

11/24/99

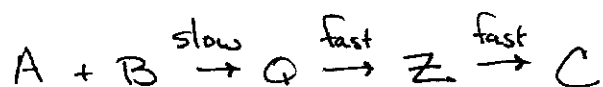
①

IMPORTANT CONCEPT: — Repeated from last time

One cannot use the form of the rate law alone to deduce reaction mechanism.

However, knowing the mechanism does allow us to deduce the rate law.

In other words, for mechanism



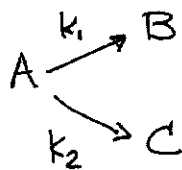
we can predict the rate law $\frac{\partial C}{\partial t} = kAB$

But knowing $\frac{\partial C}{\partial t} = kAB$ does not give us all of the mechanism above.

But Remember
Occam's
Razor!

More classes of reactions:

① Parallel
(Competing)



$$-\frac{\partial A}{\partial t} = k_1 A + k_2 A$$

$$\frac{\partial B}{\partial t} = k_1 A$$

$$\frac{\partial C}{\partial t} = k_2 A$$

$$-\frac{\partial A}{\partial t} = (k_1 + k_2)A \xrightarrow{\text{easy}} A = A_0 e^{-(k_1 + k_2)t}$$

$$\text{then } \frac{\partial B}{\partial t} = k_1 A = A_0 k_1 e^{-(k_1 + k_2)t} \Rightarrow B = \frac{k_1}{k_1 + k_2} A_0 (1 - e^{-(k_1 + k_2)t})$$

$$\frac{\partial C}{\partial t} = k_2 A = A_0 k_2 e^{-(k_1 + k_2)t} \quad C = \frac{k_2}{k_1 + k_2} A_0 (1 - e^{-(k_1 + k_2)t})$$

② Series



see p. 357

$$-\frac{\partial A}{\partial t} = k_1 A$$

$$\frac{\partial B}{\partial t} = k_1 A - k_2 B$$

$$\frac{\partial C}{\partial t} = k_2 B$$

Messy integrals



$$C = A_0 \left[1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right]$$

Check limits $A \xrightarrow{\text{slow}} B \xrightarrow{\text{fast}} C$ then $k_2 \gg k_1$

FIRST STEP RATE LIMITING

$$C = A_0 \left[1 - \frac{1}{k_2} (k_2 e^{-k_1 t} - 0) \right] = A_0 (1 - e^{-k_1 t}) \quad \text{GOOD.}$$

$A \xrightarrow{\text{fast}} B \xrightarrow{\text{slow}} C$ then $k_1 \gg k_2$

SECOND STEP RATE LIMITING

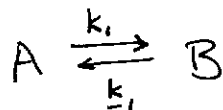
$$C = A_0 \left[1 - \frac{1}{-k_1} (0 - k_1 e^{-k_2 t}) \right]$$

$$= A_0 [1 - e^{-k_2 t}]$$

(all A quickly goes to B)
then simple kinetics

Consider reverse reactions.

Equilibrium is really just kinetics.



$$-\frac{\partial A}{\partial t} = k_1 A - k_{-1} B$$

At equilibrium $\frac{\partial A}{\partial t} = 0$

$$\therefore k_1 A = k_{-1} B$$

$$\frac{B}{A} = \frac{k_1}{k_{-1}} = K_{eq}$$

Solution (p. 361)

$$\ln \frac{A - A_{eq}}{A_0 - A_{eq}} = \ln \frac{B - B_{eq}}{B_0 - B_{eq}} = -(k_1 + k_{-1})t$$

Experimental classic T-jump

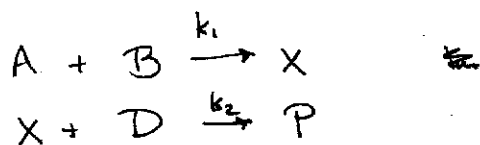
We have seen that K_{eq} is temperature dependent
So,

start with $A \rightleftharpoons B$ at equil at $T = T_0$ ~~then~~

then increase temperature to T_f with new equil

③

Steady State



initially, X increases

as it does, it begins to ~~be~~ depleted to form P

At some point, X is depleted at the same rate
that it's depleted. $\rightarrow$ i.e. $\frac{\partial X}{\partial t} = 0$

