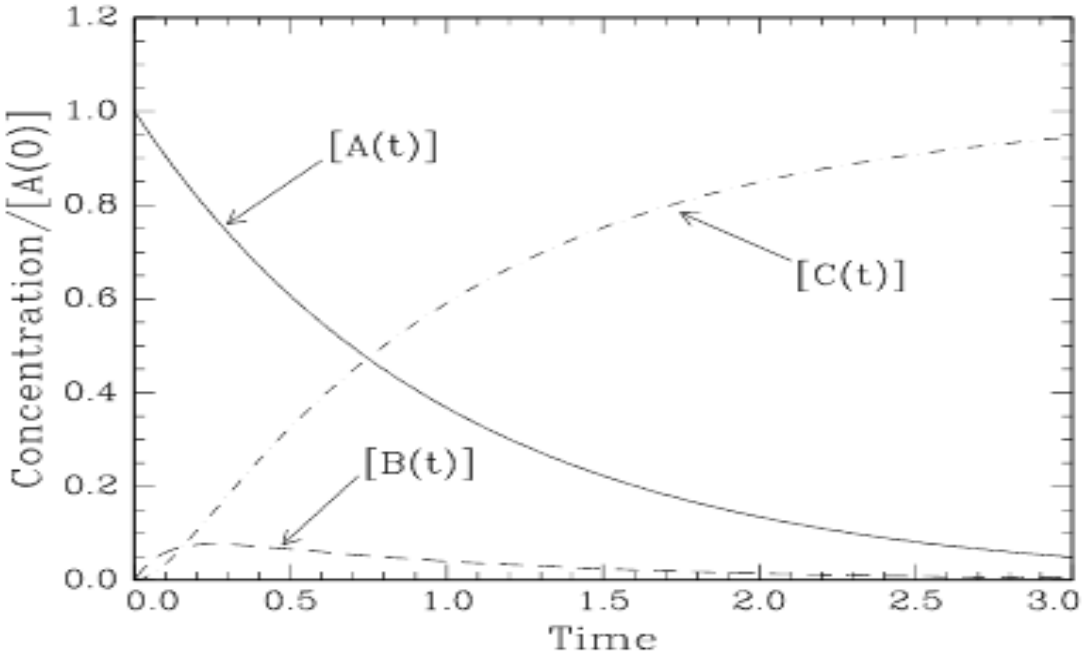
Recapitulation

Consecutive reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

Limiting case $k_1 << k_2$



Steady State Approximation

$$\frac{d[I]}{dt} = 0$$

$$[I]_{ss} = \frac{k_1[A]}{k_2}$$

$$\frac{dP}{dt} = k_2[I]$$

Excellent agreement between concentrations calculated with SSA and exact!

