A quick reminder: Chemical kinetics

Voet & Voet Chapter 14 or, for example, Atkins Chapter 10

What can we learn?

→ predict how quickly a reaction mixture approaches equilibrium

→ study the reaction mechanism (understand the elementary steps)

How do we do it?

→ determine the stoichiometry and identify any side reactions

→ determine how the reagent and/or product concentrations change with time (@ constant T)

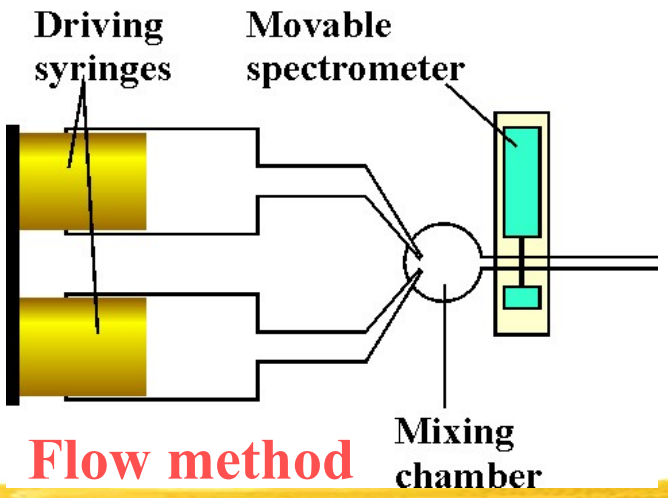
A) Quenching the reaction at defined times

B) Real-time analysis by spectroscopy

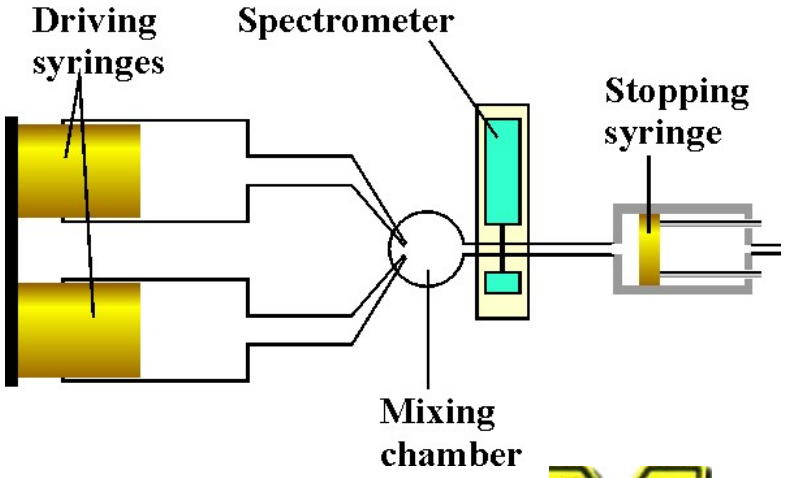
Table 10.1 *Kinetic techniques for fast reactions*

Technique	Range of time-scales/s
Femtochemistry	$>10^{-15}$
Flash photolysis	$>10^{-12}$
Fluorescence decay	10^{-10}–10^{-6}
Ultrasonic absorption	10^{-10}–10^{-4}
EPR*	10^{-9}–10^{-4}
Electric field jump	10^{-7}–1
Temperature jump	10^{-6}–1
Phosphorescence	10^{-6}–10
NMR*	10^{-5}–1
Pressure jump	$>10^{-5}$
Stopped flow	$>10^{-3}$

*EPR is electron paramagnetic resonance (or electron spin resonance); NMR is nuclear magnetic resonance; see Chapter 19.

