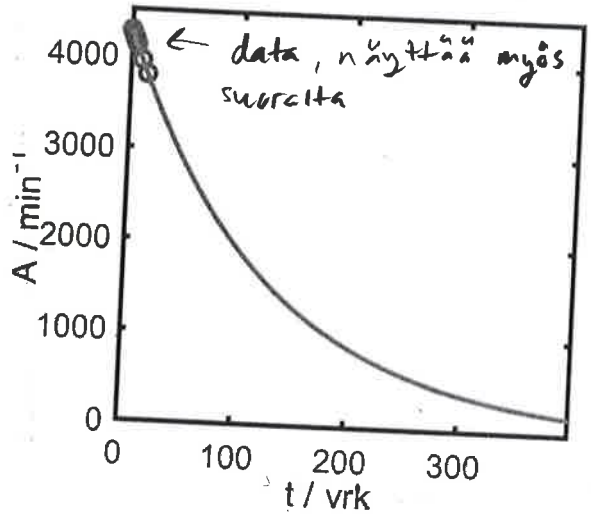
CHEM – C3220 – Kemiallinen dynamiikka
3. laskuharjoitus, ratkaisut

1. Sovitus Matlabin cftoolin avulla $A = A_0 e^{-kt}$

$$k = (0.00796 \pm 0.00002)\ \text{vrk}^{-1}$$

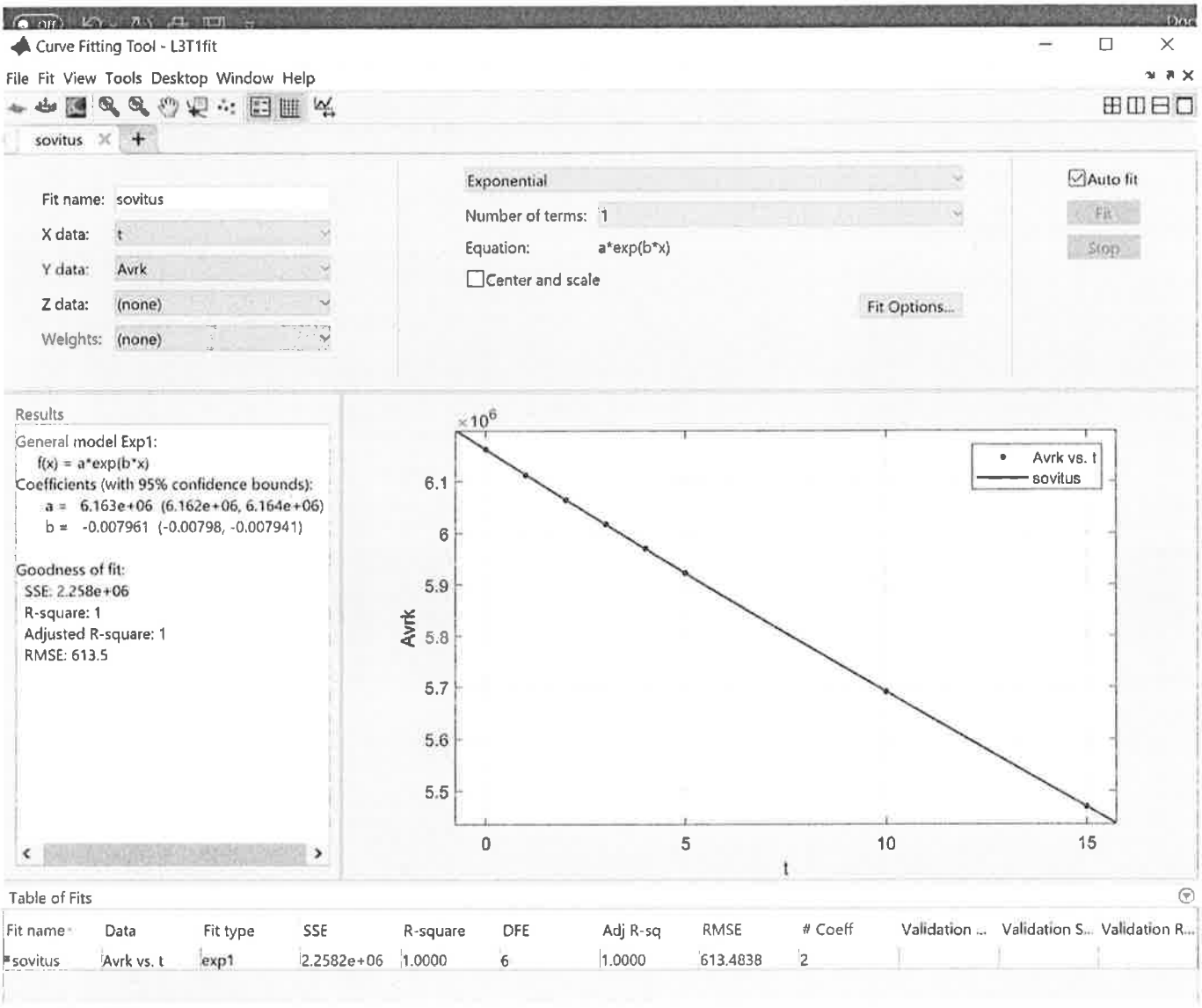
$$t_{1/2} = \frac{\ln(2)}{k} \approx 87.1\ \text{vrk}$$

