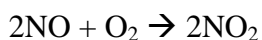


### Kinetics problems:

- Suppose an adequately stirred neutralizing tank is receiving, through the drains from a research laboratory, a steady trickle ( $0.1 \text{ L min}^{-1}$ ) of dilute hydrochloric acid ( $0.5\text{M}$ ) and that it contains  $200\text{kg CaCO}_3$ . The overflow liquid is at pH , so substantially complete removal of HCl occurs in the tank. ( $M_r(\text{CaCO}_3)=100\text{g}\cdot\text{mol}^{-1}$ )
  - What is the rate of HCL addition in  $\text{mol}\cdot\text{s}^{-1}$ ?
  - What reaction equation is involved?
  - What is the rate of this reaction?
  - If the flow continues as described, is it satisfactory to add another  $200\text{kg CaCO}_3$  to the tank each Monday?

- Why do we use initial rates to determine the order of the rate law?

- The following data has been obtained for the reaction:



Where the rate refers to:

$$\text{rate} = \frac{-d[\text{O}_2]}{dt}$$

Reaction number	$[\text{NO}]_0$ (molecules/cm <sup>3</sup> )	$[\text{O}_2]_0$ (molecules/cm <sup>3</sup> )	Initial rate (molecules/cm <sup>3</sup> s)
1	$1.00 \times 10^{18}$	$1.00 \times 10^{18}$	$2.00 \times 10^{16}$
2	$3.00 \times 10^{18}$	$1.00 \times 10^{18}$	$1.80 \times 10^{17}$
3	$3.00 \times 10^{18}$	$2.50 \times 10^{18}$	$4.50 \times 10^{17}$

- What is the order of the reaction with respect to NO?
  - What is the overall order of the reaction?
  - What is the rate constant for the reaction?
  - What would be the initial rate of reaction in an experiment where  $[\text{NO}]_0 = 6.21 \times 10^{18}$  molecules/cm<sup>3</sup> and  $[\text{O}_2]_0 = 7.36 \times 10^{18}$  molecules/cm<sup>3</sup>?
- For the following reaction

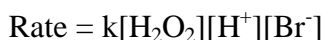


Initial concentration of $\text{CH}_3\text{COCH}_3$ (mol/L)	Initial concentration of $\text{Br}_2$ (mol/L)	Initial concentration of $\text{H}^+$ (mol/L)	Measured initial rate (mol.L <sup>-1</sup> s <sup>-1</sup> )
1.00	1.00	1.00	$4.0 \times 10^{-3}$
2.00	1.00	1.00	$8.0 \times 10^{-3}$
2.00	2.00	1.00	$8.0 \times 10^{-3}$
1.00	2.00	2.00	$8.0 \times 10^{-3}$

- What is the order of the reaction with respect to  $\text{CH}_3\text{COCH}_3$ ?
  - What is the order of the reaction with respect to  $\text{Br}_2$ ?
  - What is the order of the reaction with respect to  $\text{H}^+$ ?
  - What is the rate law?
- The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is:



Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is:



- If the concentration of  $\text{H}_2\text{O}_2$  is increased by a factor of three, by what factor is the rate of consumption of  $\text{Br}^-$  ions increased?
- If, under certain conditions, the rate of consumption of  $\text{Br}^-$  ions is  $7.2 \times 10^{-3} \text{ mol.L}^{-1}.\text{s}^{-1}$ , what is the rate of consumption of hydrogen peroxide? What is the rate of consumption of bromine?
- What is the effect on the rate constant  $k$  of increasing the concentration of bromine ions?
- If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of the concentration of  $\text{Br}^-$ ? What would be the effect on the rate constant  $k$ ?

6. A reaction obeys the stoichiometric equation

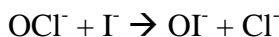


Rates of formation of Z at various concentrations of A and B are given in the following table:

$[\text{A}]$ ( $\text{mol.L}^{-1}$ )	$[\text{B}]$ ( $\text{mol.L}^{-1}$ )	Rate ( $\text{mol.L}^{-1}.\text{s}^{-1}$ )
$3.5 \times 10^{-2}$	$2.3 \times 10^{-2}$	$5.0 \times 10^{-7}$
$7.0 \times 10^{-2}$	$4.6 \times 10^{-2}$	$2.0 \times 10^{-6}$
$7.0 \times 10^{-2}$	$9.2 \times 10^{-2}$	$4.0 \times 10^{-6}$

What are  $m$  and  $n$  in the rate equation  $\text{rate} = k[\text{A}]^m[\text{B}]^n$  and what is the rate constant  $k$ ?

