

First Order Processes

These **INCREDIBLY IMPORTANT** types of processes include: growth of living objects, e.g., humans, decline of populations, growth and decay of bank accounts and investments, etc.

EXPONENTIAL decay or growth (which has same math except for sign)

$$\text{rate} = \frac{dN}{dt} = \pm kN \quad \text{where } N \text{ can be in any units} \quad \text{WHY?}$$

in words: rate of **loss** or **growth** of A is **directly proportional to A**

or, if we divide both sides by N and multiply by dt **(which changes nothing)**

$$\text{fractional change} = \frac{dN}{N} = \pm k dt \quad \text{in words this says: **fractional change** is **directly proportional to time**}$$

SUM of FRACTIONAL changes =integrated form

$$\int \frac{dN}{N} = \pm k \int dt = \ln\left(\frac{N_2}{N_1}\right) = \pm k(t_2 - t_1) \quad \text{or} \quad \frac{N(t_2)}{N(t_1)} = f = e^{\pm k(t_2 - t_1)}$$

Given any 2 of k, t, or f, find the 3rd

half life: $f = 0.5 = \exp(-kt_{1/2})$
 $\ln(0.5) = -kt_{1/2}$
 $-\ln(0.5)/k = t_{1/2}$

$t_f = -\ln(f)/k = \text{time for } N_{t_2}/N_{t_1} \text{ to } = f$

exponential increase instead of decrease

$\frac{dN}{dt} = +kN$ gives $\frac{N(t_2)}{N(t_1)} = f = e^{+k(t_2 - t_1)}$

Doubling time

$f=2$

$t_{\text{double}} = \ln(2)/k = -\ln(0.5)/k = \text{half life}$

half life: $f = 0.5 = \exp(-kt_{1/2})$
 $\ln(0.5) = -kt_{1/2}$
 $-\ln(0.5)/k = t_{1/2}$

$t_f = -\ln(f)/k = \text{time for } N_{t_2}/N_{t_1} \text{ to } = f$

“lifetime”, “relaxation time”, “time constant”, etc.
 This when the fraction $f=1/e$

$\tau = -\ln(1/e)/k = \ln(e)/k = 1/k$ “life time”

The average lifetime is $1/k$, the $1/e$ time, **not** $t_{1/2}$

$\frac{dN}{dt} = -kN$ gives $\frac{N(t_2)}{N(t_1)} = f = e^{-k(t_2 - t_1)} = e^{-\frac{(t_2 - t_1)}{\tau}}$

Sedimentation Coefficient

when something starts falling in air,
it approaches **terminal velocity exponentially**

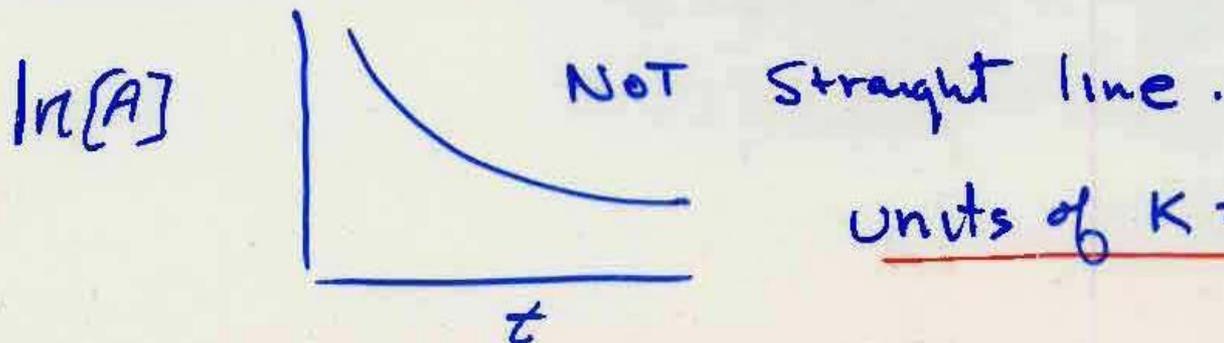
wind resistance is force opposite velocity
mass x acceleration = force = $mg - \text{velocity} \times \text{frictional coef}$
 $m \, dv/dt = mg - vf$

$$dv/dt = -(f/m)v + g = -(1/s)v + g$$

$$**v = v_t(1 - e^{-t/s})** ,$$

so **s** = sedimentation coef. is the 1/e time to reach terminal velocity

IF 2nd order & rate = $k[A]^2$



units of $k = ?$

if rate = $k[A][B]$ and $[B] \gg [A]$ then what will
plot of $\ln[A]$ vs t look like?
(pseudo first order)

A **mechanism** predicts a rate law, **but**

A rate law **CANNOT** be deduced from a **STOICHIOMETRIC** Equation. This is **abundantly** clear from the table below.

