Chemical Principles Atkins – Notes

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Conteúdo

Topic 17A – Rates of Chemical reactions

17A.1 Monitoring the progress of a reaction

Exemplo 17A.1 1

Self test 17A.1

$$2\,\mathrm{NOBr_{(g)}} \longrightarrow 2\,\mathrm{NO_{(g)}} + \mathrm{Br_{2(g)}}$$

Resposta

$p(\mathrm{NOBr_{(g)}})$	$p(\mathrm{NO_{(g)}})$	$p(\mathrm{Br_{2(g)}})$	p
p_0	0	0	p_0
$p_0 - 2\ \Delta p$	$2\ \Delta p$	Δp	$p_0 + \Delta p$
$3\,p_0 - 2\,p$	$2(p - p_0)$	$p - p_0$	

$$\Delta p = p - p_0$$

17A.2 Definition of Rate

$$\mathrm{A} + 2\,\mathrm{B} \longrightarrow 3\,\mathrm{C} + \mathrm{D}$$

Rate for each substance

$$v = \frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = \frac{1}{3}\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}$$

17A.2.1 Extend of reaction (ξ)

Define a universal rate of the reaction

$$\mathrm{d}n_J = v_J \ \mathrm{d}\xi$$

v_J Is the stoichiometric number of the species

17A.2.2 Rate of reaction

$$v = \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{V\,v_J}\frac{\mathrm{d}n_J}{\mathrm{d}t} \underset{\text{const}\,V}{=} \frac{1}{v_J}\frac{\mathrm{d}[\mathrm{J}]}{\mathrm{d}t}$$

V Volume of the system

Heterogeneous reaction

$$v = \frac{1}{v_J}\frac{\mathrm{d}\sigma_J}{\mathrm{d}t} \qquad \sigma_J = \frac{n_J}{A}$$

A Surface area

Topic 17B – Integrated Rate Laws

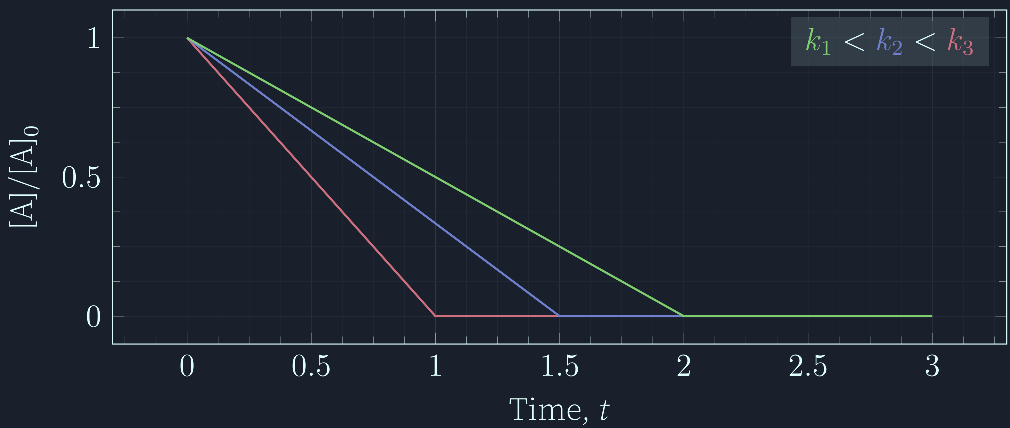
17B.1 Zeroth-Order reaction A $\longrightarrow$ P

$$\boldsymbol{v} = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}\boldsymbol{t}} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\boldsymbol{t}} = \boldsymbol{k_r}$$

$$[\mathrm{A}] = \begin{cases} [\mathrm{A}]_0 - \boldsymbol{k_r}\,\boldsymbol{t} & \boldsymbol{t} \leq [\mathrm{A}]_0/\boldsymbol{k_r} \\ 0 & \boldsymbol{t} > [\mathrm{A}]_0/\boldsymbol{k_r} \end{cases}$$

Intregration

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_r \implies$$
$$\implies \int \mathrm{d}[\mathrm{A}] = \Delta[\mathrm{A}] = [\mathrm{A}] - [\mathrm{A}]_0 = -\int k_r\,\mathrm{d}t = -k_r\,\Delta t = -k_r\,t \implies$$
$$\implies [\mathrm{A}] = [\mathrm{A}]_0 - k_r\,t$$



