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10.1 Rate expression (rate law)

rate of rxn \propto (proportional) to $\Delta []$

reaction rate = k [compd] ($k \rightarrow$ rate constant)

first order rate expression \rightarrow [reactant]¹
(remember rate = $[R]$)

Generally: $A + B \rightarrow$ products

rate = $k[A]^m[B]^n$ (expression / law)

k = rate constant (affected only by T) - specific to each

$[A]$ & $[B]$ = conc. of reactants rxn

$m + n$ = order w/ respect to $A + B$

* cannot be determined from mole ratios,
done experimentally

* order is an expression of the relationships
b/w each reactant & its rate

- overall order \rightarrow sum of ind. orders

- determine through rate mechanism

once k & orders known \rightarrow determine rate for
any $[R]$

ex: pg 289

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units of k vary depending on overall order of rxn

Zero order	1^0	2^0	3^0
rate = k	rate = $k[A]$	= $k[A]^2$	= $k[A]^3$

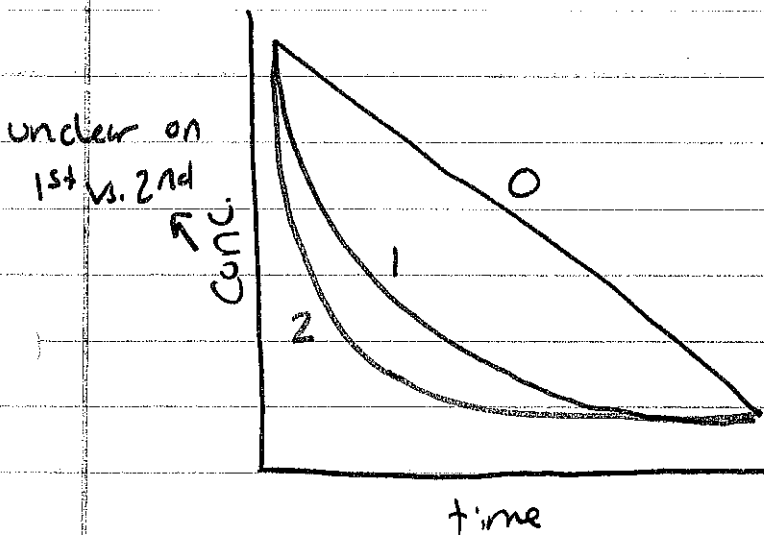
$$k = \frac{\text{units of rate}}{(\text{units of } [A])^{\text{order}}}$$

rate = $\text{mols dm}^{-3} \text{s}^{-1}$	$\text{mols dm}^{-3} \text{s}^{-1}$	$\text{mols dm}^{-3} \text{s}^{-1}$	$\text{mols dm}^{-3} \text{s}^{-1}$
	mols dm^{-3}	$(\text{mols dm}^{-3})^2$	$(\text{mols dm}^{-3})^3$
	= s^{-1}	= $\text{mols}^{-1} \text{dm}^3 \text{s}^{-1}$	= $\text{mols}^{-2} \text{dm}^6 \text{s}^{-1}$

k can be calculated from rate expression when
 $[R]$ + rate are known
 $\neq k$ will \uparrow w/ temp (16.2)

pg 290 (worked ex)

Graphical Representations

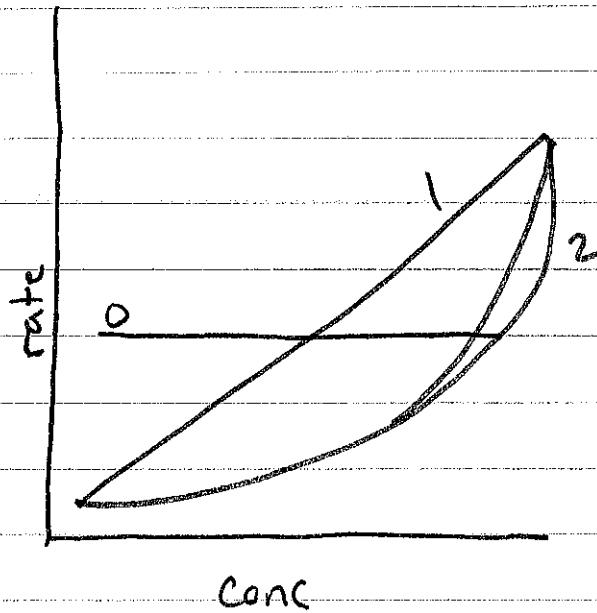


Zero order: rate = k
 : constant rate

1-order: rate \downarrow w/ conc
 : rate = $k[A]$

2 order: rate = $k[A]^2$
 : steeper at 1st, levels off more

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zero order: no change in rate