TABLE 9.1 Rate Laws and Kinetic Order for Some Reactions

Stoichiometric reaction	Rate law	Kinetic order
sucrose + H ₂ O → fructose + glucose	$v = k[\text{sucrose}]$	1
L-isoleucine → D-isoleucine	$v = k[\text{L-isoleucine}]$	1
¹⁴ C → ¹⁴ N + β ⁻	$v = k[^{14}\text{C}]$	1
2 proflavin → proflavin dimer	$v = k[\text{proflavin}]^2$	2
<i>p</i> -nitrophenylacetate + 2 OH ⁻ → <i>p</i> -nitrophenolate + acetate + H ₂ O (pH 9)	$v = k[\textit{p}\text{-nitrophenylacetate}][\text{OH}^-]$	2 (overall)
hemoglobin·3O ₂ + O ₂ → hemoglobin·4O ₂	$v = k[\text{Hb}\cdot 3\text{O}_2][\text{O}_2]$	2 (overall)
H ₂ + I ₂ → 2 HI	$v = k[\text{H}_2][\text{I}_2]$	2 (overall)
H ₂ + Br ₂ → 2 HBr	$v = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{k' + [\text{HBr}]/[\text{Br}_2]}$	Complex
CH ₃ CHO → CH ₄ + CO	$v \cong [\text{CH}_3\text{CHO}]^{3/2}$	3/2 (approx.)
C ₂ H ₅ OH → CH ₃ CHO (liver enzymes)	v constant	0

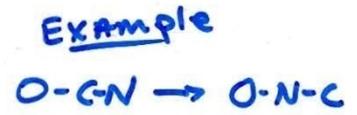
MECHANISM: a set of hypothetical

ELEMENTARY REACTIONS that are microscopic descriptions of supposed events.

Mechanism MAY ^{←(might)} be correct IF it predicts the observed rate law (or might be wrong.)

→ 3 Types only:

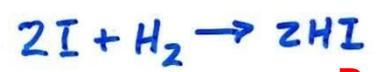
1. UNIMOLECULAR



2. BI MOLECULAR



RARE! 3. TER MOLECULAR



MOLECULARITY DOES imply ORDER

But, experimentally observed order does not imply molecularity

UNIMOLECULAR	STEP	IS	1 ST order	$K[O-G-N]$
BI MOLECULAR	"	"	2 ND "	$K[H_2][I_2]$
TER MOLECULAR	"	"	3 RD "	$K[I]^2[H_2]$

SUM OF STEPS MUST = STOICHIOMETRIC EQ.

STEPS → predicted rate law

STOICHIOMETRIC CHEMICAL EQ SAYS NOTHING ABOUT THE RATE LAW

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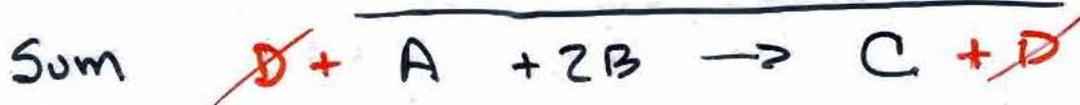
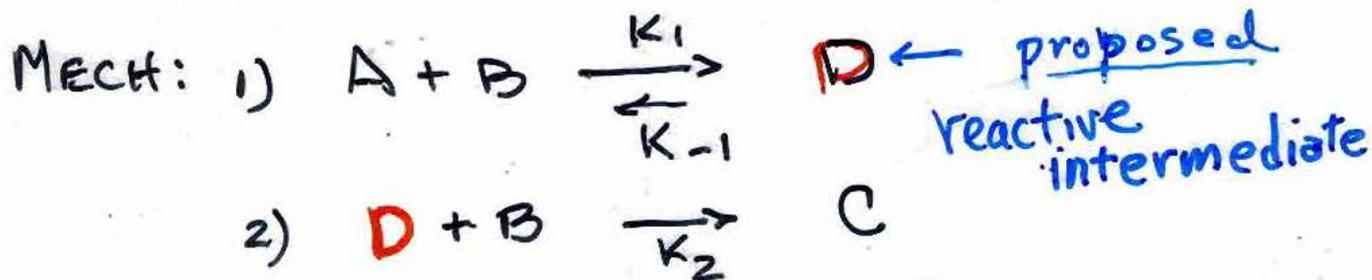
FIND RATE LAW (OVERALL) FROM MECHANISM:

- THE RATE-DETERMINING STEP (RDS)
SLOWEST STEP & THE BOTTLENECK

BE ABLE TO "FIND" RATE LAW GIVEN A
TWO-STEP MECHANISM & WHICH STEP
IS RDS.