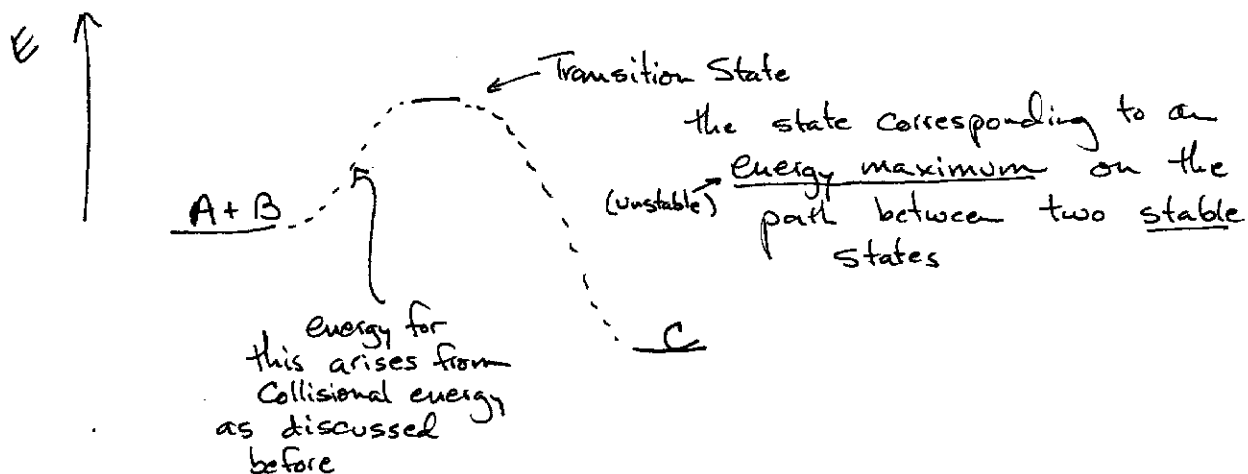
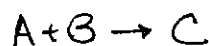
but

$$\frac{\partial X}{\partial t} = k_1 AB - k_2 XD = 0$$

$$v = \frac{\partial P}{\partial t} = k_2 XD = k_1 AB$$

This is not the steady
state used in classic
biochem texts.
LATER

Transition State ← IMPORTANT CONCEPT!



Temperature Dependence (more collisional energy at higher T) of Kinetics

Arrhenius showed that for most chemical reactions:

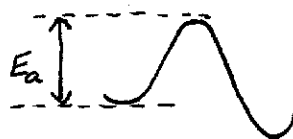
$$\ln k = -\left(\frac{E_a}{RT}\right) + \ln A$$

Empirical

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

IMPORTANT

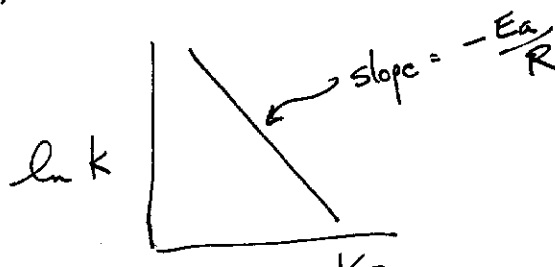
E_a = activation energy
(easy to understand)