- What would be the units for the rate constant of a  $3/2$  order reaction? Use concentration in  $\text{mol.L}^{-1}$  and time in seconds.
- T. Y. Chin and R. E. Connich measured the data below for the  $\text{OH}^-$  catalysed reaction:



Determine the rate law and constant.

$[\text{OCl}^-]$ ( $\text{mol.L}^{-1}$ )	$[\text{I}^-]$ ( $\text{mol.L}^{-1}$ )	$[\text{OH}^-]$ ( $\text{mol.L}^{-1}$ )	Initial rate ( $\text{mol.L}^{-1}.\text{s}^{-1}$ )
0.0017	0.0017	1.00	$1.75 \times 10^{-4}$
0.0034	0.0017	1.00	$3.50 \times 10^{-4}$
0.0017	0.0034	1.00	$3.5 \times 10^{-4}$
0.0017	0.0017	0.50	$3.5 \times 10^{-4}$

(Hint: don't worry about the fact that  $\text{OH}^-$  doesn't feature in the total equation – work it out anyway)

- Use the data below for the decomposition of diacetylene at 1173 K to determine the reaction order.  
(Hint: careful of units)

$10^3 C \text{ (mol.mL}^{-1}\text{)}$	$t \text{ (s)}$
0.532	0
0.454	0.030
0.420	0.050
0.364	0.100
0.298	0.150
0.267	0.200
0.237	0.250

10. Use the data below for the partial pressure of  $N_2O_2$  during a thermal decomposition at  $45^\circ C$  to determine the reaction order and rate constant.

$t \text{ (min)}$	$P \text{ (torr, } N_2O_2\text{)}$
0	348.4
20	185.2
40	105.4
60	58.6
80	33.1
100	18.6
160	2.8

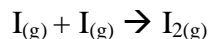
11. The reaction:



was studied and found to be first order. Use the data below to calculate the rate constant. (The measured pressures include 4.2 torr due to nitrogen that was present in the reaction container).

$t \text{ (min)}$	$P \text{ (torr)}$	$t \text{ (min)}$	$P \text{ (torr)}$
0	173.5	12	244.4
2	187.3	14	254.4
3	193.4	15	259.2
5	205.3	17	268.7
6	211.3	18	273.9
8	222.9	20	282.0
9	228.6	21	286.8
11	239.8		

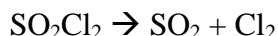
12. Iodine atoms combine to form molecular iodine in the gas phase:



The reaction follows second order kinetics and has a rate constant of  $7.0 \times 10^{-1} \text{ M}^{-1} \cdot \text{s}^{-1}$  at  $23^\circ C$ .

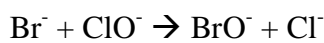
- If the initial concentration of iodine atoms was 0.086 M, calculate the concentration of iodine atoms after 2 mins.
  - Calculate the half-life of the reaction if the initial concentration of I was 0.16 M.
13. A substance decomposes at 600 K with a rate constant of  $3.72 \times 10^{-5} \text{ s}^{-1}$ .
- Calculate the half life of the reaction
  - What fraction remains undecomposed if the substance is heated for three hours at 600 K?

14. How does the time required for a first order reaction to go to 99% completion relate to the half life of the reaction?
15. The first order gas reaction:



has  $k = 2.20 \times 10^{-5} \text{ s}^{-1}$ . What percentage of the  $\text{SO}_2\text{Cl}_2$  would be decomposed after five hours?

16. A first order reaction has a half life of 26.2 minutes. At what time will the reaction be 90% complete?
17. A second order reaction  $\text{A} + \text{B} \rightarrow \text{products}$ , has a rate law rate =  $k[\text{A}][\text{B}]$ , has  $k = 1.23 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ . If A and B are mixed with equal initial concentrations of 0.365 M, at what time will the reaction be 90% complete?
18. For the reaction

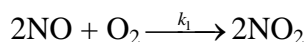


in water at 25°C. With initial concentrations  $[\text{ClO}^-] = 3.230 \times 10^{-3} \text{ M}$ ,  $[\text{Br}^-] = 2.508 \times 10^{-3} \text{ M}$ , the results were:

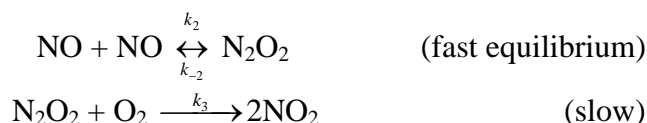
$t \text{ (min)}$	$[\text{BrO}^-] \text{ (mM)}$
0	0
3.65	0.560
7.65	0.953
15.05	1.420
26.00	1.800
47.60	2.117
90.60	2.367

Assume a second order rate law and calculate the rate constant.