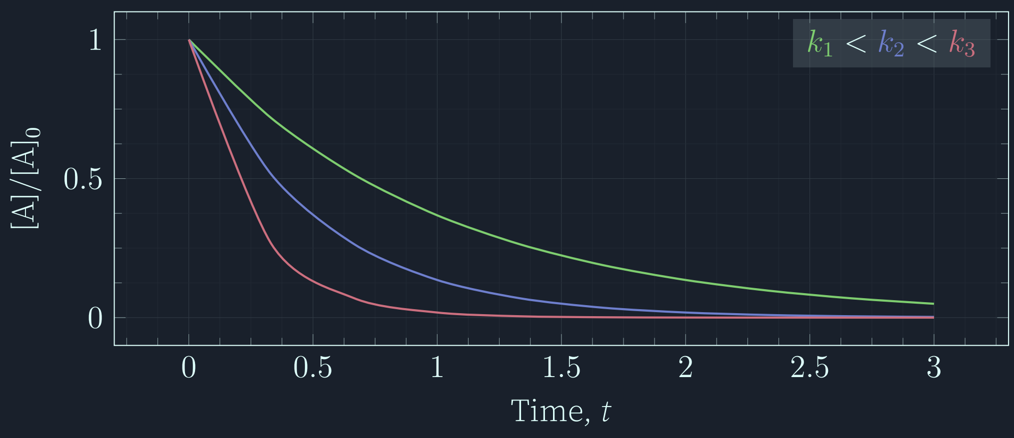
17B.2 First-order reaction A $\longrightarrow$ P

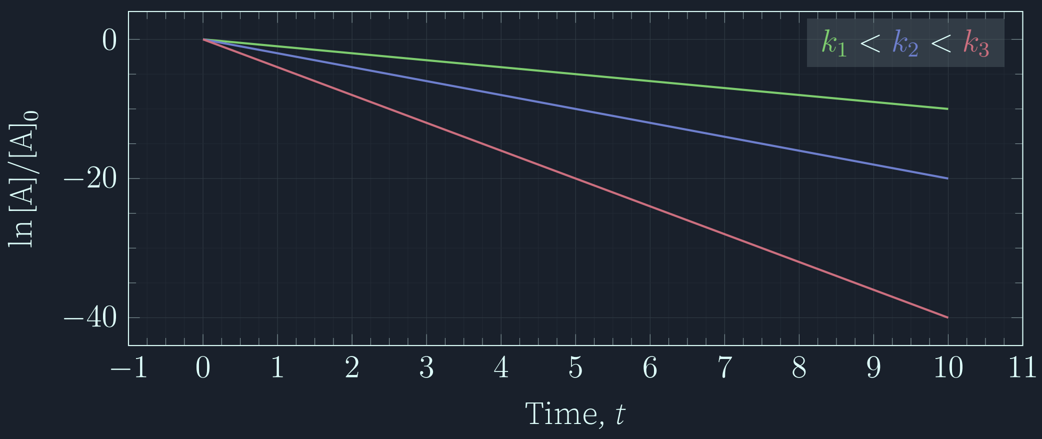
$$v = \frac{\mathrm{d[P]}}{\mathrm{d}t} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = k_r\,\mathrm{[A]}$$

$$\ln\frac{\mathrm{[A]}}{\mathrm{[A]_0}} = -k_r\,t \iff \mathrm{[A]} = \mathrm{[A]_0}\,e^{-k_r\,t}$$

Intregration

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_r\,\mathrm{[A]} \implies$$
$$\implies \int\frac{\mathrm{d[A]}}{\mathrm{[A]}} = \Delta\ln\mathrm{[A]} = \ln\frac{\mathrm{[A]}}{\mathrm{[A]_0}} = -\int k_r\,\mathrm{d}t = -k_r\,t \implies$$
$$\implies \mathrm{[A]} = \mathrm{[A]_0}\,e^{-k_r\,t}$$