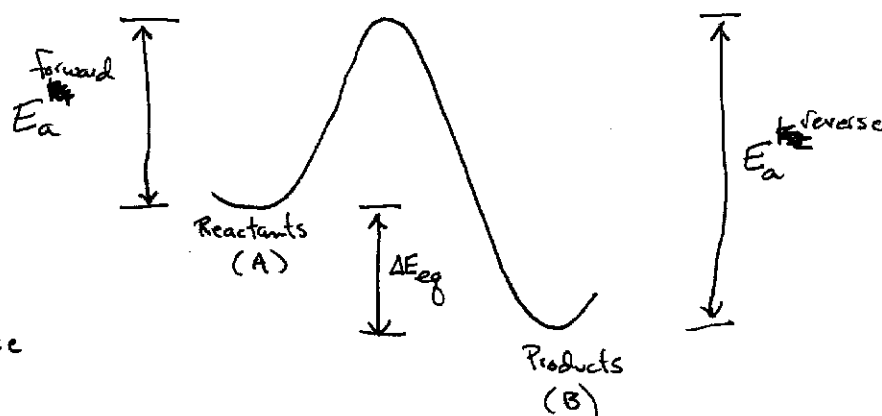
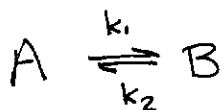


But try to interpret

A = pre-exponential factor
(harder to understand)

How to measure?





Note relationship:

$$E_a^{\text{forward}} + \Delta E_{eg} = E_a^{\text{reverse}}$$

Assume a bucket-full of A molecules, with a distribution of translational speeds (and therefore energy)

Some will have enough energy for a collision to yield reaction (get to transition state)

Some will not have enough energy.

The overall reaction rate will reflect this ratio

$\frac{\text{ready}}{\text{not ready}}$ high means lots of reaction (e.g. high T)

$\frac{\text{ready}}{\text{not ready}}$ low means little reaction (e.g. low T)

At $T \rightarrow \infty$, all will be ready

$$k = A e^{-\frac{E_a}{R(\infty)}} \rightarrow A e^{-0} = A$$

So A is the rate when all have sufficient energy

⑥

Arrhenius theory is an empirical relation, which tries to develop a theory to explain

Not perfect. "A" is often much lower than simple analyses would predict...

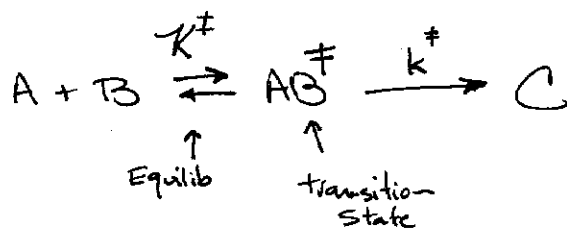
Alternative → TRANSITION STATE THEORY

IMPORTANT
CONCEPT

1935 - Eyring



is really



then

$$\frac{\partial C}{\partial t} = k^\ddagger [AB^\ddagger]$$

but (pre-)equilibrium says $K^\ddagger = \frac{AB^\ddagger}{A \cdot B} \therefore [AB^\ddagger] = K^\ddagger A \cdot B$

then $\frac{\partial C}{\partial t} = k^\ddagger K^\ddagger A \cdot B$

i.e. $k \text{ (normal)} = k^\ddagger K^\ddagger$

From thermo:

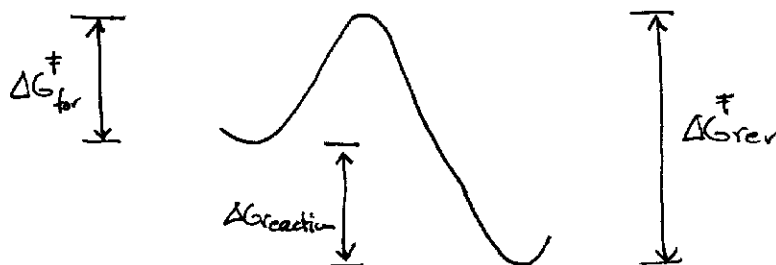
$$\Delta G^\ddagger = -RT \ln K^\ddagger$$

Transition state theory says:
(not shown)

$$k^\ddagger = \frac{k_B T}{h}$$

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

As before:



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

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

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

different
from Arrhenius
equation! →

But most of T-dependence is
in the $e^{-\Delta H^{\ddagger}/RT}$ term, so
not that dissimilar.

This, in principle, allows us to
determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and
so gives us more information
on the transition state.

eq.