19. What is the half life for the reaction  $\text{A} \rightarrow \text{D}$  when  $[\text{A}]_0$  is 0.02M and the reaction constant  $k = 2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ ?
20. The reaction of NO with  $\text{O}_2$  obeys the stoichiometry

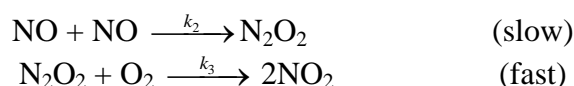


The collision of three molecules simultaneously is a very rare event at low pressure, so the following mechanism has been proposed.



- a. What would be the overall rate law in terms of  $k_2$ ,  $k_{-2}$ ,  $k_3$  and the concentrations of NO and  $\text{O}_2$  if this mechanism is true?

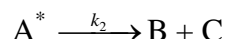
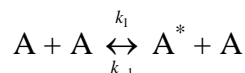
b. What would be the rate law if the following mechanism prevailed?



21. Consider the reaction



The reaction mechanism is thought to be:

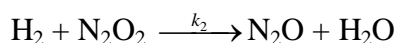
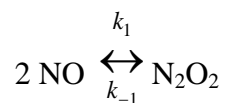


- Derive the rate law for production of C using the steady-state approximation. Remember that  $\text{A}^*$  is removed via two processes.
- What are the assumptions of the steady state approximation?
- Assume the rate is known experimentally to be first-order. Under what conditions will the answer from a) be consistent with this?

22. Consider the reaction:



The reaction mechanism is thought to be:



- Which reaction is likely to be rate determining in this mechanism?
- Apply the steady state approximation to the concentration of  $\text{N}_2\text{O}_2$  and derive an equation for the rate of production of  $\text{H}_2\text{O}$ .
- Under what conditions will the reaction show first order dependence on the concentration of hydrogen?

23. For a reaction  $\text{A} \rightarrow \text{product}$ , taking place at  $25^\circ\text{C}$ , the reactant concentration fell from 0.1M to 0.05M in 10 minutes and had fallen to 0.033M after a further 10 minutes.

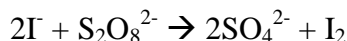
- By inspection, the reaction is clearly not first order. Briefly explain this conclusion
- Use the data provided to show that the reaction follows second order kinetics
- The reaction has a rate constant  $k = 1.67 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$  and an activation energy of  $100 \text{ kJ mol}^{-1}$ . Use the Arrhenius equation ( $k = A\exp(-E_a/RT)$ ) to calculate the rate constant at  $40^\circ\text{C}$ .
- What fraction of collisions between molecules have the necessary energy to allow formation of products when the temperature is  $25^\circ\text{C}$ ?

24. The dependence of the rate of reaction on temperature is described by the Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

where  $E_a$  is the activation energy of the reaction (J/mol),  $R$  the gas constant,  $T$  the absolute temperature and  $A$  is the collision frequency.

a. The rate of reaction for the oxidation of iodide ion by persulfate ion:



was found to be  $5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  at 298 K and  $6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  at 350 K. What is the value of the activation energy,  $E_a$  and the Arrhenius parameter  $A$ ?

b. The rate of decomposition of species A was measured as a function of time. Determine graphically or otherwise the rate constant for the reaction.

[A] (M)	Time (s)
0.1000	0
0.0666	10
0.0500	20
0.0333	40
0.0200	80

25. The gas phase reaction:



has a rate constant of  $3.5 \times 10^{-5} \text{ s}^{-1}$  at 298 K, and  $5.0 \times 10^{-4} \text{ s}^{-1}$  at 318 K.

- Calculate the activation energy (in J/mol) using the Arrhenius equation
- Calculate the value of the Arrhenius parameter  $A$  (in  $\text{s}^{-1}$ )
- Calculate the rate constant at 338 K.

26. The rate constant for a reaction at 30°C is found to be exactly twice the value at 20°C. Calculate the activation energy.

27. The rate of the following reaction was measured at two temperatures:



The rate constant,  $k$ , was found to be  $2.0 \times 10^{-5} \text{ s}^{-1}$  at 20°C and  $2.9 \times 10^{-3} \text{ s}^{-1}$  at 60°C. Determine the activation barrier,  $E_a$ , and the collision frequency,  $A$ , assuming the Arrhenius equation holds.