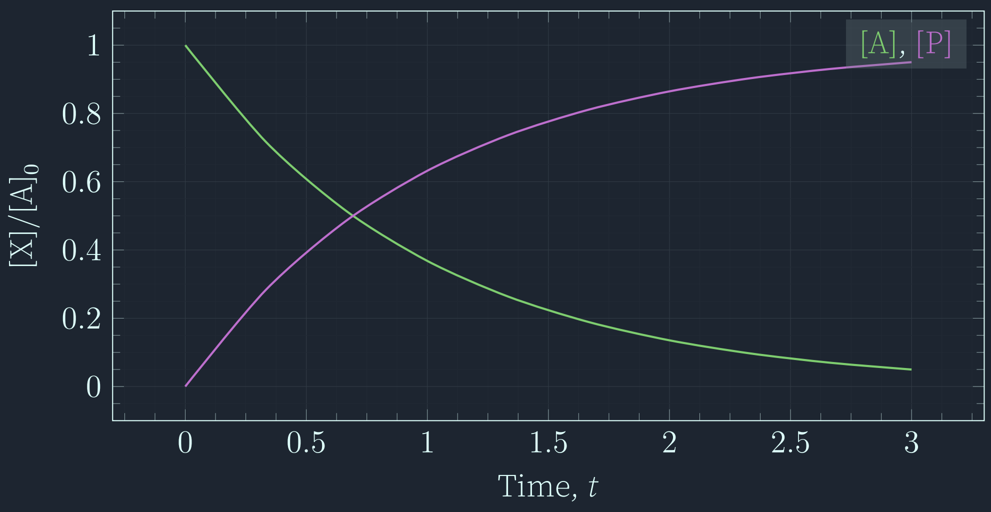




17B.2.1 Reaction

A $\longrightarrow$ P	
[A]	[P]
$\mathrm{[A]_0}$	0
$\mathrm{[A]_0} - \mathrm{[P]}$	[P]
$\mathrm{[A]} = \mathrm{[A]_0} - \mathrm{[P]}$	

$$\ln\frac{\mathrm{[A]}}{\mathrm{[A]_0}} = \ln\frac{\mathrm{[A]_0}-\mathrm{[P]}}{\mathrm{[A]_0}} = -k_r\,t \implies \mathrm{[P]} = \mathrm{[A]_0}\left(1 - e^{-k_r\,t}\right)$$



17B.2.2 Half Life

$$t_{1/2} = \frac{\ln 2}{k_r}$$

$$\ln\frac{\mathrm{[A]_0}/2}{\mathrm{[A]_0}} = \ln 1/2 = -\ln 2 = -k_r\,t_{1/2} \implies t_{1/2} = \frac{\ln 2}{k_r}$$

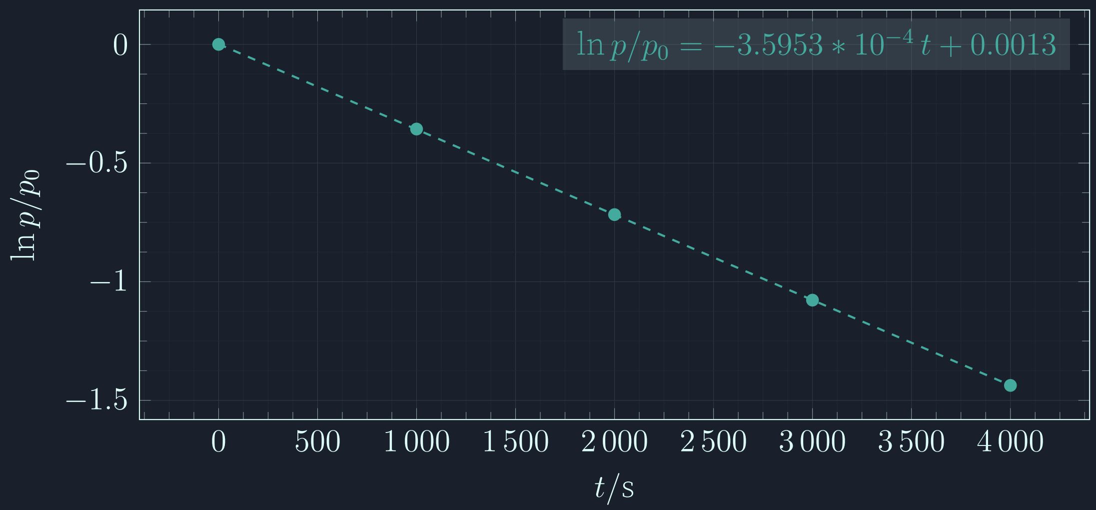
Exemplo 17B.2 1

The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition $CH_3N_2CH_{3(g)} \longrightarrow CH_3CH_{3(g)} + N_{2(g)}$ is first-order in azomethane, and find the rate constant and half-life at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Resposta