GUIDING PRINCIPLE: Rate Law = THAT FROM RDS^{*}
* BUT MUST NOT CONTAIN ANY
HYPOTHETICAL TRANSIENT SPECIES

EXAMPLE: STOICH: $A + 2B \rightarrow C$ overall balanced reaction



• IF 1ST step is RDS, RATE = $k_1[A][B]$

• IF 2ND step is RDS, RATE = $k_2[B][D]$ ← unseenn

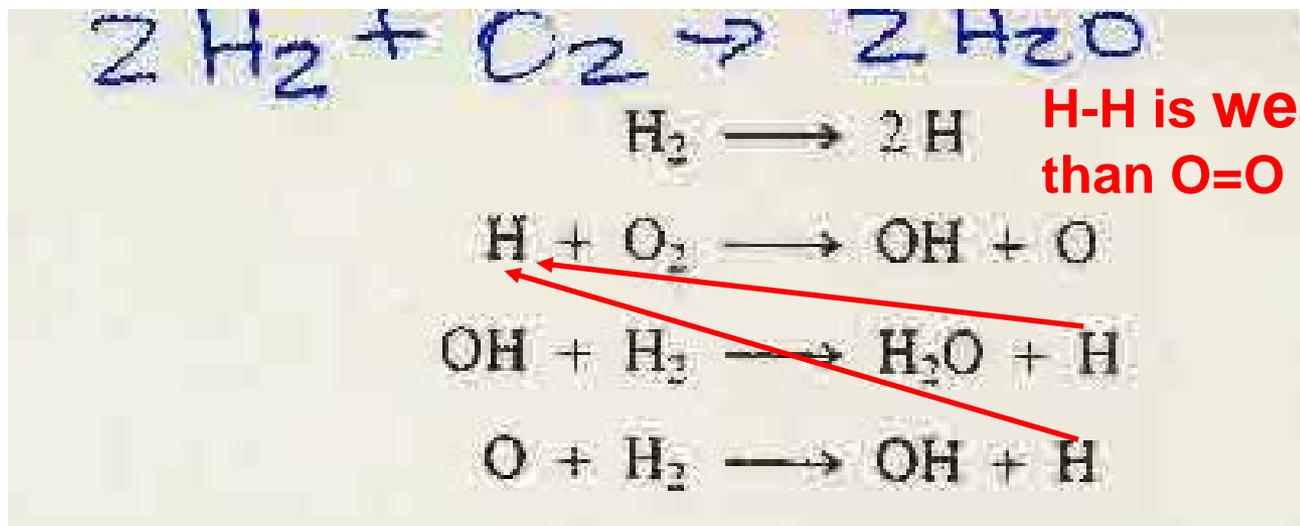
must reexpress $[D]$ by saying step (1) reaches EQUILIBRIUM

BACK rate = FORWARD RATE $k_{-1}[D] = k_1[A][B]$

$[D] = \frac{k_1}{k_{-1}} [A][B]$ RATE = $\frac{k_2[B]}{k_{-1}} \frac{k_1[A][B]}{k_{-1}} = \frac{k_2 k_1}{k_{-1}} [A][B]^2$

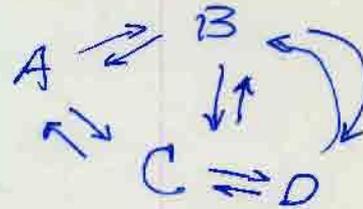
What about really fast, violent reactions, i.e.,
EXPLOSIONS?

Chain reaction mechanism (typical of explosions):



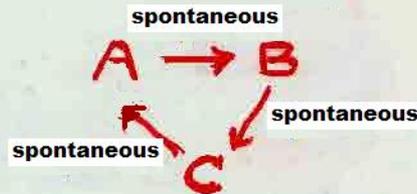
MICROSCOPIC REVERSIBILITY

MUST ACCOUNT FOR
REVERSE OF ALL
PROPOSED PROCESSES



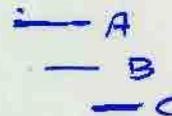
AT EQUILIBRIUM: FORWARD RATE = BACKWARD RATE
FOR ANY PAIR

NEVER

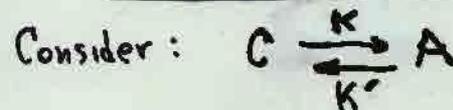


Perpetual
Motion!

implies that $G_A > G_B > G_C > G_A$



But $\Delta G = 0$ for cyclic process.



