Kinetics Problem Sheet

1. The initial rate of the reaction $CO + Cl_2 \rightarrow COCl_2$ at 300 K is given for different initial pressures of the reactants. Determine the rate law.

$[Cl_2]$ / atm	0.7	0.4	0.5	0.5	0.5
[CO] / atm	1.0	1.0	1.0	0.5	0.3
ν / atm min^{-1}	0.586	0.253	0.354	0.177	0.106

2. The data below refer to the rearrangement of N-bromoacetanilide (A) to 4-bromoacetanilide in chlorobenzene at 288 K. Determine the order of the reaction with respect to A and the rate constant, *k*. [If you are interested, you can also deduce the work patterns of the scientist!].

time / h	0.0	4.0	10.5	23.0	31.5	45.0	48.0
10^2[A] / mol dm^{-3}	1.00	0.907	0.762	0.566	0.466	0.348	0.321

3. Iodine was allowed to react with an equimolar amount of propanone in acidic solution. The transmittance of the solution at a concentration where only I_2 absorbs was followed as a function of time. Determine the order of the reaction and, if possible, obtain the rate constant.

time / mins	0	5	10	15	20
transmission / %	10	19.6	31.6	44.3	56.2

4. A proposed mechanism for the reaction of HCl with propene is shown below. Determine the rate law for this mechanism.

$$2HCl \overset{K_1}{\rightleftharpoons} (HCl_2)$$

$$HCl + CH_3CH{=}CH_2 \overset{K_2}{\rightleftharpoons} \text{complex}$$

$$(HCl)_2 + \text{complex} \overset{k\ (\text{slow})}{\rightarrow} CH_3CHClCH_2 + 2HCl$$

5. The mechanism originally proposed for hte pyrolysis of ethanal was as follows:

$$CH_3CHO \overset{k_1}{\rightarrow} CH_3 + CHO$$

$$CH_3 + CH_3CHO \overset{k_2}{\rightarrow} CH_4 + CH_3CO$$

$$CH_3CO \overset{k_3}{\rightarrow} CH_3 + CO$$

$$2CH_3 \overset{k_4}{\rightarrow} C_2H_6$$

Apply the steady-state approximation to the radicals CH_3 and CH_3CO to obtain the rate law predicted by this mechanism ($\nu = d[CH_4]/dt$). Ignore the fate of CHO.

6. The enzyme catalase catalyses the decomposition of hydrogen peroxide. The initial rate of reaction was determined as a function of the initial peroxide concentration $[H_2O_2]_0$.

$[H_2O_2]_0$ / mol dm^{-3}	0.001	0.002	0.005
$10^3\nu$ / mol dm^{-3}	1.38	2.67	6.00

Determine ν_{max} and K_M. Given that the concentration of catalase is 4.0 x 10^{-9} mol dm^{-3}, calculate the turnover number, k_{cat}.

7. The major reactions in the pyrolysis of ethane to produce ethene and hydrogen at 1100 K are

$$C_2H_6 \xrightarrow{k_1} 2CH_3 \qquad \text{Initiation}$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5 \qquad \text{Initiation}$$

$$C_2H_5 \xrightarrow{k_3} H + C_2H_4 \qquad \text{Propagation}$$

$$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5 \qquad \text{Propagation}$$

$$2C_2H_5 \xrightarrow{k_5} C_4H_{10} \qquad \text{Termination}$$

(a) Show that the steady-state concentration $[CH_3]$ is given by $2k_1/k_2$.

(b) Determine the steady-state concentration of C_2H_5.

(c) Determine the rate law for the production of ethene.

(d) Calculate the chain length.