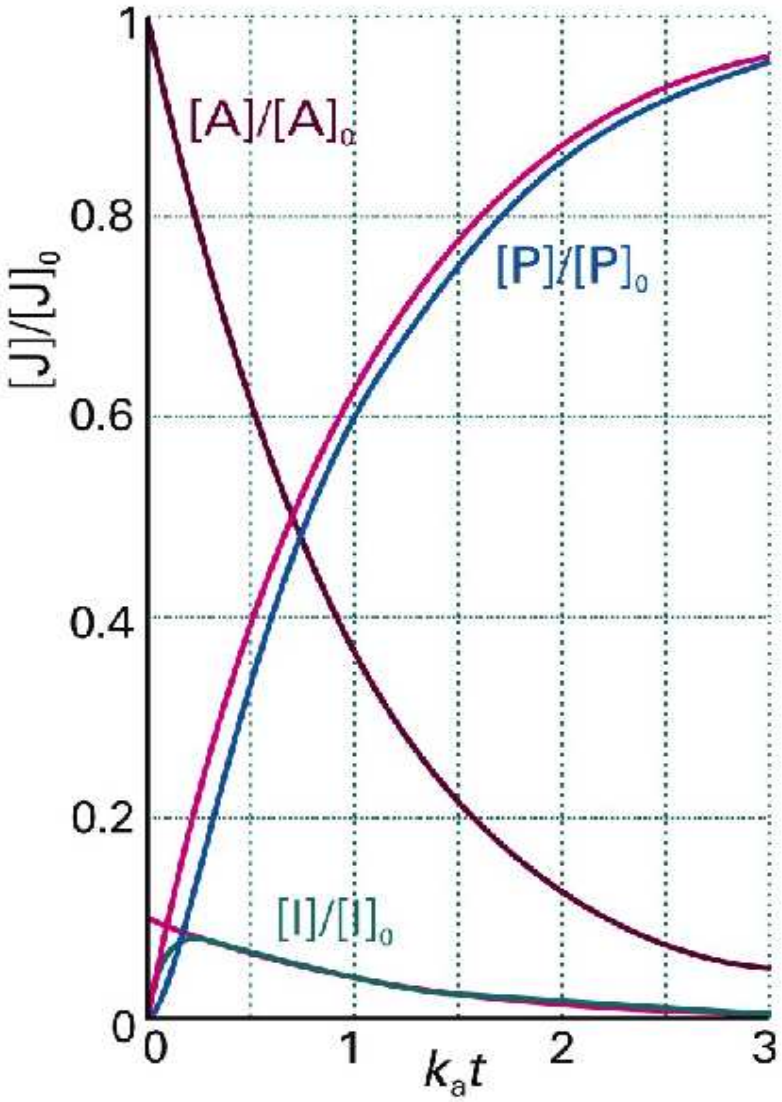


Figure 22-15
Atkins Physical Chemistry, Eighth Edition

In-class question: Apply the SSA for the mechanism

Reaction:

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

Mechanism:

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2\,NO_2$$

Apply the SSA (rate fo change of the concentration is zero) to all intermediates - here NO3 and NO.

For example:

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_3][NO_2] - k_3[NO_3][NO] - k_2[NO_3][NO_2] = 0$$

For NO it is:

$$\frac{d[NO]}{dt} = 0 = \ldots$$

The SSA is useful in deriving rate laws for mechanisms.

Most reactions do not occur in a single step.

Seemingly simple reactions could involve many steps. For example

$$2H_2 + O_2 \rightarrow 2H_2O$$

involves 19 steps!