IF BOTH ARE 1st order:

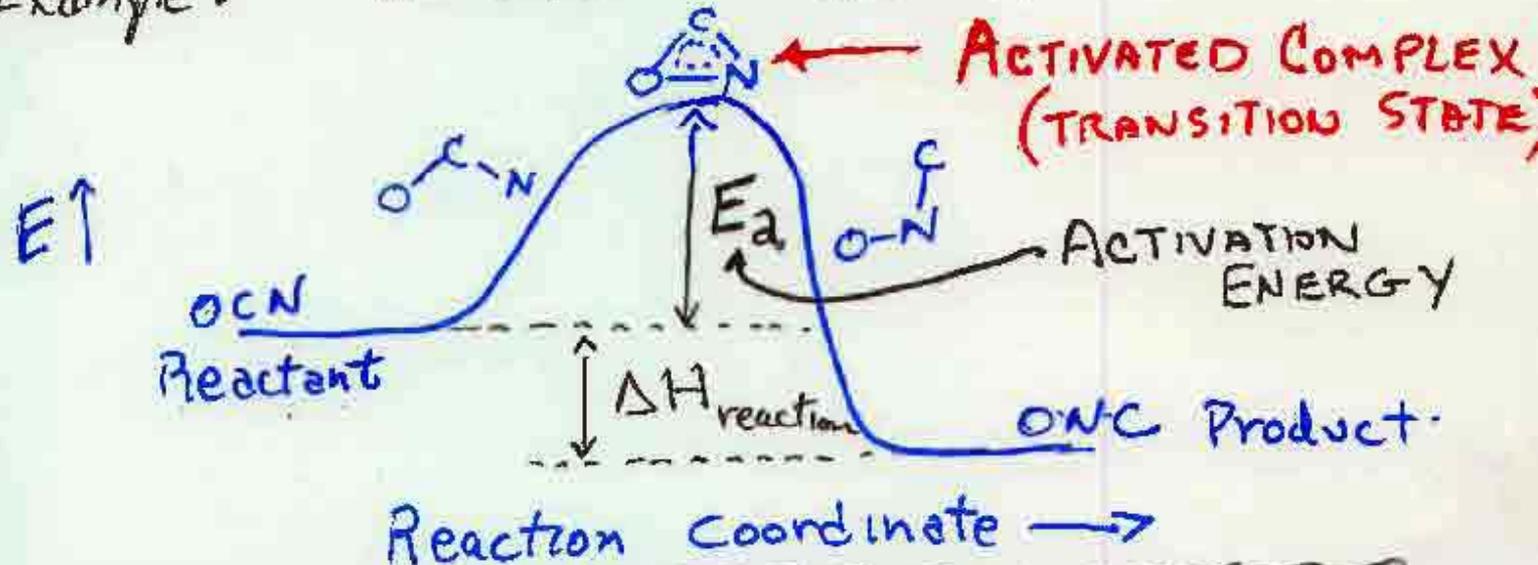
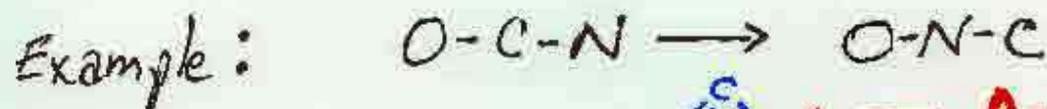
AT EQUIL: $k[C] = k'[A]$

Forward rate = $k[C]$
Back rate = $k'[A]$
 $K_{eq} = \frac{[A]}{[C]}_{eq} = \frac{k}{k'}$

TEMPERATURE DEPENDENCE OF RATES

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Arrhenius: Explanation of why most reactions have rate increase as temp. increases.



Arrhenius was a student of Boltzmann

Boltzmann distribution

Arrhenius: rate constant = $k = A e^{-\frac{E_a}{RT}}$

↑
frequency factor

(preexponential factor)

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Exactly the form as Van't Hoff when applied to equilibrium constants!

↑
ratio of rates or rate constants

RULE OF THUMB: 10°C doubles rate

WHAT IS E_a ?