1st order: direct relationship
b/w rate & conc

2nd order: exponential relationship
(square function)

Generally:

0 order: $2[C]$, no effect

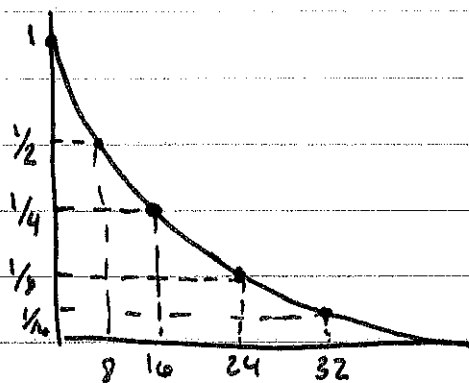
1st order: $2[C]$, double rate; $3[C]$, triple rate

2nd order: $2[C]$, quadruple rate

1st order rxn have a constant $t_{1/2}$ life

$t_{1/2}$ life - time it takes for a reactant to $1/2$ its
conc, regardless of starting conc ($t_{1/2}$)

• used to establish 1st order rxn
- shorter $t_{1/2}$, faster rxn



Calculating order of rxn

Initial rates method

- run multiple exp changing $[]$ of 1 reactant at a time
- Compare initial rate of rxn to deduce order of rxn

1. Change $[]$ has no effect on rate = 0
2. change $[]$ has proportional change = 1
double $[]$, double rate
3. change $[]$ has squared effect = 2
double $[]$, quadruple rate

examples pg 295

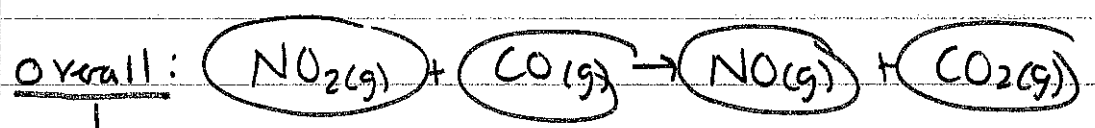
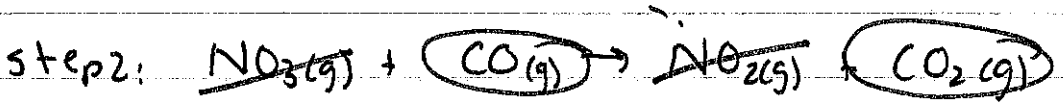
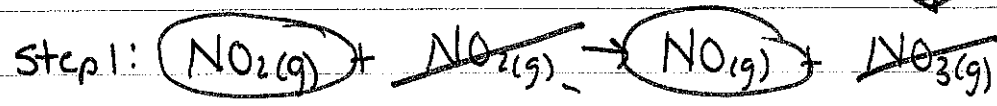
Most rxns involve a series of small steps (each involving a small # of particles)

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Reaction Mechanism

theory about sequence of events (R → P)
↳ consistent w/ data

intermediate
↓



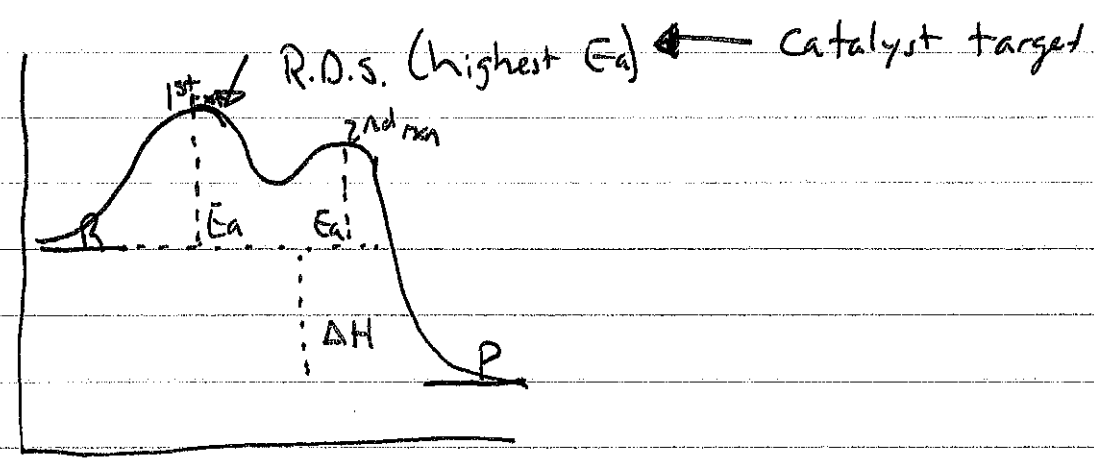
elementary steps
(usually can't be obs.)

