Temperature Dependence

Arrhenius and others: EMPIRICAL

$$\ln k = \frac{-E_a}{RT} + \ln A$$

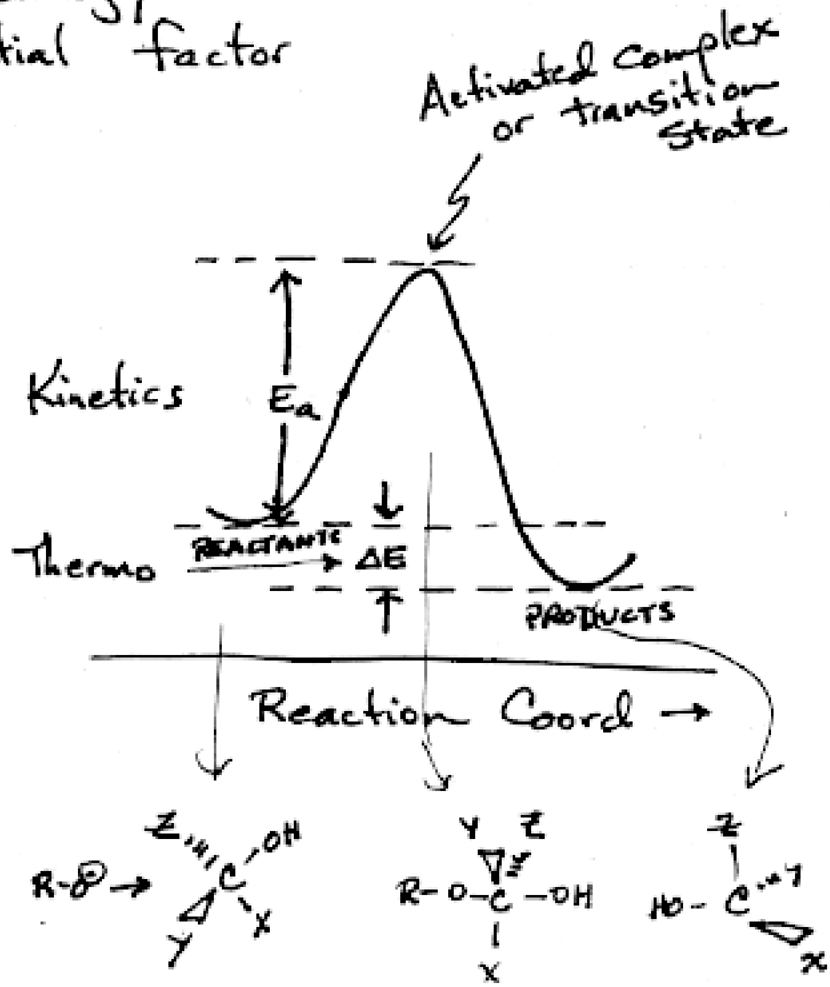
$$y = mx + b$$

OR

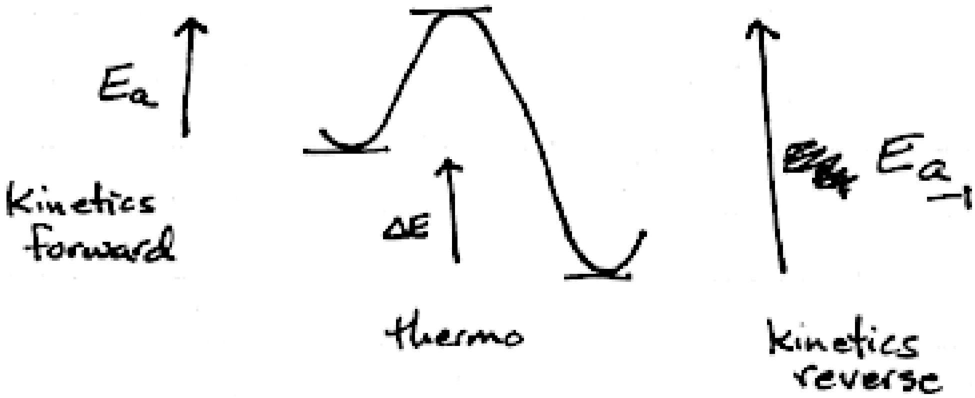
$$k = Ae^{-E_a/RT}$$ empirical

E_a = activation energy

A = preexponential factor



Example

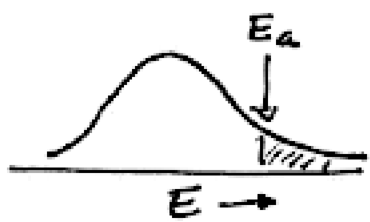


$$E_a - E_{a_{-1}} = \Delta E$$

Explain → a molecule must have enough energy to get over barrier ($\geq E_a$).