$t = 60$ vrk $\Rightarrow A = 265\ \text{min}^{-1}$
$t = 1$ vuosi $\Rightarrow A = 23\ \text{min}^{-1}$



Seuraavalla sivulla Matlab-lasku.

```
>> data=[0     1       2       3       4       5       10      15
4280    4245    4212    4179    4146    4113    3952    3798];
>> t=data(1,:);
>> A=data(2,:);
>> Avrk=A*60*24;
>> figure(1),plot(t,Avrk,'o-','linewidth',2),xlabel('t / vrk'),ylabel('A / vrk^{-1}')
>> cftool
```




```
>> T=0:1:400;
>> Afit=A(1)*exp(-0.007961*T);
>> figure(2),plot(t,A,'o',T,Afit,'linewidth',2),xlabel('t / vrk'),ylabel('A / min^{-1}')
>> set(gca,'linewidth',2,'fontsize',12)
```

2. $2\,NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

(1) (2) (3) (4)

$$R_0 = k P_{1,0}^{\alpha} P_{2,0}^{\beta}$$

$$\frac{R_{0,1}}{R_{0,2}} = \left(\frac{P_{1,1}}{P_{1,2}}\right)_0^{\alpha} \Rightarrow \alpha = \frac{\ln\left(R_{0,1}/R_{0,2}\right)}{\ln\left(P_{1,1}/P_{1,2}\right)_0}$$

$$a = \frac{\ln(0.137/0.033)}{\ln(40/20.3)} = 2.0987 \approx \underline{\underline{2}}$$

$$\frac{R_{0,3}}{R_{0,4}} = \left(\frac{P_{2,3}}{P_{2,4}}\right)_0^{\beta} \Rightarrow \beta = \frac{\ln(0.213/0.105)}{\ln(38.5/19.6)} = 1.0477 \approx \underline{\underline{1}}$$

$$k = \frac{R_0}{P_{1,0}^2 P_{2,0}}$$

sijoitetaan lukuarvot

$$\Rightarrow \underline{k \approx (1.74 \pm 0.22)\cdot 10^{-6}\ kPa^{-2}\,s^{-1}}$$

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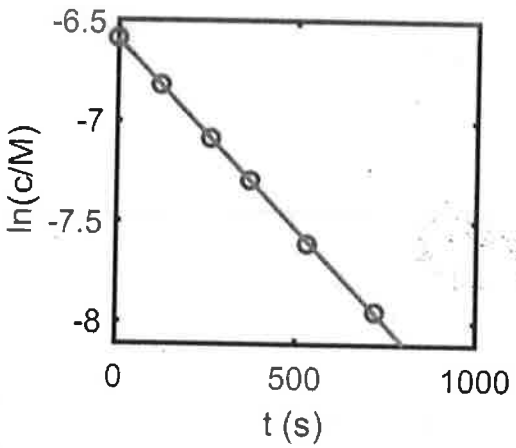
3. Ratkaisu Matlabin avulla. 1. kertaluku sopii hyvin!

