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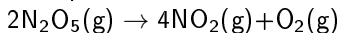Monitor quantities that change during the reaction
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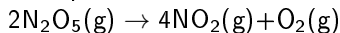$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

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initial amount of $N_2O_5 = n$ mols
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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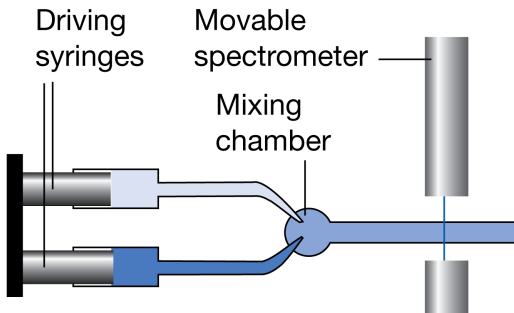Let initial pressure$=p_0$
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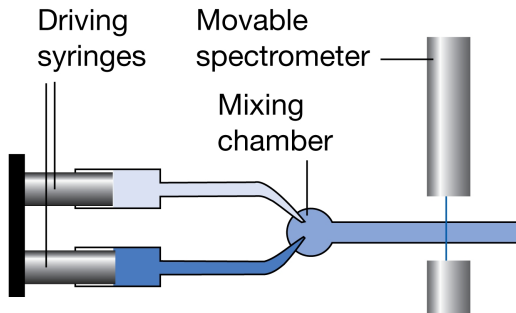|	N_2O_5	NO_2	O_2	total
amount	$n(1-\alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n\left(1+\frac{3}{2}\alpha\right)$

When $\alpha = 0$, $p = p_0$ $\quad$ $\therefore$ 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 $Br_2(g)$

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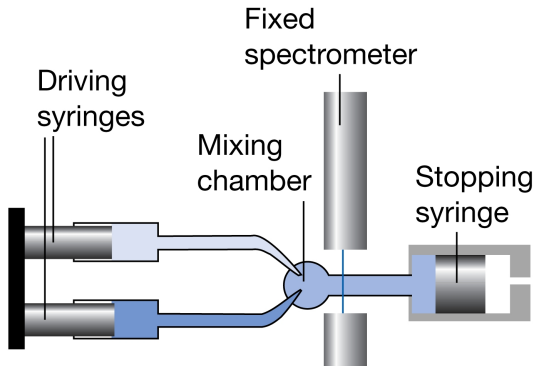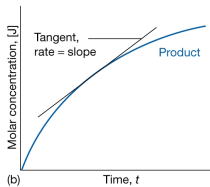monitoring the progress of a reaction
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$(CH_3)_3CCl(aq)+H_2O(l)\rightarrow(CH_3)_3COH(aq)+H^+(aq)+Cl^-(aq)$

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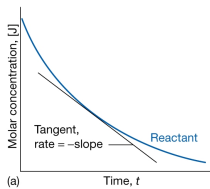
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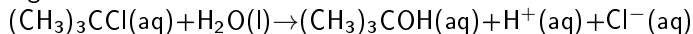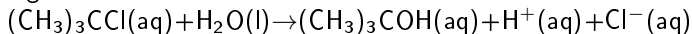
can be monitored by measuring either conductivity or pH

Driving
syringes

Fixed
spectrometer

Mixing
chamber

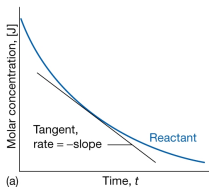Stopping
syringe

instantaneous rate

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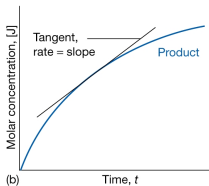
extent of reaction

$\xi = \frac{n_J - n_{J,0}}{\nu_J}$; J refers to a species in a reaction mixture

$n_J =$ amount of J at some time

$n_{J,0} =$ amount of J at initial time

$\nu_J =$ stoichiometric number of species J (negative for reactants and positive for products)

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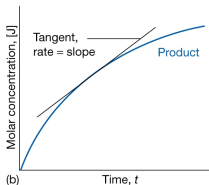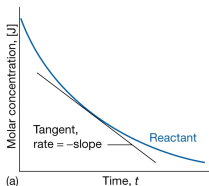

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$v = \frac{1}{V} \frac{d\xi}{dt}$; $V =$ vol. of reaction mix.

$\quad = \frac{1}{V} \frac{1}{\nu_J} \frac{dn_J}{dt}$

or, $v = \frac{1}{\nu_J} \frac{d[J]}{dt}$ (mol.dm^{-3}s^{-1})

for gas phase, (molecules.cm^{-3}s^{-1})

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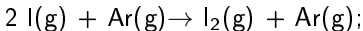
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$v = f(p_A \, p_B \cdots)$: Rate law in terms of pressures
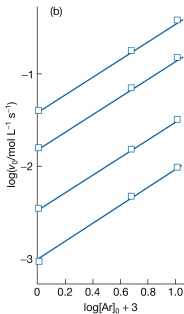
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$[I]_0/(10^{-5} \ mol \ dm^{-3})$		1.0	2.0	4.0	6.0
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	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
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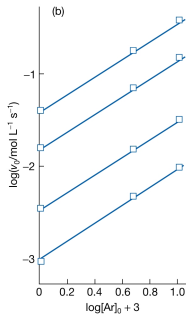
slope=2   slope=1

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half-life

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

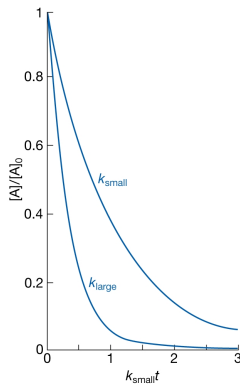time constant, $\tau = \frac{1}{k}$

integrated rate law: 1st order rxn

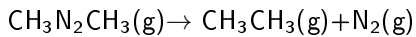integrated rate law: 1st order rxn

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$$[A] = [A]_0 \, e^{-kt}$$

$CH_3N_2CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59
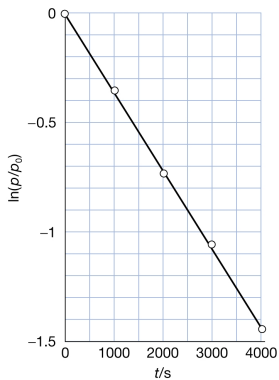
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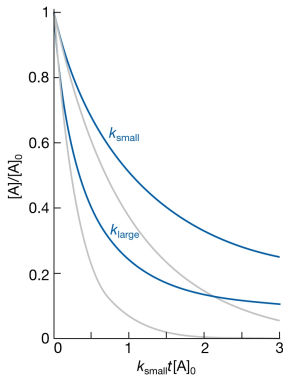
$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$[A] = \frac{[A]_0}{1+kt[A]_0}$$

$k_{\text{large}} = 3k_{small}$
(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: $t_{\frac{1}{2}} = \frac{1}{k[A]_0^{n-1}}$

General second-order reaction:

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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	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$[A]_0/2k$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \dfrac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \dfrac{x}{[A]_0([A]_0 - x)}$	$1/k[A]_0$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \dfrac{1}{[B]_0 - 2[A]_0} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \dfrac{1}{[A]_0 + [P]_0} \ln \dfrac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k[A][B]^2$ $kt = \dfrac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0}$ $\qquad + \dfrac{1}{(2[A]_0 - [B]_0)^2} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	$A \rightarrow P$	$v = k[A]^n$ $kt = \dfrac{1}{n-1} \left\{ \dfrac{1}{([A]_0 - x)^{n-1}} - \dfrac{1}{[A]_0^{n-1}} \right\}$	$\dfrac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$