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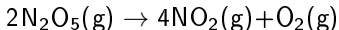$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

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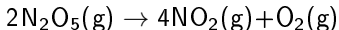If at least one component is a gas, we can monitor the change in pressure.
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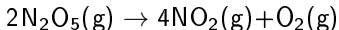initial amount of $N_2O_5 = n$ mols

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at time t, degree of dissociation $= \alpha$

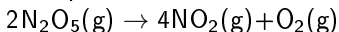|	N_2O_5	NO_2	O_2	total
amount	$n(1 - \alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n\left(1 + \frac{3}{2}\alpha\right)$

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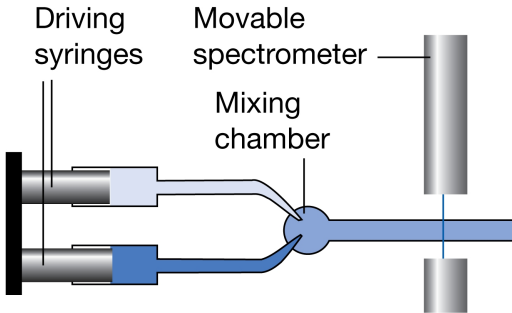Let initial pressure$=p_0$
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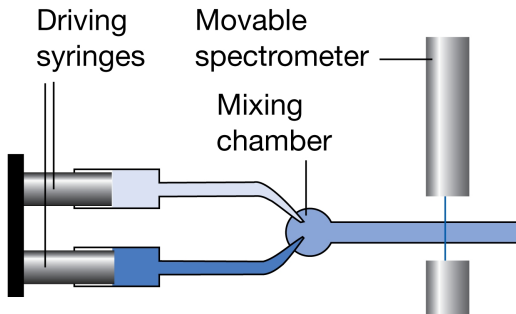|	N_2O_5	NO_2	O_2	total
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When $\alpha = 0$, $p = p_0$ $\qquad \therefore$ at time t, $p(t) = \left(1+\frac{3}{2}\alpha\right)p_0$

real-time-analysis: flow technique

location of the spectrometer corresponds to different times after initiation

real-time-analysis: flow technique

Driving syringes

Movable spectrometer

Mixing chamber

location of the spectrometer corresponds to different times after initiation

e.g., progress of the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
can be followed by measuring amount of visible light absorbed by $Br_2(g)$

Similarly, changes in conductivity and pH can be used as means of monitoring the progress of a reaction

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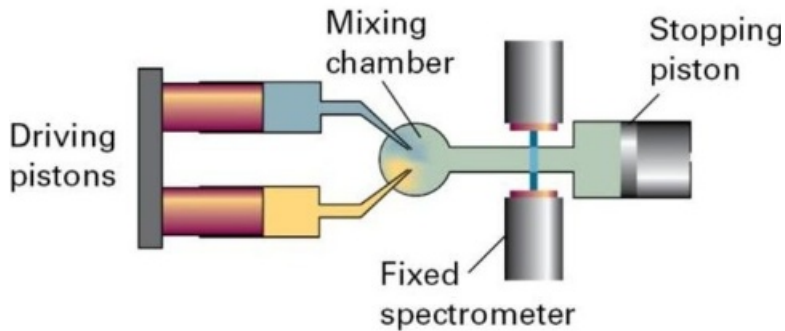e.g., the reaction $(CH_3)_3CCl(aq) + H_2O(l) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)$

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stopped-flow technique

instantaneous rate
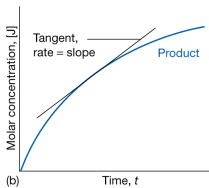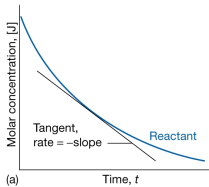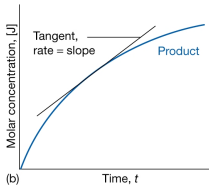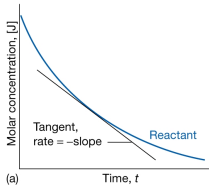
(a) Tangent, rate = −slope — Reactant

Molar concentration, [J]

Time, t

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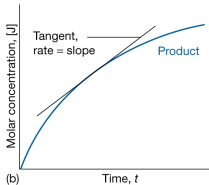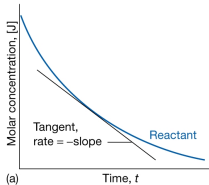J refers to species in a reaction mixture

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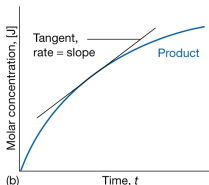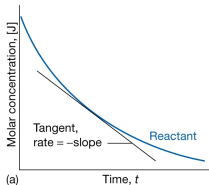J refers to species in a reaction mixture

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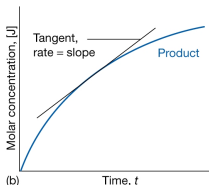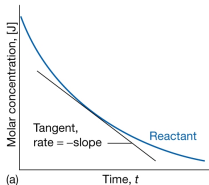$n_J =$ amount of J at some time

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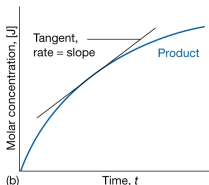$\nu_J =$ stoichiometric number of species J

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Typical rate expression, $v = k\,[A]^m\,[B]^n$; $k =$ rate constant

order w.r.t. A$= m \in \mathbb{R}$; order w.r.t. B$= n \in \mathbb{R}$; overall order$= m + n \in \mathbb{R}$