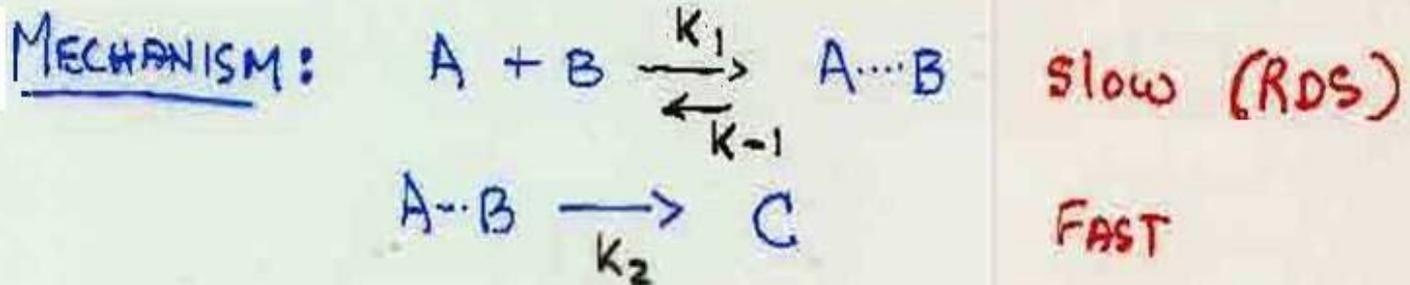
$$\ln 2 = -\frac{E_a}{R} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$E_a = \frac{-R \ln 2}{\frac{1}{310} - \frac{1}{300}} = \frac{-8.3145 (0.693)}{-1.075 \times 10^{-4}} = 52,500 \frac{\text{J}}{\text{mol}} \approx \sqrt{50 \text{ kJ mol}^{-1}}$$

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DIFFUSION LIMITED (CONTROLLED) REACTION

REACTION ON EVERY ENCOUNTER ($E_A \approx 0$)



$$k_2 \gg k_{-1}$$

$$\text{RATE LAW} = k_1[A][B]$$

$$\text{RATE LAW} = k_1[A][B]$$

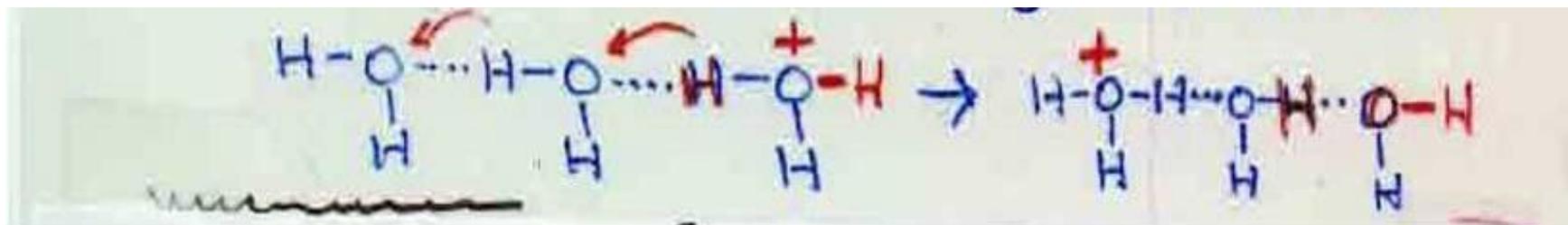
$$k_1 \equiv 4\pi (D_A + D_B) \left(\frac{\text{cm}^2}{\text{s}} \right) \frac{G_{AB}(\text{cm})}{(\text{molecule})} \frac{6 \times 10^{23} (\text{molecules mol}^{-1})}{1000 (\text{cm}^3 \text{L}^{-1})}$$

* $\approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $D \approx 2 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$

But, $k_1 \approx 10^{11}$ for $\text{H}^+(\text{aq})$

ANOMALOUS BECAUSE H_2O^+ not so small!

Why???



Can confidently ESTIMATE upper limit of a rate:

Suppose you read that a reaction rate for

$A + B \rightarrow C$ has a rate = 1×10^7 M per second

when both $[A]$ and $[B] = 0.01$ M, and it is claimed that the reaction must be diffusion controlled because it is so fast.

Find rate of a diffusion controlled reaction:

Mechanism: $A + B \rightleftharpoons C$

if both A and B are both 0.01 M

$$\text{Rate} = k [A][B] = 5 \times 10^9 \times 10^{-2} \times 10^{-2}$$

$$= 5 \times 10^5 \text{ Ms}^{-1}$$

Therefore the **claim was FALSE!** The rate constant would be impossibly fast unless H^+ is involved because:

$$1 \times 10^7 = 1 \times 10^{11} \times 0.01 \times 0.01$$