t/s	0	1000	2000	3000	4000
$\ln(p/p_0)$	0	-0.357	-0.717	-1.08	-1.44



$$k_r \cong 3.5953 * 10^{-4}; \quad t_{1/2} = \frac{\ln 2}{k_r} \cong \frac{\ln 2}{3.5953 * 10^{-4}} \cong 1.93\,\mathrm{E3}\,\mathrm{s}$$

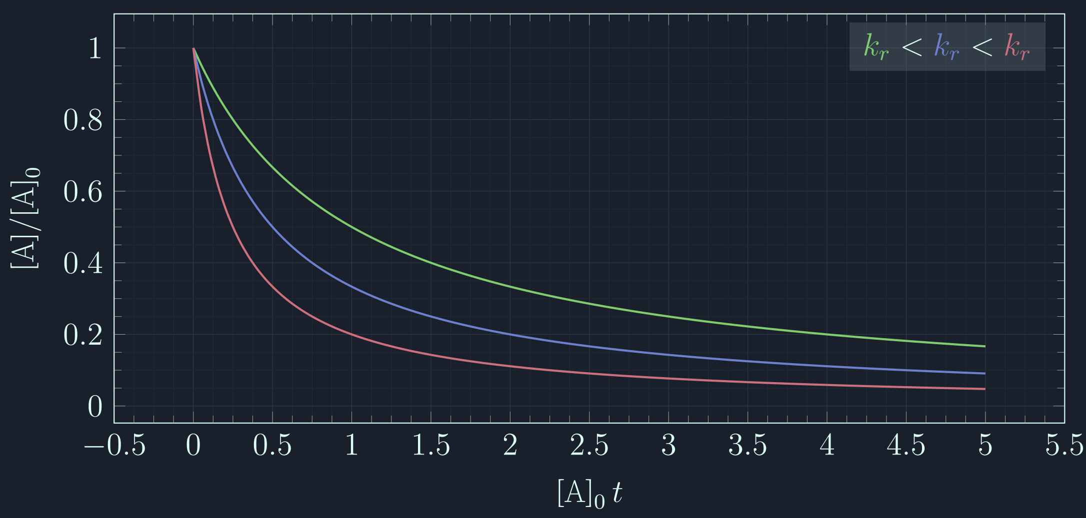
17B.3 Second-order reaction $2\,A \longrightarrow P$

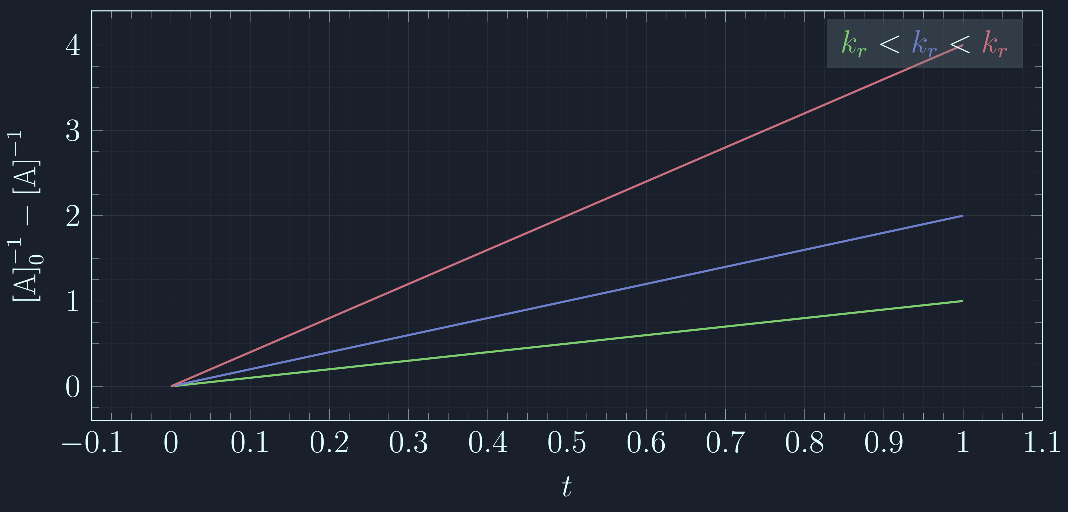
$$v = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_r\,[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_r\,t \iff [A] = \frac{[A]_0}{1 + k_r\,t\,[A]_0}$$