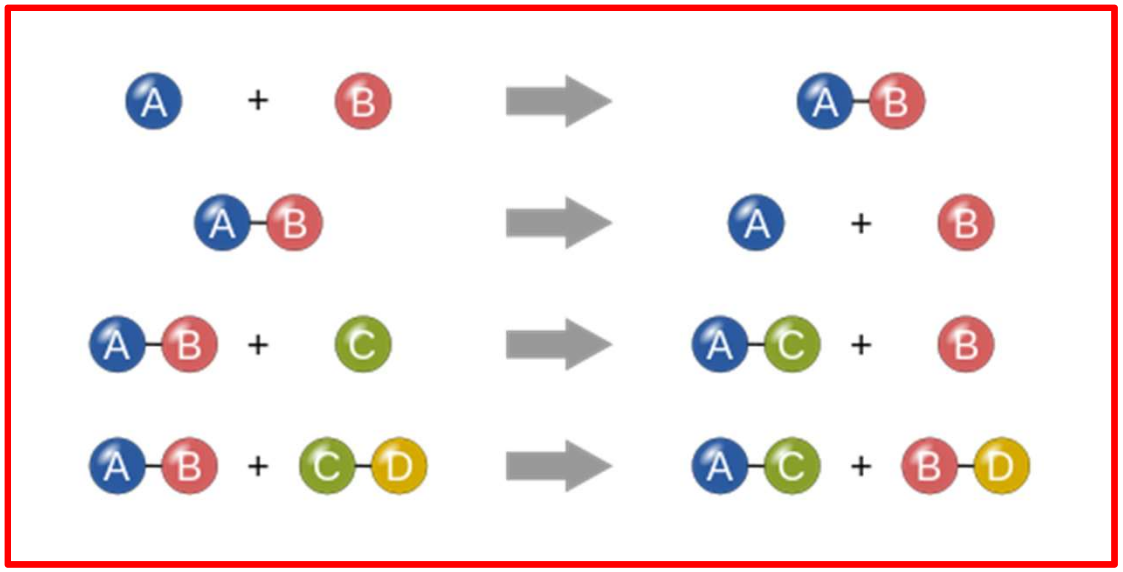


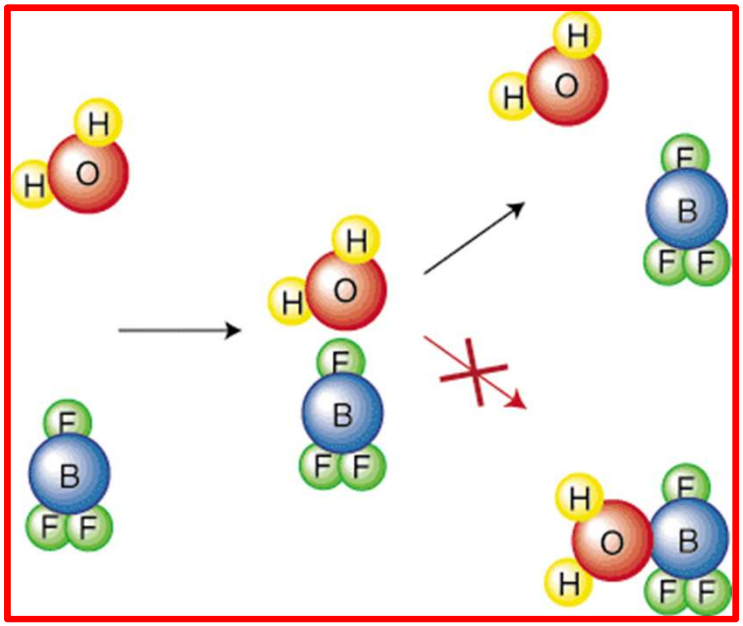
Flow method

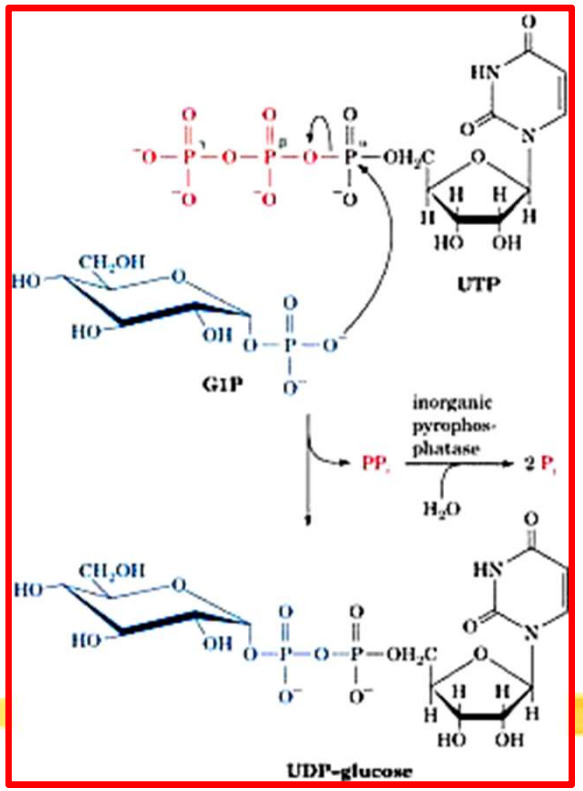


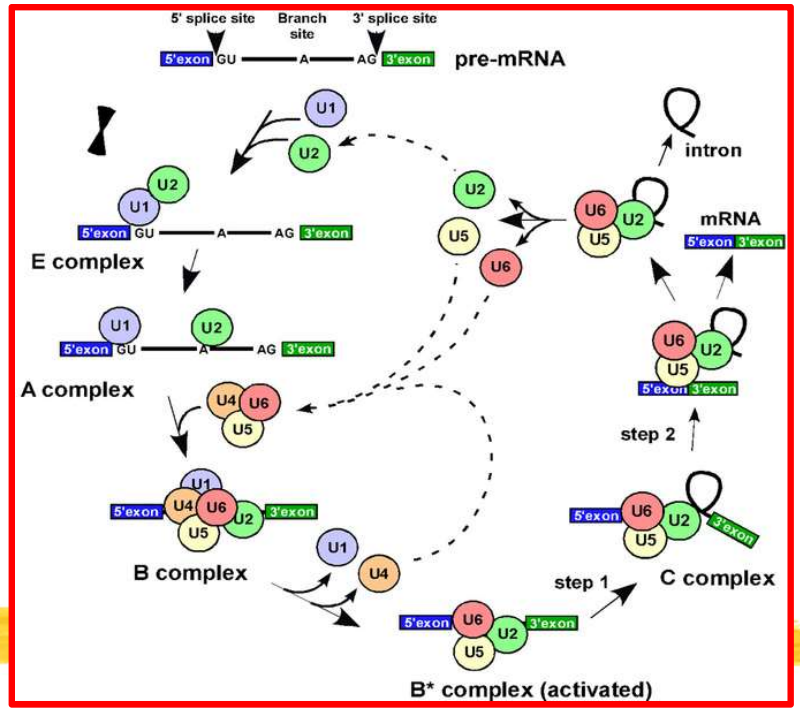
Stopped-flow method

Kinetics


A + B
A B
A B + C
A B + C D
A B
A + B
A C + B
A C + B D

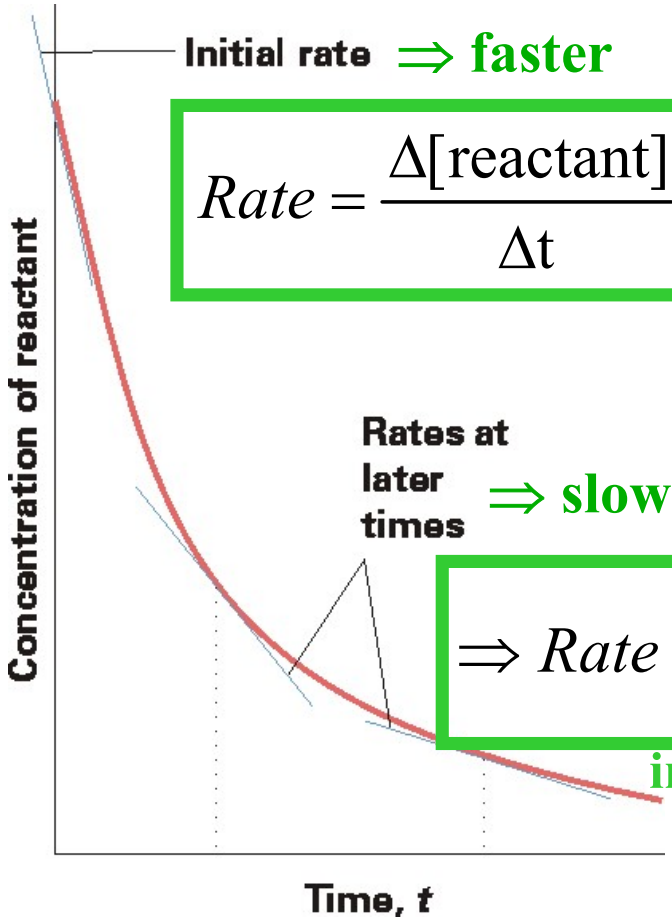

H O H
F B F F
H O H
F B F F
H O H
F B F F


UTP
G1P
inorganic pyrophos-phatase
PP$_i$
2 P$_i$
H$_2$O
UDP-glucose


5' splice site
Branch site
3' splice site
5'exon GU A AG 3'exon
pre-mRNA
U1
U2
U4
U5
U6
intron
mRNA
E complex
A complex
B complex
C complex
step 1
step 2
B* complex (activated)

Reaction rates

Raw kinetic data: [reactant](t)



$$Rate = \frac{\Delta[\text{reactant}]}{\Delta t} \quad (M\ s^{-1})$$

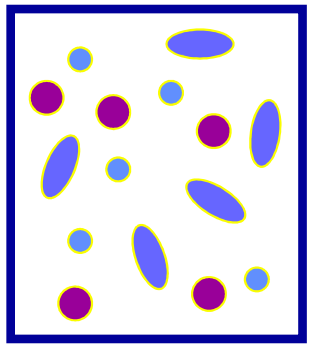
$$\Rightarrow Rate = \frac{d[\text{reactant}]}{dt}$$