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example : unimolecular, $N_2O_4 \rightarrow 2NO_2$

bimolecular, $O + H_2 \rightarrow OH + H$

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Recombination of I atoms in the gas phase in the presence of Ar,
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$[I]_0/(10^{-5} \text{ mol dm}^{-3})$	1.0	2.0	4.0	6.0
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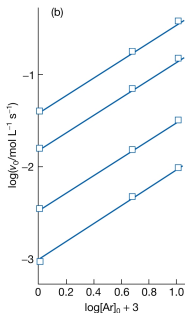
slope=2   slope=1

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  - ▶ full rate law depends on [HBr]

half-life

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1st order reaction: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

time constant, $\tau = \frac{1}{k}$

integrated rate law: Zero- order rxn

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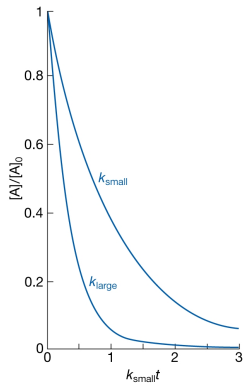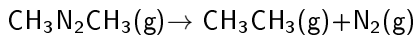
t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59
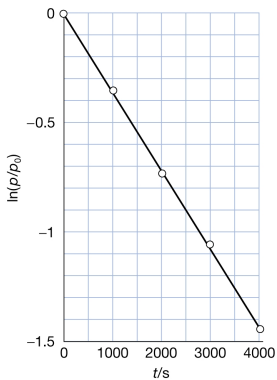
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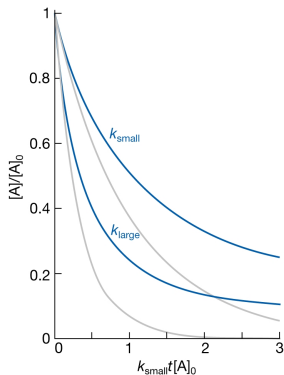
$k_{\text{large}} = 3k_{\text{small}}$
(grey lines for first order)

half life for second order reaction: $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

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In general, for $n-$th order reaction: $t_{\frac{1}{2}} = \frac{1}{k[A]_0^{n-1}}$

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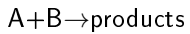
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$$\ln\left(\frac{\frac{[B]}{[B]_0}}{\frac{[A]}{[A]_0}}\right) = \left([B]_0 - [A]_0\right)kt$$

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k_r$	$[A]_0/2k_r$
		$k_r t = x$ for $0 \le x \le [A]_0$	
1	$A \rightarrow P$	$v = k_r[A]$	$(\ln 2)/k_r$
		$k_r t = \ln \dfrac{[A]_0}{[A]_0 - x}$	
2	$A \rightarrow P$	$v = k_r[A]^2$	$1/k_r[A]_0$
		$k_r t = \dfrac{x}{[A]_0([A]_0 - x)}$	
	$A + B \rightarrow P$	$v = k_r[A][B]$	
		$k_r t = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k_r[A][B]$	
		$k_r t = \dfrac{1}{[B]_0 - 2[A]_0} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k_r[A][P]$	
		$k_r t = \dfrac{1}{[A]_0 + [P]_0} \ln \dfrac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k_r[A][B]^2$	
		$k_r t = \dfrac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0}$ $+ \dfrac{1}{(2[A]_0 - [B]_0)^2} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \ge 2$	$A \rightarrow P$	$v = k_r[A]^n$	$\dfrac{2^{n-1} - 1}{(n-1)k_r[A]_0^{n-1}}$
		$k_r t = \dfrac{1}{n-1} \left\{ \dfrac{1}{([A]_0 - x)^{n-1}} - \dfrac{1}{[A]_0^{n-1}} \right\}$	

* $x = [P]$ and $v = dx/dt$

Statistics of Birth-Death processes applied to chemical kinetics :

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Consider a first order decay process,

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probability that at time we have n molecules at time t : $P_n(t)$

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This is a differential-difference equation (also called a master equation) with the

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This can be solved as before and we get,

$P_{n_0-2}(t) = \frac{n_0(n_0-1)}{2} \left(e^{-kt}\right)^{n_0-2} \left(1 - e^{-kt}\right)^2$

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$\left[\text{using } \sum_0^m p \left(\begin{array}{c} m \\ p \end{array}\right) a^p b^{m-p} = \right.$

$\left. ma\sum_{p-1=0}^{m-1} \frac{(m-1)!}{(p-1)!\{(m-1)-(p-1)\}!} a^{p-1}b^{\{(m-1)-(p-1)\}} = ma(a + b)^{m-1} \text{ and } a + b = 1\right]$

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2. We could have obtained the final result above by starting from first order decay, such that the probability of a molecule remaining unreacted after time t is e^{-kt} and not reacting is $1 - e^{-kt}$

$\implies$ the probability of n molecules remaining unreacted after time t is $\left(e^{-kt}\right)^n$ and not reacting is $\left(1 - e^{-kt}\right)^{n_0-n}$

3. The variance $= n_0 e^{-kt}(1 - e^{-kt})$

$$\left[\text{using } \sum_{p=0}^{m} p^2 \begin{pmatrix} m \\ p \end{pmatrix} a^p b^{m-p} \overset{a+b=1}{=\!=\!=} m(m-1)a^2 + ma\right.$$

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i.e., the larger the number of molecules, the relative deviation from the mean will be smaller. This is why the phenomenological results work - at the macroscopic level, the deviation is negligible.

4. The assumption that the transition is occurring in a single step from n to $n-1$ and not to $n-2$ is tantamount to Markovian statistics.