Intregration

$$\frac{d[A]}{dt} = -k_r\,[A]^2 \implies$$
$$\implies \int \frac{d[A]}{[A]^2} = \Delta\big(-[A]^{-1}\big) = [A]_0^{-1} - [A]^{-1} =$$
$$= -\int k_r\,dt = -k_r\,t \implies$$
$$\implies [A]^{-1} = k_r\,t + [A]_0^{-1} \iff [A] = \frac{[A]_0}{1 + k_r\,t\,[A]_0}$$

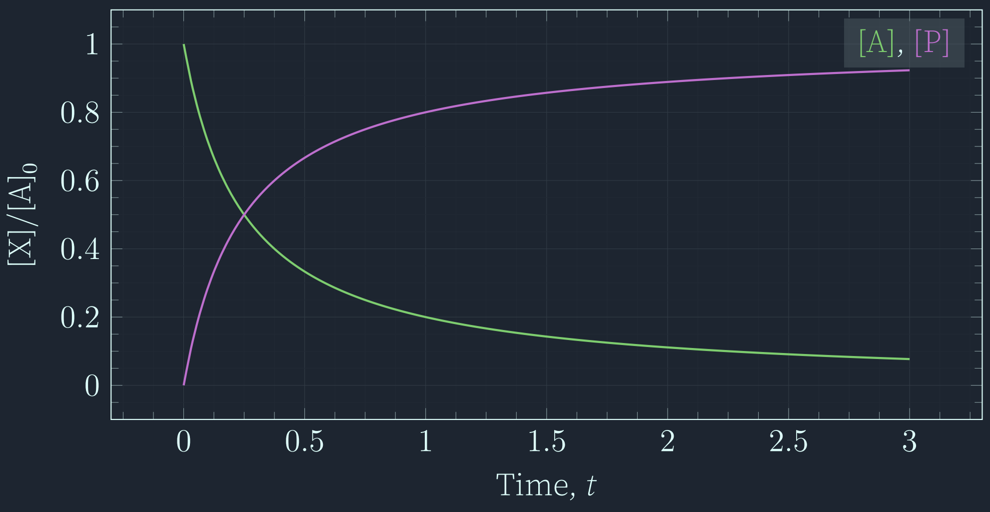




17B.3.1 Reaction

$$[P] = \frac{k_r\,t\,[A]_0^2}{1 + [A]_0\,k_r\,t} \iff \frac{1}{[P]} - \frac{1}{[A]_0} = \frac{1}{k_r\,t\,[A]_0^2}$$

$$[A] = [A]_0 - [P] = \frac{[A]_0}{1 + k_r\,t\,[A]_0} \implies k_r\,t\,[A]_0 = \frac{[P]}{[A]_0 - [P]} \implies$$
$$\implies [P] = \frac{k_r\,t\,[A]_0^2}{1 + k_r\,t\,[A]_0} \iff \frac{[A]_0}{[P]} - 1 = \frac{1}{k_r\,t\,[A]_0}$$



17B.3.2 Half life

$$t_{1/2} = \frac{1}{k_r\,[A]_0}$$

17B.4 Second-order reaction $A + B \longrightarrow P$

$$v = \frac{\mathrm{d[P]}}{\mathrm{d}t} = -\frac{\mathrm{d[A]}}{\mathrm{d}t} = -\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_r\,[\mathrm{A}][\mathrm{B}]$$

$$\ln\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0} = ([\mathrm{B}]_0 - [\mathrm{A}]_0)\,k_r\,t \qquad : \mathrm{A}_0 \neq [\mathrm{B}]_0$$