instantaneous rates

Stoichiometry and rate:

$$A + B \rightarrow C$$

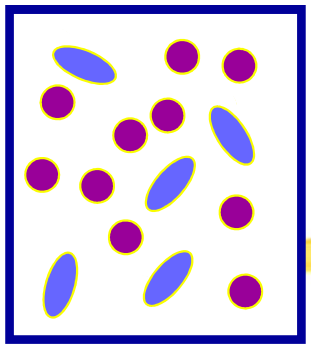
E.g., $I_2 + C_2H_4 \rightarrow C_2H_4I_2$



- $\Delta A = -5$
- $\Delta B = -5$
- $\Delta C = 5$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

$2A \rightarrow C$



- $\Delta A = -10$
- $\Delta C = 5$

$$-\frac{d[A]}{dt} = 2\frac{d[C]}{dt} \Rightarrow -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[C]}{dt}$$

Summary of rate laws

	Differential Rate Law	Integral Rate Law	Half-Life
0th Order:	$-\frac{d[A]}{dt} = k$	$[A](t) = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1st Order:	$-\frac{d[A]}{dt} = k[A]$	$[A](t) = [A]_0 e^{-kt}$	$t_{1/2} = \frac{\ln 2}{k}$
2nd Order:	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$	$t_{1/2} = \frac{1}{k[A]_0}$