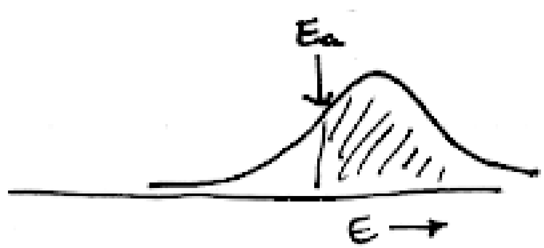
Boltzmann

T_1



$T_2 > T_1$

T_2



FOR BIMOLECULAR COLLISION $\quad M + N \rightarrow P$

$$v = k[M][N]$$

$$= [M][N]\,A\,e^{-E_a/RT}$$

$$e^{-\frac{E_a}{\infty}} = e^{0}$$

As $T \rightarrow \infty \qquad e^{-E_a/RT} \rightarrow 1$

$$v = A[M][N] \qquad k \rightarrow A$$

So A = preexponential = k at $T = \infty$

SIMPLE VIEW $\Rightarrow$ POST-EMPERICAL RATIONALIZATION

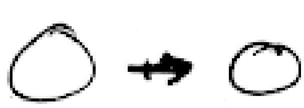
Example before: in-line attack.

Not all collisions occurs with the right orientation

$A < 1$

GOOD BAD BAD

If reaction were two spheres,



all orientations good

$A = 1$

Transition State Theory

1935 Eyring — Reactive Intermediate
a.k.a. transition state

Unstable high-E state between reactants and products
Exists transiently.

$$\underbrace{M + N \overset{K^\ddagger}{\rightleftharpoons} MN^\ddagger}_{\text{Pre-equilib}} \underbrace{\xrightarrow{k^\ddagger} P}$$

$$K^\ddagger = \frac{[MN^\ddagger]}{[M][N]} \quad \therefore \quad [MN^\ddagger] = K^\ddagger [M][N]$$

$$v = \frac{dP}{dt} = k^\ddagger [MN^\ddagger] = K^\ddagger k^\ddagger [M][N]$$

$$\therefore \quad k = K^\ddagger k^\ddagger$$

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

Out of a hat $\Rightarrow$ $k^{\ddagger} = \dfrac{k_B T}{h}$

Boltzmann k

Temperature (K)

Planck

Then

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

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

looks like Arrhenius except theirs T in the pre-exponential. Over narrow ranges of T near 300, impact of this is small!

MORE $\Rightarrow$

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

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

$$= \left[\frac{k_B T}{h} e^{\Delta S^{\ddagger}/R}\right] e^{-\Delta H^{\ddagger}/RT}$$

* DISCUSS HERE *

Compare Eyring to Arrhenius

$$A \approx \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R}$$

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

OR

$$\Delta S^{\ddagger} \approx R \ln \frac{Ah}{k_B T}$$

SKIP Marcus Theory (pp 361 – 362 a bit)
SKIP Salt Effects pp 362 –

Experimental approaches

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad K = \frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}}$$

How to measure k_1 and k_{-1}?

Relaxation Methods
Temperature Jump
Pressure Jump
Laser Photo-Init

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$$

$$\frac{dP}{dt} = k_1 AB - k_{-1} P$$

$$P = P_{eq} + x$$
$$A = A_{eq} - x$$
$$B = B_{eq} - x$$

$$\frac{dP}{dt} = \frac{dx}{dt} = k_1 (A_{eq} - x)(B_{eq} - x) - k_{-1}(P_{eq} + x)$$

$$\frac{dx}{dt} = k_1 x^2 - [k_1 A_{eq} + k_1 B_{eq} + k_{-1}]x + \underbrace{k_1 A_{eq} B_{eq} - k_{-1} P_{eq}}_{\Rightarrow 0}$$

SMALL

$$= k_1 x^2 - [k_1 A_{eq} + k_1 B_{eq} + k_{-1}]x$$

$$-\frac{dx}{dt} \approx [k_1 (A_{eq} + B_{eq}) + k_{-1}]x$$

$$-\frac{dx}{dt} = k' x \qquad \therefore \quad x = x_0 e^{-kt}$$

$$k' = k_1 (A_{eq} + B_{eq}) + k_{-1}$$