Note: Behaves as $2\,\mathrm{A} \longrightarrow \mathrm{P}$ if $[\mathrm{A}]_0 = [\mathrm{B}]_0$

Integration

[A]	[B]	[P]
$[\mathrm{A}]_0$	$[\mathrm{B}]_0$	0
$[\mathrm{A}]_0 - x$	$[\mathrm{B}]_0 - x$	x

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{A}]_0 - x}{\mathrm{d}t} = -\frac{\mathrm{d}x}{\mathrm{d}t} =$$

$$= -k_r\,[\mathrm{A}][\mathrm{B}] = -k_r\,([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) \implies$$

$$\implies \int_0^x \frac{\mathrm{d}x}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left(\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0 - x} - \ln\frac{[\mathrm{B}]_0}{[\mathrm{B}]_0 - x}\right) =$$

$$\underset{[\mathrm{A}]_0 \neq [\mathrm{B}]_0}{=} \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\left(\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]} - \ln\frac{[\mathrm{B}]_0}{[\mathrm{B}]}\right) = \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\ln\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0} =$$

$$= \int_0^t k_r\,\mathrm{d}t = k_r\,t \implies$$

$$\implies \ln\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0} = ([\mathrm{B}]_0 - [\mathrm{A}]_0)\,k_r\,t$$

17B.5 n-th order reaction nA $\longrightarrow$ P

$$v = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_r\,[\mathrm{A}]^n$$

$$k_r\,t = \frac{1}{n-1}\left(([\mathrm{A}]_0 - [\mathrm{P}])^{1-n} - [\mathrm{A}]_0^{1-n}\right); \quad n \geq 2$$

17B.5.1 Half life

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)\,k_r\,[\mathrm{A}]_0^{n-1}} \quad : n > 1$$

Topic 17C – Reactions approaching equilibrium

17C.1 First-Order reactions approaching equilibrium

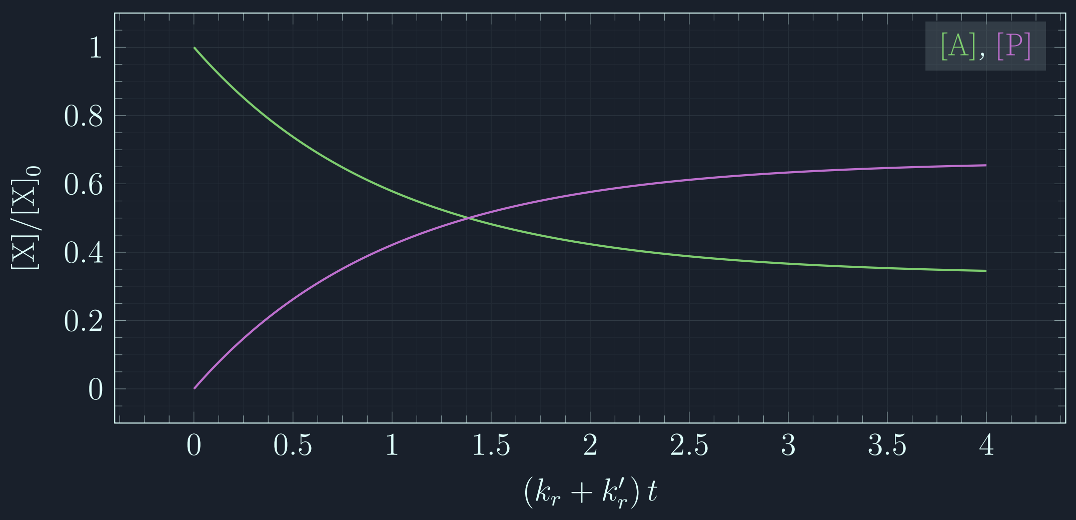
$$\mathrm{A} \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} \mathrm{P}$$

$$\boldsymbol{K} = \frac{[\mathrm{A}]_{\mathrm{eq}}}{[\mathrm{P}]_{\mathrm{eq}}} = \frac{\boldsymbol{k_r}}{\boldsymbol{k_r'}} \qquad \begin{cases} [\mathrm{P}] = [\mathrm{A}]_0 - [\mathrm{A}] \\ [\mathrm{P}]_0 = 0 \end{cases}$$

