3. Systems of reactions. Reversible, parallel, consecutive reactions. Complex reaction systems.

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MINISTRY OF EDUCATION,
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Summary

- Simple systems of elementary reactions
- Open x Closed sequence of elementary steps
- Quasi Steady State Hypothesis
- Practically important examples

Elementary (one step) reactions between stable molecules are very rare. Rather, a sequence of elementary steps is necessary.

Examples

- Polymerization
- Catalytic and enzymatic reactions
- Combustion
- Catalytic reactions (homogeneous, heterogeneous)

Basic characteristics

- large number of species ($N > 10^6$)
- complex mechanism
- effect of environment (e.g. effect of solid surface on reaction rate)
- highly exothermic or endothermic processes

Basic types of complex reactions

1) Reversible reactions
2) Parallel reactions
3) Consecutive reactions

Homework 3

To find $c_1(t)$, $c_2(t)$,$c_3(t)$ in the closed isotherm constant volume reaction system, in which the first order irreversible consecutive reactions take place

$$A_1 \rightarrow A_2 \qquad r_{V1} = k_1 c_1 \qquad t = 0,\ c_1 = 1\ \text{mol/l},\ c_2 = c_3 = 0$$

$$A_2 \rightarrow A_3 \qquad r_{V2} = k_2 c_2 \qquad t \in (0;5)$$

$$a) k_1 = 2\ \text{min}^{-1}, k_2 = 1\ \text{min}^{-1}$$

$$b) k_1 = k_2 = 1\ \text{min}^{-1}$$

$$c) t_{opt}\ \text{for}\ c_2$$

HW 3

$A_1 \rightarrow A_2 \qquad r_{V1} = k_1 c_1 \qquad t = 0,\ c_1 = 1\ \text{mol/l},\ c_2 = c_3 = 0$

$A_2 \rightarrow A_3 \qquad r_{V2} = k_2 c_2 \qquad t \in (0;5)$

$a) k_1 = 2\ \text{min}^{-1}, k_2 = 1\ \text{min}^{-1}$

$b) k_1 = k_2 = 1\ \text{min}^{-1}$

$c) t_{opt}\ \text{for}\ c_2$

LINEAR 1ST ORDER DIFFERENTIAL EQUATION ⟹ INTEGRATION FACTOR

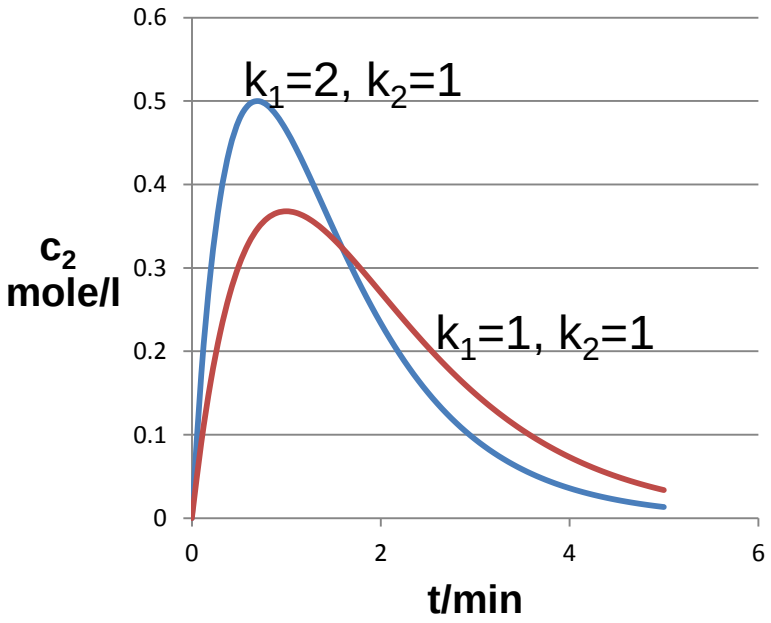
Solution

$$a) c_2 = c_1^o \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$b) c_2 = c_1^o k_1 t e^{-k_1 t}$$

$$c) k_1 \neq k_2, t_{opt} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1} = 0.693, c_2(t_{opt}) = c_1^o \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}} = \frac{1}{2}\ \text{mol/l}$$

$$k_1 = k_2, t_{opt} = \frac{1}{k_1} = 1, c_2(t_{opt}) = \frac{c_1^o}{e} = 0.368\ \text{mol/l}$$



Open x Closed sequence of elementary steps

- **In the sequence of elementary steps, the reactants and products of these are not stable reactants or products but are highly reactive intermediates.**

- **The reactive intermediates can be of several different chemical types : free radicals, free ions, solvated ions, complexes at solid surfaces, complexes in homogeneous phase, complexes with enzymes.**

- **Many intermediates may be involved in a given reaction, however the advancement of the reaction can still be described by means of a single parameter – extent of reaction or fractional conversion of key component.**

- **There are two types of sequences leading from reactants to products through intermediates: OPEN or CLOSED.**

- **An open sequence is one in which an intermediate is not reproduced in any other step of the sequence.**

- **A closed sequence is one in which an intermediate is reproduced so that a cyclic reaction pattern repeats itself and a large number of molecules of products can be made through only one intermediate. (Catalysis)**

$$O_{3(g)} \rightleftarrows O_{2(g)} + O_{(g)}$$

$$O_{3(g)} + O_{(g)} \rightarrow 2O_{2(g)}$$

$$2O_{3(g)} \rightarrow 3O_{2(g)}$$

Open

$$O_{3(g)} + Cl_{(g)} \rightleftarrows ClO_{(g)} + O_{2(g)}$$

$$ClO_{(g)} + O_{3(g)} \rightarrow Cl_{(g)} + 2O_{2(g)}$$

$$2O_{3(g)} \rightarrow 3O_{2(g)}$$

Closed (catalytic)

Quasi Steady State Hypothesis – QSSH

The concentrations of the intermediates remain low and constant → these intermediate concentrations can be expressed using reactant and product concentrations

Example

Fosgen ($COCl_2$) is manufactured by gas phase reaction between CO and Cl_2

$$CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$$

It follows from experimental data :

$$r_V = k c_{CO} c_{Cl_2}^{3/2} \quad [\mathrm{mol.m^{-3}.s^{-1}}]$$

The proposed mechanism involves 2 intermediates Cl and COCl.

Reaction	Kinetic equation
1. $Cl_{2(g)} \leftrightarrow 2Cl_{(g)}$	$r_1 = k_{f,1} c_{Cl_2} - k_{b,1} c_{Cl}^2$
2. $CO_{(g)} + Cl_{(g)} \leftrightarrow COCl_{(g)}$	$r_2 = k_{f,2} c_{CO} c_{Cl} - k_{b,2} c_{COCl}$
3. $COCl_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)} + Cl_{(g)}$	$r_3 = k_{f,3} c_{COCl} c_{Cl_2}$

The balances of intermediates at steady state:

$$R_{Cl} = 2r_1 - r_2 + r_3 = 0$$

$$R_{COCl} = r_2 - r_3 = 0$$

$$\mathbf{\nu} = \begin{array}{c} \begin{array}{ccccc} Cl_2 & Cl & CO & COCl & COCl_2 \end{array} \\ \begin{pmatrix} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 0 \\ -1 & 1 & 0 & -1 & 1 \end{pmatrix} \end{array}$$

By adding above equations

$$2r_1 = 0 = r_1 = k_{f,1} c_{Cl_2} - k_{b,1} c_{Cl}^2$$

$$c_{Cl} = \left(\frac{k_{f,1}}{k_{b,1}} c_{Cl_2} \right)^{1/2}$$

Concentration of COCl:

$$R_{COCl} = r_2 - r_3 = k_{f,2} c_{CO} c_{Cl} - k_{b,2} c_{COCl} - k_{f,3} c_{COCl} c_{Cl_2} = 0$$

$$c_{COCl} = \frac{k_{f,2} c_{CO} c_{Cl}}{k_{b,2} + k_{f,3} c_{Cl_2}} = \frac{k_{f,2} c_{CO} \left(\frac{k_{f,1}}{k_{b,1}} c_{Cl_2} \right)^{1/2}}{k_{b,2} + k_{f,3} c_{Cl_2}} = \frac{k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} c_{CO} \left(c_{Cl_2} \right)^{1/2}}{k_{b,2} + k_{f,3} c_{Cl_2}}$$

Rate of $COCl_2$ production is given by equation (3) in which we substitute for COCl concentration

$$R_{COCl_2} = r_3 = k_{f,3} c_{COCl} c_{Cl_2} = \frac{k_{f,3} k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} c_{CO} \left(c_{Cl_2} \right)^{3/2}}{k_{b,2} + k_{f,3} c_{Cl_2}}$$

If Cl_2 concentration is low or $k_{b,2} >> k_{f,3}$ is valid, we get

$$R_{COCl_2} = \frac{k_{f,3} k_{f,2}}{k_{b,2}} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} c_{CO} \left(c_{Cl_2} \right)^{3/2} = k c_{CO} \left(c_{Cl_2} \right)^{3/2}$$

$$k = \frac{k_{f,3} k_{f,2}}{k_{b,2}} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2}$$

Validity of QSSH

$Cl_{2(g)} \leftrightarrow 2\underline{Cl}_{(g)}$	$r_{V,1} = k_{f,1} c_{Cl_2} - k_{b,1} c_{Cl}^2$
$CO_{(g)} + Cl_{(g)} \leftrightarrow \underline{COCl}_{(g)}$	$r_{V,2} = k_{f,2} c_{CO} c_{Cl} - k_{b,2} c_{COCl}$
$\underline{COCl}_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)} + \underline{Cl}_{(g)}$	$r_{V,3} = k_{f,3} c_{COCl} c_{Cl_2}$

Isothermal batch constant volume reactor

$$\frac{dc_{Cl_2}}{dt} = -r_{V,1} - r_{V,3}$$

$$\frac{dc_{Cl}}{dt} = 2r_{V,1} - r_{V,2} + r_{V,3}$$

$$\frac{dc_{CO}}{dt} = -r_{V,2}$$

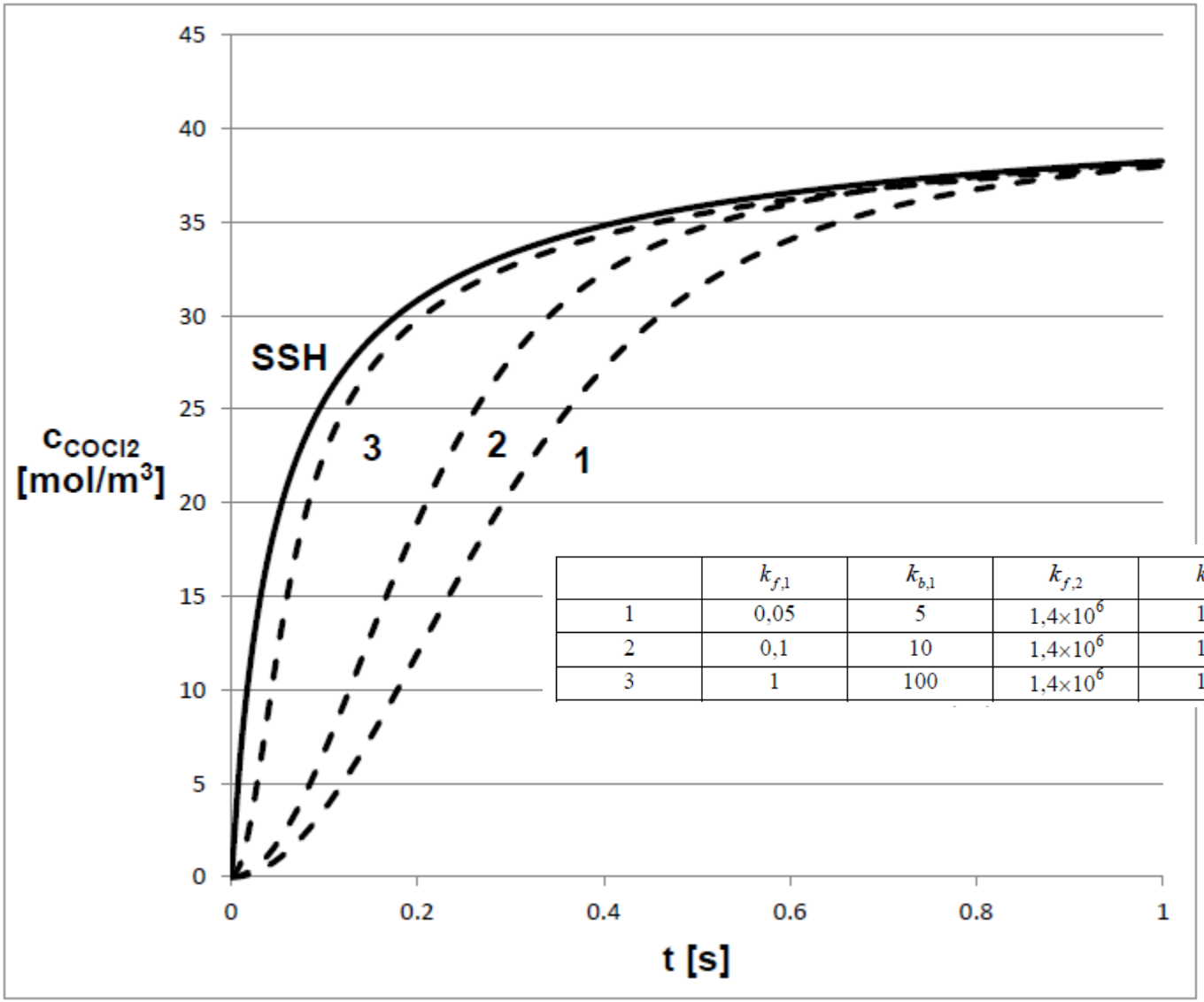
$$\frac{dc_{COCl}}{dt} = r_{V,2} - r_{V,3}$$

$$\frac{dc_{COCl_2}}{dt} = r_{V,3}$$

$$k = \frac{k_{f,3} k_{f,2}}{k_{b,2}} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} = 0.07 \ (m^3 mol^{-1})^{3/2} s^{-1}$$

Kinetic parameters used in numerical simulation

	$k_{f,1}$	$k_{b,1}$	$k_{f,2}$	$k_{b,2}$	$k_{f,3}$
1	0,05	5	$1{,}4\times10^6$	10^7	5
2	0,1	10	$1{,}4\times10^6$	10^7	5
3	1	100	$1{,}4\times10^6$	10^7	5



	$k_{f,1}$	$k_{b,1}$	$k_{f,2}$	$k_{b,2}$	$k_{f,3}$
1	0,05	5	$1{,}4\times10^{6}$	10^{7}	5
2	0,1	10	$1{,}4\times10^{6}$	10^{7}	5
3	1	100	$1{,}4\times10^{6}$	10^{7}	5

Concentration profiles of $COCl_2$

Homework 4 (due after Chapter 4)

Calculate volumes of CSTR a PFR working at 150 ^{o}C and 300 kPa to produce 1 t $COCl_2$/day with CO conversion equal to 95 %. A mixture of CO and Cl_2 (molar ratio 1:1) is fed at 300 kPa and 150 ^{o}C.

Data

k(423 K) = 0.07 $(m^3mol^{-1})^{3/2}.s^{-1}$

M_{COCl2} = 98.92 kg/kmol.

Answer:

V_{CSTR} = 0.053 m^3 V_{PFR} = 0.0021 m^3

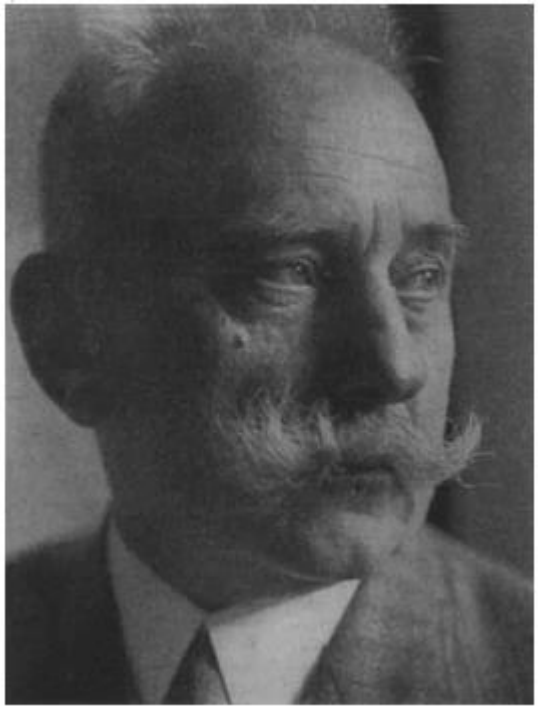
Example

$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$

Mechanism:

$2NO_{(g)} \leftrightarrow (NO)_{2(g)} \cong$equlibrium(1)

$(NO)_{2(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ (2)



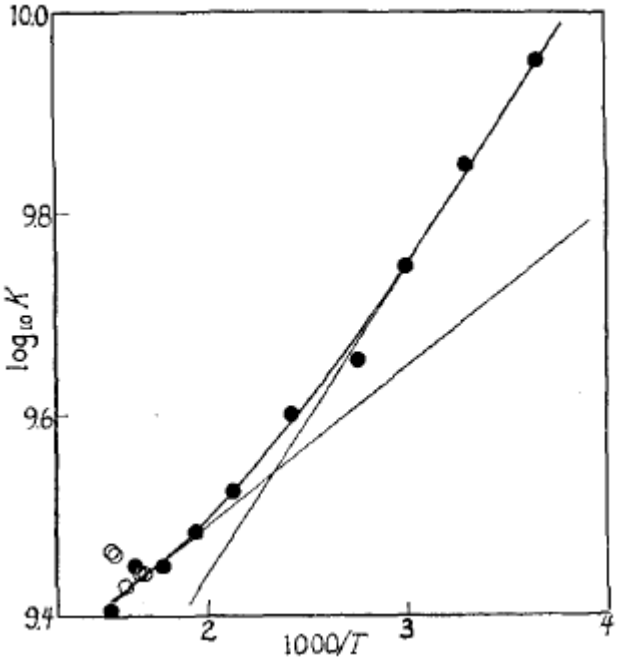
Max Bodenstein, 1941

$$K_1 = \frac{c_{(NO)_2}}{c_{NO}^2}$$

$$r_2 = k_{f,2} c_{(NO)_2} c_{O_2} - k_{b,2} c_{NO_2}^2 = k_{f,2} K_1 c_{NO}^2 c_{O_2} - k_{b,2} c_{NO_2}^2 = k_f' c_{NO}^2 c_{O_2} - k_b c_{NO_2}^2$$

$$k_f' = k_{f,2} K_1 = A_{of,2} e^{-\frac{E_{f,2}}{RT}} e^{-\frac{\Delta_r G_1^o}{RT}} = A_{of,2} e^{\frac{\Delta_r S_1^o}{R}} e^{-\frac{\left(E_{f,2} + \Delta_r H_1^o\right)}{RT}} = A_{of}' e^{-\frac{E_f'}{RT}}$$

$$A_{of}' = A_{of,2} e^{\frac{\Delta_r S_1^o}{R}}, E_f' = E_{f,2} + \Delta_r H_1^o$$



Radical polymerization

Inicialization

$I \xrightarrow{k_d} 2R\bullet$ $R\bullet + M \xrightarrow{k_i} P_1\bullet$	$r_d = k_d c_I$ $r_{init} = k_i c_{R\bullet} c_M$

Propagation

$P_1\bullet + M \xrightarrow{k_p} P_2\bullet$	$r_1 = k_p c_{P_1\bullet} c_M$
$P_2\bullet + M \xrightarrow{k_p} P_3\bullet$	$r_2 = k_p c_{P_2\bullet} c_M$
.	.
.	.
$P_{i-1}\bullet + M \xrightarrow{k_p} P_i\bullet$	$r_{i-1} = k_p c_{P_{i-1}\bullet} c_M$
.	.

Termination

$P_k\bullet + P_l\bullet \xrightarrow{k_t} P_{k+l}$	$r_{t,k+l} = k_t c_{P_k\bullet} c_{P_l\bullet}$

Intermediates

$$\frac{dc_{P_i\bullet}}{dt} = \frac{dc_{R\bullet}}{dt} = 0$$

Balance of initiator

$$2r_d - r_{init} = 0$$

$$2k_d c_I = k_i c_{R\bullet} c_M$$

$$c_{R\bullet} = \frac{2k_d c_I}{k_i c_M}$$

Balance of $P_1\bullet$

$$R_{P_1\bullet} = r_{init} - r_1 - r_{t,1} = k_i c_{R\bullet} c_M - k_p c_{P_1\bullet} c_M - k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

Balance of $P_k\bullet, k = 2,3,\ldots$

$$R_{P_k\bullet} = k_p c_{P_{k-1}\bullet} c_M - k_p c_{P_k\bullet} c_M - k_t c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

By summing the last equation from k=2,3,… and adding balance equation of $P_1\bullet$

$$k_i c_{R\bullet} c_M - k_t \left(\sum_{j=1}^{\infty} c_{P_j\bullet} \right)^2 = 0 \quad \longrightarrow \quad \sum_{j=1}^{\infty} c_{P_j\bullet} = \sqrt{\frac{k_i c_{R\bullet} c_M}{k_t}} = \sqrt{\frac{2k_d c_I}{k_t}}$$

Monomer consumption

$$R_M = -r_{init} - k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} = -\left(k_i c_{R\bullet} c_M + k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} \right) =$$

$$= -\left(2k_d c_I + k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M \right) \cong -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M$$

Polymer P_n production

$$R_{P_n} = \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}\bullet} c_{P_k\bullet}$$

