

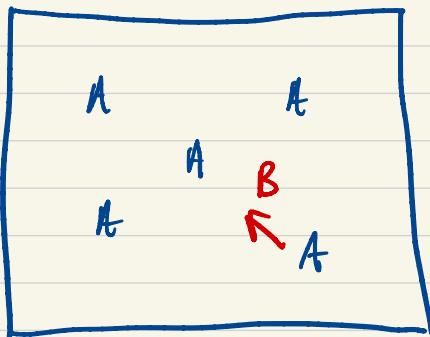
Chemical Kinetics

Thermo tells us what can happen

Kinetics tells us what will, how fast

Consider $A \rightarrow B$

Expressed in terms of \propto rate



$\frac{\# \text{ events}}{\text{time} \cdot \text{something}}$
 something: { volume
 area
 mass
 ...

rate is in general some function of T, P , concentrations (or pressures)

$$\text{eg } r_A = f(T, P, C_A, C_B)$$

Sometime can factor

$$r_A = k(T) \cdot g(p, c_A, c_B)$$

$$\rightarrow k(T) C_A^\alpha C_B^\beta$$

$k(T)$: rate constant

generally
strong T-depend.

α, β : rate orders unpredictable!!

$\alpha + \beta$: overall order

Sometime cannot:



$$-r_{H_2} = \frac{k P_{H_2} P_{Br_2}^{1/2}}{P_{Br_2} + k' P_{HBr}}$$

$$\frac{H_2}{1}$$

$$\frac{Br_2}{\text{undef}}$$

$$\frac{HBr}{\text{undef}}$$

$$Br_2 \gg k' HBr \quad 1$$

$$Br_2 \ll k' HBr \quad 1$$

$$0 \quad -1$$

"pseudo" orders

$$\text{Br}_2 \gg k' \text{HBr} \quad -r_{\text{H}_2} = k P_{\text{H}_2} P_{\text{Br}_2}^{-1/2}$$

$$\text{Br}_2 \ll k' \text{HBr} \quad -r_{\text{H}_2} = \left(\frac{k}{k'}\right) \frac{P_{\text{H}_2} P_{\text{Br}_2}^2}{P_{\text{HBr}}}$$

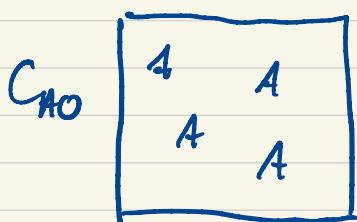
So rate laws can have complicated forms and behave differently in different limits

Simple cases

A → ?

$$r = k C_A$$

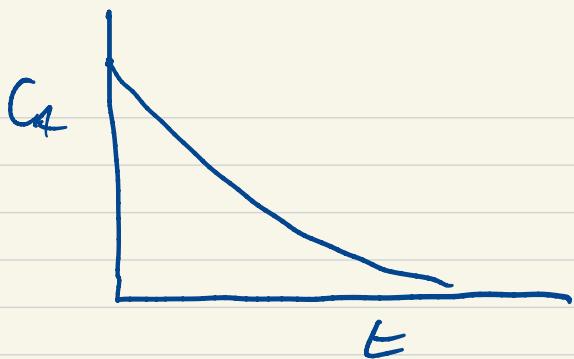
"first order"
differential rate



$$t=0 \quad C=C_{A0}$$

$$\frac{dN_A}{dt} = \cancel{\text{in}^\circ - \text{out}^\circ} + \text{gen} - \text{con}$$
$$= -k C_A \cdot V$$

$$\frac{dC_A}{dt} = -k C_A \Rightarrow C_A = C_{A0} e^{-kt}$$



half-life time for $C_A = \frac{1}{2} C_{A0}$

$$\frac{1}{2} C_{A0} = C_{A0} e^{-kt/2}$$

$$\Rightarrow t_{1/2} = \ln 2 / k$$

2nd order

$$\frac{dC_A}{dt} = -k C_A^2$$

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + kt$$

$$t_{1/2} = 1/k C_{A0}$$



$$\text{rate} = k C_A C_B$$

relate $C_A + C_B$ through an advancement

rate constant k

units depend on rate expression

1st order $1/\text{time}$

2nd order $1/\text{conc.} \cdot \text{time}$

Empirically observed to follow Arrhenius behavior.

$$k = A e^{-E_a/k_b T}$$

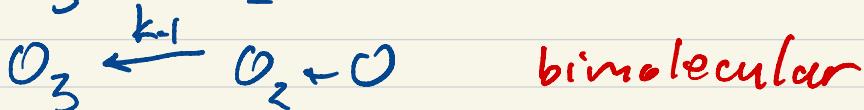
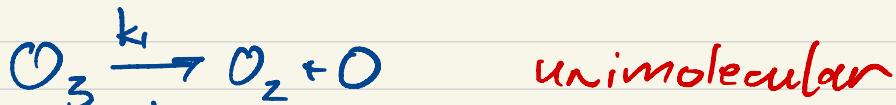
prefactor activation energy

$\ln k$ vs $1/T$ called an Arrhenius plot.