$$k = 0.00190\ s^{-1}$$

```
t=[0 120 260 370 530 720];
c=[1.378 1.091 0.837 0.680 0.496 0.353]*0.001;
figure(1),plot(t,log(c),'o-','linewidth',2)
set(gca,'linewidth',2,'fontsize',12),xlabel('t (s)'),ylabel('ln(c/M)')
y=log(c);
p=polyfit(t,y,1)
=  -0.00190   -6.5916
T=0:10:800;
f=polyval(p,T);
figure(1),plot(t,log(c),'o',T,f,'linewidth',2)
set(gca,'linewidth',2,'fontsize',12),xlabel('t (s)'),ylabel('ln(c/M)')
```



$$t_{1/2} = \frac{\ln(2)}{k} \approx 365\ s = \underline{\underline{6\ min\ 5\ s}}$$

4. $\overset{1}{2\,NOCl(g)} \longrightarrow \overset{2}{2\,NO(g)} + \overset{3}{Cl_2(g)}$

$$v = -\frac{dp_1}{dt} = k p_1^2 \qquad p_i = \frac{n_i RT}{V}$$

$$\left.\begin{aligned} n_1 &= n_0 - 2x \\ n_2 &= 2x \\ n_3 &= x \end{aligned}\right\} \quad n_T = n_0 + x = \frac{p_T V}{RT}$$

$$p_T = \frac{(n_0 + x)RT}{V} = p_0 + \frac{xRT}{V}$$

$$\frac{RT}{V}x = p_T - p_0$$

$$p_1 = (n_0 - 2x)\frac{RT}{V} = p_0 - \frac{2xRT}{V} = p_0 - 2(p_T - p_0)$$

$$= \underline{3p_0 - 2p_T}$$

$$-\frac{dp_1}{dt} = +2\frac{dp_T}{dt} = \underline{\underline{k(3p_0 - 2p_T)^2}}$$

$$\underline{\underline{\frac{dp_T}{dt} = k'(3p_0 - 2p_T)^2 = -\frac{1}{2}\frac{dp_1}{dt}}}$$

5.

Jokeri:

$(CH_3)_2O$ hajoaa lämpötilassa 777 K siten, että aika jona alkukonsentraatio alenee 69%:iin alkuperäisestä riippuu alkukonsentraatiosta seuraavasti:

c_0 (mM)	8.13	6.44	3.10	1.88
$t_{0.69}$ (s)	590	665	900	1140

Etsi reaktion $dc/dt = -kc^n$ kertaluku n ja nopeusvakio k.

$$\left(\frac{[A]}{[A]_0}\right)^{1-n} = 1 + (n-1)[A]_0^{n-1} kt \qquad \frac{[A]}{[A]_0} = 0.69$$

$$t_{0.69} = \frac{0.69^{1-n} - 1}{(n-1)[A]_0^{n-1} k}$$

Arvataan Excelissä n:n arvo, jokaantaa suoran viivan Excel-file liitteenä!

$$\Rightarrow n = 1.5$$

$$k = \frac{0.69^{-0.5} - 1}{0.5\,[A]_0^{0.5}\, t_{0.69}}$$

$[A]_0$ (mM)	$t_{0.69}$ (s)	fit		k ($mM^{-½}\,s^{-1}$)
8.13	590	-0.1188		2.424E-04
6.44	665	-0.1335		2.416E-04
3.10	900	-0.1924		2.573E-04
1.88	1140	-0.247		2.608E-04
			k.a.	2.505E-04
	n:	1.5	std. virhe	9.977E-06