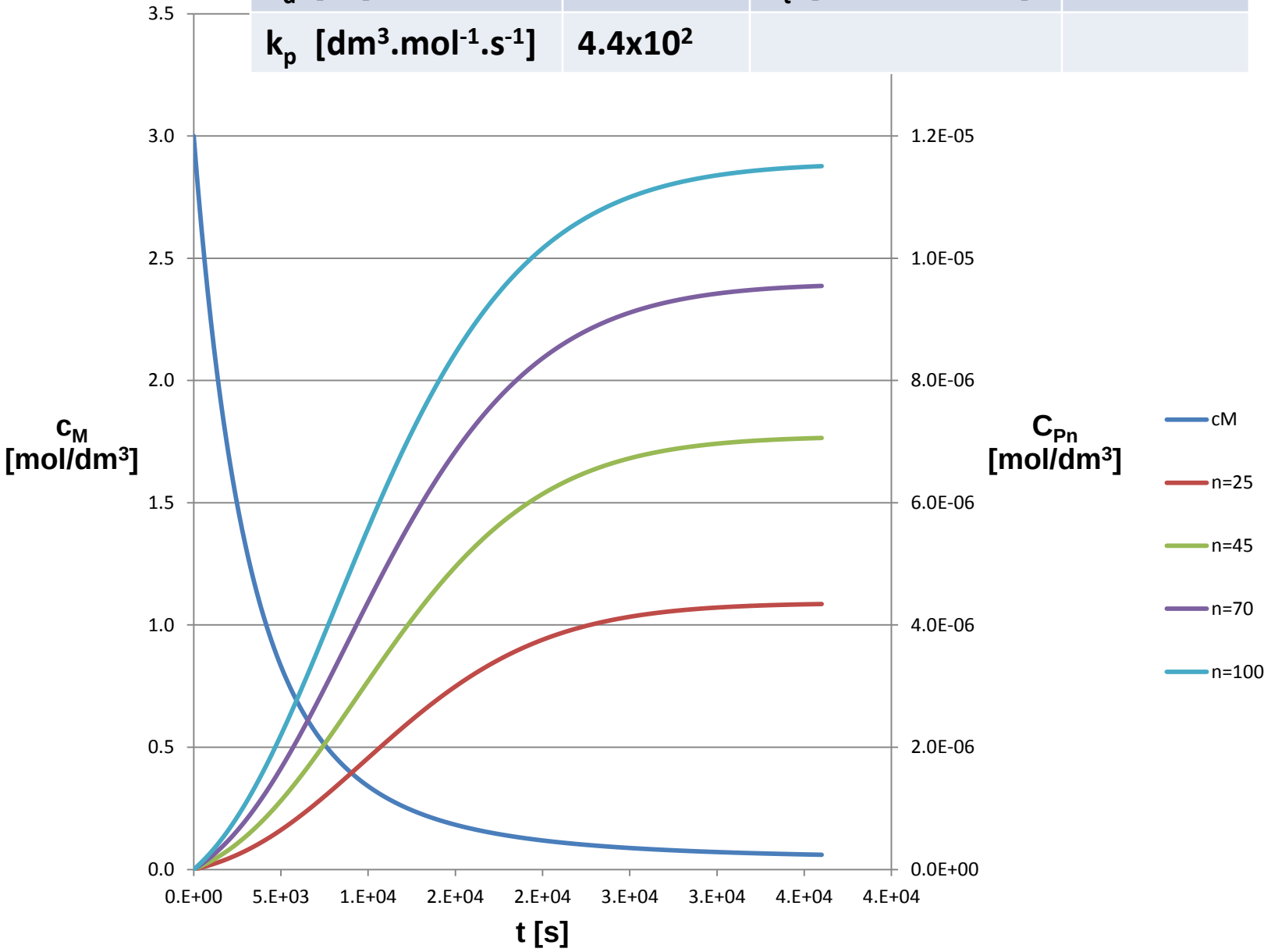
Homework 5: to justify these equations

From balance of $P_k\bullet$

$$c_{P_k\bullet} = \frac{k_p c_{P_{k-1}\bullet} c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \longrightarrow c_{P_k\bullet} = \frac{k_p c_{P_{k-1}\bullet} c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} = \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \left[\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^{k-1}$$

$$R_{P_n} = \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}\bullet} c_{P_k\bullet} = \frac{(n-1)k_t}{2} \left[\frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^2 \left[\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^{n-2}$$

$c_M^o\,[\mathrm{mol/dm^3}]$	3.0	$c_I^o\,[\mathrm{mol/dm^3}]$	1.0×10^{-2}
k_d [s^{-1}]	1.45×10^{-5}	k_t [$dm^3.mol^{-1}.s^{-1}$]	1.2×10^{6}
k_p [$dm^3.mol^{-1}.s^{-1}$]	4.4×10^{2}		



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