Slope $-E_a/R$

Form of rate expression depends
on underlying mechanism

Imagine reactions to occur
through a sequence of elementary
steps



O is an intermediate - created &
destroyed in overall reaction

rate of individual step goes as
molecularity

$$r_1 = k_1 C_{O_3} \quad r_1 = k_{-1} C_{O_2} C_O$$

$$r_2 = k_2 C_O \cdot C_{O_3} \quad r_{-2} = k_{-2} C_{O_2}^2 \approx 0$$

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

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

Principle of microscopic reversibility says every step can go either way.



characteristic of elementary step

At equilibrium, must have

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

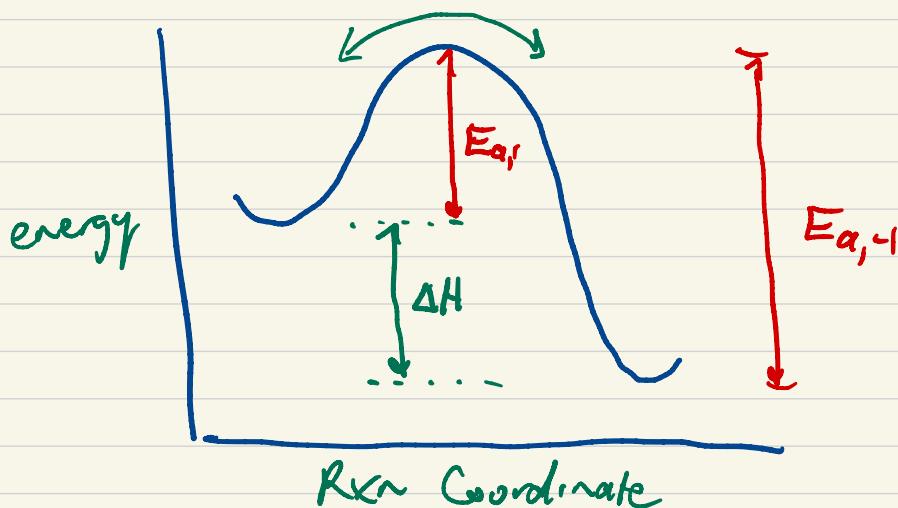
$$k_1 C_A = k_{-1} C_B$$

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

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

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

ΔH $E_{a,1}$ $E_{a,-1}$



Suggests "collision theory"

- Reactions occur when molecules collides
- 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



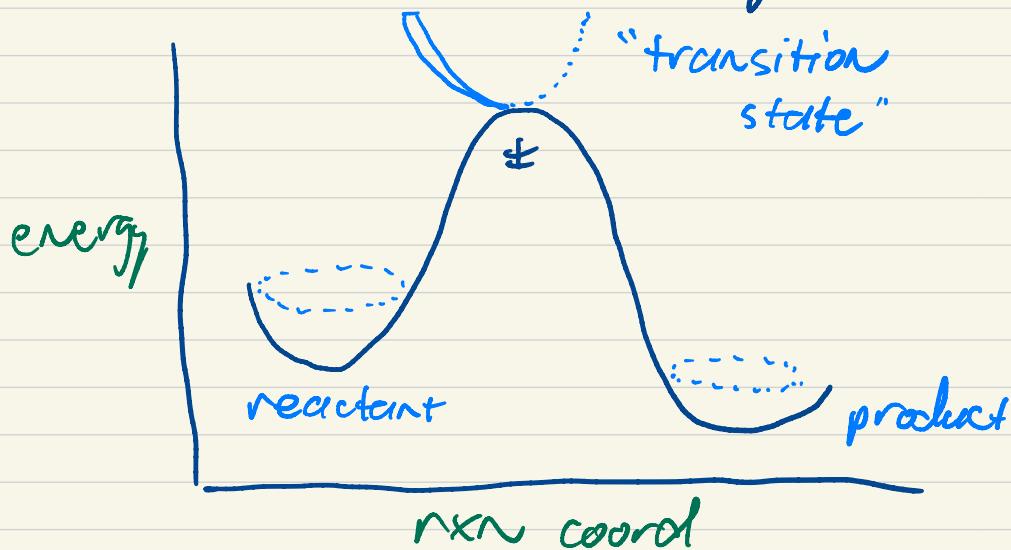
$$k_{\text{pred}} \sim 10^{12} \text{ M}^{-1}\text{s}^{-1}$$

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

} ouch
not great

Assumption that all collisions are successful
is too generous.

transition state theory



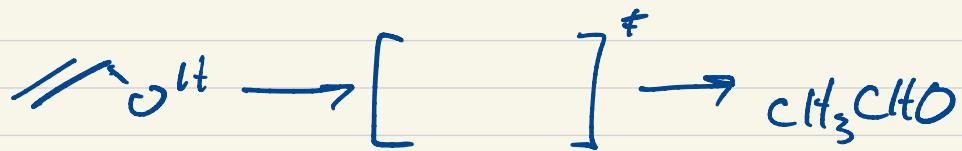
"Landscape" that connects reactants to products.

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

Key assumption of TST is that there is a "reaction coordinate" along which there is a "point of no return".

Called the "transition state". Lowest "free" energy passage from

reactants to products.



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

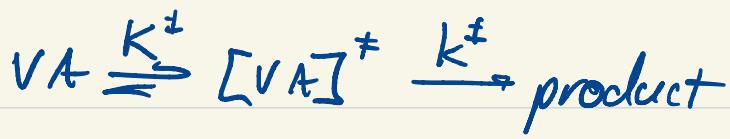
"imaginary mode"

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

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

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

$$C_\pm = K^\pm C_{VA}$$

$$= k^\pm K^\pm C_{VA}$$

If we assume motion along rxn coord is harmonic:

prefactor

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

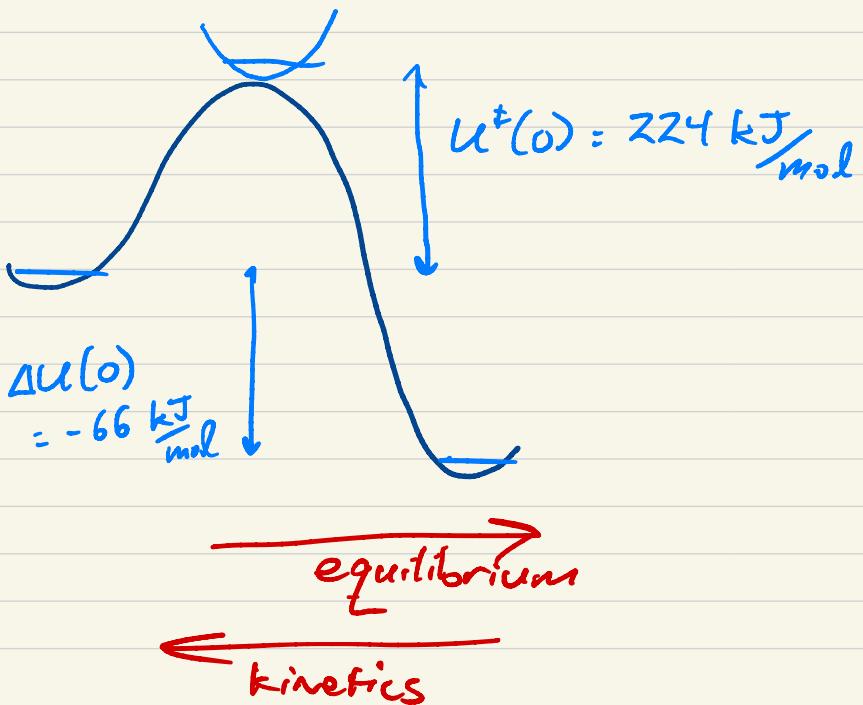
From our previous work, we know how to get an equilibrium const:

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

$$k(T) = \frac{k_B T}{h} \frac{\mathcal{E}^\circ(T)}{\mathcal{E}_{\text{vib}}^\circ(T)} e^{-\Delta U(0)/(k_B T)}$$

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

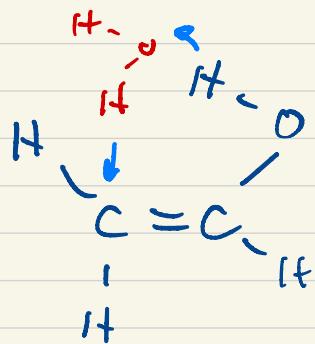
Same sum as before, except, $\mathcal{E}_{\text{vib}}^\circ$ has only $3n-7$ contributions — reaction coord “vibration” excluded.



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



Alternative view

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

$$K^\ddagger(T) = e^{-\Delta G^\ddagger(T)/kT}$$
$$= e^{\Delta S^\ddagger/k} e^{-\Delta H^\ddagger/kT}$$

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

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

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

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

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

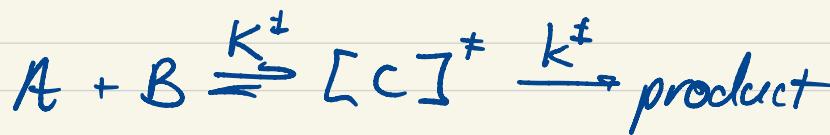
highlights fact that it intimately related to entropy

Typically $\Delta S^\ddagger < 0$

$\Delta H^\ddagger > 0$

By measuring $k(T)$, can extract
 ΔS^\ddagger , ΔH^\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:

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

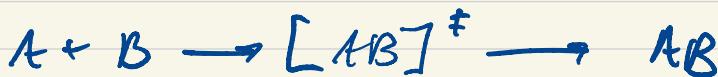
We know a molecular perspective
on $K(T)$

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

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

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

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

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