$2H_2 + O_2 \rightarrow 2H_2O$

			A	n	E_a
(1)	$H + O_2 = O + OH$		1.04E+14	0.00	1.531E+04
(2)	$O + H_2 = H + OH$	Duplicate	3.82E+12	0.00	7.948E+03
		Duplicate	8.79E+14	0.00	1.917E+04
(3)	$H_2 + OH = H_2O + H$		2.16E+08	1.51	3.430E+03
(4)	$OH + OH = O + H_2O$		3.34E+04	2.42	−1.930E+03
(5)	$H_2 + M = H + H + M$		4.58E+19	−1.40	1.040E+05
	$\varepsilon_{H2} = 2.5$, $\varepsilon_{H2O} = 12.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO2} = 3.8$, $\varepsilon_{Ar} = 0.0$, $\varepsilon_{He} = 0.0$				
	$H_2 + Ar = H + H + Ar$		5.84E+18	−1.10	1.040E+05
	$H_2 + He = H + H + He$		5.84E+18	−1.10	1.040E+05
(6)	$O + O + M = O_2 + M$		6.16E+15	−0.50	0.000E+00
	$\varepsilon_{H2} = 2.5$, $\varepsilon_{H2O} = 12.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO2} = 3.8$, $\varepsilon_{Ar} = 0.0$, $\varepsilon_{He} = 0.0$				
	$O + O + Ar = O_2 + Ar$		1.89E+13	0.00	−1.790E+03
	$O + O + He = O_2 + He$		1.89E+13	0.00	−1.790E+03
(7)	$O + H + M = OH + M$		4.71E+18	−1.00	0.000E+00
	$\varepsilon_{H2} = 2.5$, $\varepsilon_{H2O} = 12.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO2} = 3.8$, $\varepsilon_{Ar} = 0.75$, $\varepsilon_{He} = 0.75$				
(8)	$H_2O + M = H + OH + M$		6.06E+27	−3.32	1.208E+05
	$\varepsilon_{H2} = 3.0$, $\varepsilon_{H2O} = 0.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO2} = 3.8$, $\varepsilon_{O2} = 1.5$, $\varepsilon_{N2} = 2.0$, $\varepsilon_{He} = 1.1$				
	$H_2O + H_2O = H + OH + H_2O$		1.01E+26	−2.44	1.202E+05
(9)	$H + O_2 (+M) = HO_2 (+M)^a$	k_∞	4.65E+12	0.44	0.000E+00
		k_0	6.37E+20	−1.72	5.250E+02
	$F_c = 0.5$, $T^{***} = 1.0E{-}30$, $T^* = 1.0E{+}30$				
	$\varepsilon_{H2} = 2.0$, $\varepsilon_{H2O} = 14.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO2} = 3.8$, $\varepsilon_{O2} = 0.78$, $\varepsilon_{Ar} = 0.67$, $\varepsilon_{He} = 0.8$				
	$H + O_2 (+M) = HO_2 (+M)^b$	k_∞	4.65E+12	0.44	0.000E+00
		k_0	9.04E+19	−1.50	4.920E+02
	$F_c = 0.5$, $T^{***} = 1.0E{-}30$, $T^* = 1.0E{+}30$				
	$\varepsilon_{H2} = 3.0$, $\varepsilon_{H2O} = 21.0$, $\varepsilon_{CO} = 2.7$, $\varepsilon_{CO2} = 5.4$, $\varepsilon_{O2} = 1.1$, $\varepsilon_{He} = 1.2$, $\varepsilon_{N2} = 1.5$				
(10)	$HO_2 + H = H_2 + O_2$		2.75E+06	2.09	−1.451E+03
(11)	$HO_2 + H = OH + OH$		7.08E+13	0.00	2.950E+02
(12)	$HO_2 + O = O_2 + OH$		2.85E+10	1.00	−7.239E+02
(13)	$HO_2 + OH = H_2O + O_2$		2.89E+13	0.00	−4.970E+02
(14)	$HO_2 + HO_2 = H_2O_2 + O_2$	Duplicate	4.20E+14	0.00	1.200E+04
	$HO_2 + HO_2 = H_2O_2 + O_2$	Duplicate	1.30E+11	0.00	−1.630E+03
(15)	$H_2O_2(+M) = OH + OH(+M)$	k_∞	2.00E+12	0.90	4.875E+04
		k_0	2.49E+24	−2.30	4.875E+04
	$F_c = 0.42$, $T^{***} = 1.0E{-}30$, $T^* = 1.0E{+}30$				
	$\varepsilon_{H2O} = 7.5$, $\varepsilon_{H2O2} = 7.7$, $\varepsilon_{CO2} = 1.6$, $\varepsilon_{O2} = 1.2$, $\varepsilon_{N2} = 1.5$, $\varepsilon_{He} = 0.65$				
	ε_{H2}=3.7, $\varepsilon_{CO} = 2.8$				
(16)	$H_2O_2 + H = H_2O + OH$		2.41E+13	0.00	3.970E+03
(17)	$H_2O_2 + H = HO_2 + H_2$		4.82E+13	0.00	7.950E+03
(18)	$H_2O_2 + O = OH + HO_2$		9.55E+06	2.00	3.970E+03
(19)	$H_2O_2 + OH = HO_2 + H_2O$	Duplicate	1.74E+12	0.00	3.180E+02
		Duplicate	7.59E+13	0.00	7.270E+03

Units are cm^3 mol s cal K; $k = AT^n \exp(-E_a/RT)$.

While complicated reactions could proceed by one step!
For example the Diels-Alder reaction: