begin{matrix} k^\pm \text{ 1st order} \\ \text{'time} \end{matrix}$$

$$C_\pm = K^\pm C_A C_B$$
$$= k^\pm K^\pm C_A C_B$$

If we assume motion along rxn coord is harmonic:

$$\text{prefactor} \quad \overbrace{\frac{k_B T}{h}}$$
$$\text{rate} = \frac{k_B T}{h} \cdot K^\pm C_A C_B$$
$$\underbrace{s^{-1}}$$

We know a molecular perspective
on $K(T)$

$$K^{\pm}(T) = \frac{g^{\pm\circ}(T)}{g_A^{\circ}(T) g_B^{\circ}(T)} e^{-\Delta E(0)/RT}$$

computed from
exactly same information

pay
attention
to std
state

Two atoms colliding



$$g_{\pm}^{\circ} = g_{trans}^{\circ} g_{rot}^{\pm} \quad \text{no vib!!}$$

$$g_A^{\circ} = g_{trans}^{\circ} \quad g_B^{\circ} = g_{trans}^{\circ}$$

$$k = \frac{k_B T}{h} \frac{g_{trans}^{\circ} (m_A + m_B) \cdot g_{rot}^{\pm}}{g_{trans}^{\circ} (m_A) g_{trans}^{\circ} (m_B)} e^{-\Delta U / kT}$$

math. \rightsquigarrow collision theory result!!

$$\text{with } \sigma_{AB} = \pi \cdot (R_{A-B}^{\pm})^2$$

More real things will have contributions from all degrees of freedom, especially loss of translational @ TS.

$$E_a = -R \frac{\partial \ln k}{\partial T} \rightarrow E_a = \Delta H^\ddagger + 2RT$$

gas-phase
ideal gas
1 bar std state

$$A = \frac{k_B T}{h} \left(\frac{RT}{P_0} \right) e^{\Delta S^\ddagger / R} e^z$$

Diels-Alder



$$k = 9.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1} e^{-9915/J/K}$$

$$\Delta H^\ddagger = 91 \text{ kJ/mol}$$

500 K

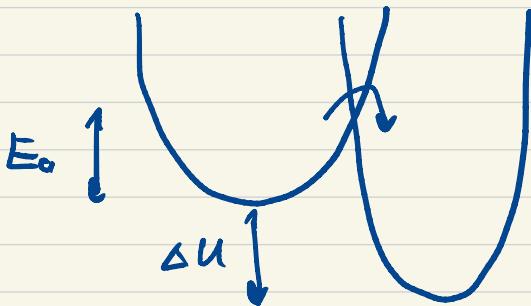
$$\Delta S^\ddagger = -164 \text{ J/mol K}$$

$$\Delta G^\ddagger = 173 \text{ kJ/mol}$$

Compensation effect

$\Delta H^\ddagger + \Delta S^\ddagger$ often correlated

Correlations



Rxn coord can
be thought of
as intersection
of 2 parabolas

Suggests height of barrier +
reaction energy may be correlated!
Initially observed in terms of free
energies $\ln\left(\frac{k_2}{k_1}\right) \propto \ln\left(\frac{E_{rxn2}}{E_{rxn1}}\right)$.

Called a linear (free) energy relationship
Commonly observed for a series of
reactions that follow the same path.

A corollary is that TS's of very
exothermic reactions will be product -
like - "late" TS
endothermic - "early" TS

Compensation effect

LFER

Unimolecular reactions

Modern methods - NEB

sampling
scaling

Alternative view

Because K^\ddagger is an equilibrium const,
can write

$$\begin{aligned} \text{in pressure std state} \\ K^\ddagger(T) &= e^{-\Delta G^\ddagger(T)/kT} \\ &= e^{\Delta S^\ddagger/k} e^{-\Delta H^\ddagger/kT} \end{aligned}$$

$$k(T) = \frac{k_B T}{h} e^{\Delta S^\ddagger/k} e^{-\Delta H^\ddagger/kT}$$

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

$$-\frac{E_a}{R} = \frac{\partial \ln k}{\partial 1/T} = \frac{\partial \ln \left(\frac{k_B T}{h} \right)}{\partial 1/T} + \frac{1}{k_B} \frac{\partial \Delta S^\ddagger}{\partial 1/T} - \frac{1}{k_B} \frac{\partial \Delta H^\ddagger}{\partial 1/T}$$

$$E_a \approx \Delta H^\ddagger + k_B T$$

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger/k_B} \cdot e'$$

Examples

C₂H₆ pyrolysis

Xu, 2011 JPC-A

Surface-catalyzed reactions
Practical rxns carried out in
catalytic reactors, rxns @
solid surfaces.

NH₃ oxidation

Ma, 2019, ACS Catalysis