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{\boldsymbol{k_r'} + \boldsymbol{k_r}} \left(\boldsymbol{k_r'} + \boldsymbol{k_r} \, \exp\left(-(\boldsymbol{k_r'} + \boldsymbol{k_r})\boldsymbol{t}\right)\right)$$

$$[\mathrm{A}]_{\mathrm{eq}} = \frac{[\mathrm{A}]_0}{(\boldsymbol{k_r}/\boldsymbol{k_r'}) + 1}; \quad [\mathrm{P}]_{\mathrm{eq}} = \frac{[\mathrm{A}]_0}{(\boldsymbol{k_r'}/\boldsymbol{k_r}) + 1}$$

$$\boldsymbol{v} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}\boldsymbol{t}} = \boldsymbol{k_r}\,[\mathrm{A}] - \boldsymbol{k_r'}\,[\mathrm{B}]$$



integration

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} =$$

$$= -k_r\,[\mathrm{A}] + k_r'\,[\mathrm{P}] \underset{\mathrm{P}_0=0}{=} -k_r\,[\mathrm{A}] + k_r'\,([\mathrm{A}]_0 - [\mathrm{A}]) = -(k_r' + k_r)\,[\mathrm{A}] + k_r'\,[\mathrm{A}]_0 \implies$$

$$\implies \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{\mathrm{d}[\mathrm{A}]}{-(k_r' + k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0} =$$

$$= \int_{-(k_r'+k_r)[\mathrm{A}]_0 + k_r'[\mathrm{A}]_0}^{-(k_r'+k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0} \frac{\frac{\mathrm{d}(-(k_r'+k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0)}{-(k_r'+k_r)}}{-(k_r' + k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0} =$$

$$= \frac{-1}{k_r' + k_r}\,\Delta\,(\ln -(k_r' + k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0) =$$

$$= \frac{-1}{k_r' + k_r}\left(\ln \frac{-(k_r' + k_r)[\mathrm{A}] + k_r'[\mathrm{A}]_0}{-(k_r' + k_r)[\mathrm{A}]_0 + k_r'[\mathrm{A}]_0}\right) =$$

$$= \frac{-1}{k_r' + k_r}\left(\ln \frac{-(k_r' + k_r)\frac{[\mathrm{A}]}{[\mathrm{A}]_0} + k_r'}{k_r}\right) =$$

$$= \frac{-1}{k_r' + k_r}\left(\ln\left(-(k_r' - k_r)\frac{[\mathrm{A}]}{[\mathrm{A}]_0} + k_r'\right) - \ln k_r\right) =$$

$$= \int_0^t \mathrm{d}t = t \implies$$

$$\implies \exp\left(\ln\left(-(k_r' + k_r)\frac{[\mathrm{A}]}{[\mathrm{A}]_0} + k_r'\right)\right) = -(k_r' + k_r)\frac{[\mathrm{A}]}{[\mathrm{A}]_0} + k_r' =$$

$$= \exp\left(-(k_r' + k_r)t + \ln k_r\right) = k_r \exp\left(-(k_r' + k_r)t\right) \implies$$

$$\implies [\mathrm{A}] = \frac{[\mathrm{A}]_0}{k_r' + k_r}\left(k_r' + k_r\,\exp\left(-(k_r' + k_r)t\right)\right)$$

$$\lim_{t\to\infty} [\mathrm{A}] = \frac{[\mathrm{A}]_0}{k_r' + k_r}\,(k_r' + k_r * 0) = \frac{[\mathrm{A}]_0\,k_r'}{k_r' + k_r}$$

17C.1.1 Chain reactions

$$\mathrm{X}_1 \longrightarrow \mathrm{X}_2 \longrightarrow \ldots \longrightarrow \mathrm{X}_{\mathrm{n+1}}$$

$$\boldsymbol{K} = \prod_{i=1}^{n} \frac{\boldsymbol{k_i}}{\boldsymbol{k_i'}}$$