Sum of individual steps must equal overall
intermediates on product & 2nd reactants cancel out

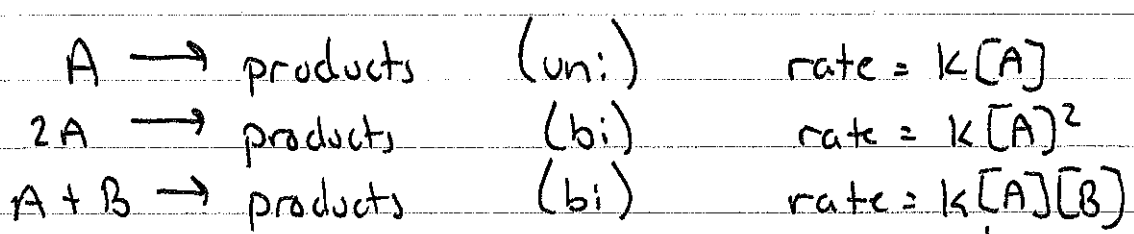
Molecularity → indicates # of reactants involved in elementary steps

- unimolecular = 1 reactant
- bimolecular = 2 reactants

Rate determining step (RDS) → slowest step in mechanism
∴ products in rxn appear as fast as products in slowest step

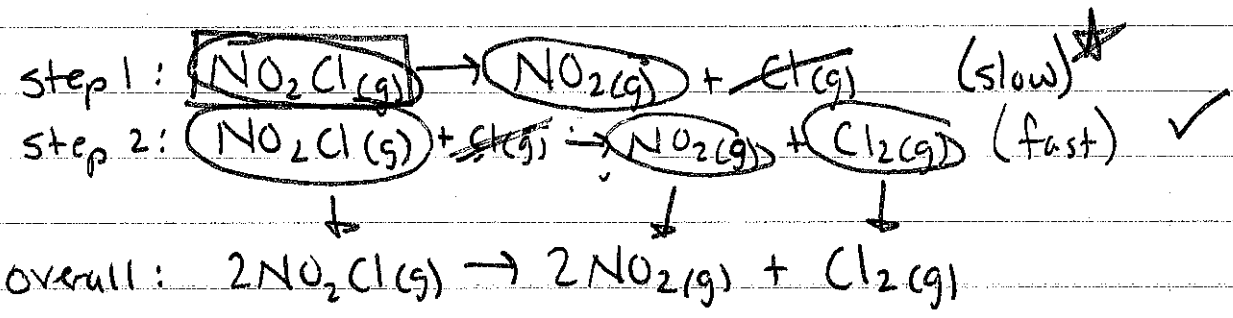


Rate Law comes directly from molecularity of RDS



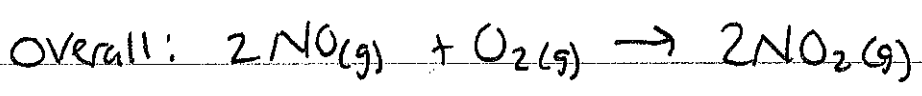
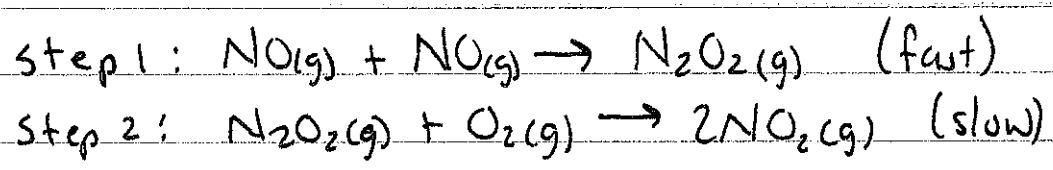
rate law from RDS \rightarrow rate expression only for elementary steps not overall rxn

1st step example



rate = $k[\text{NO}_2\text{Cl}]$ (uni) 1st order rxn

2nd step example



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$$\text{rate} = k [\text{N}_2\text{O}_2] [\text{O}_2]$$

↑ but products of 1st rxn [] depends on its reactants ∴

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2] \quad 3^{\text{rd}} \text{ order}$$

* remember: order of rxn is connected to RDS coefficients & not necessarily overall rxn

• zero order reactants exist b/c reactant does not take part in RDS

• possible 'mechanisms' due to theory (empirical findings)

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ones that do not satisfy → kinetic data & stoichiometry
must be rejected