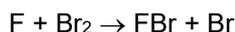


Kinetics problems

Question 1

- a) Explain the terms *order*, *overall order*, and *molecularity* as applied to the kinetics of a chemical reaction.
- b) Outline one method by which the order of a chemical reaction can be determined experimentally.
- c) The gas phase reaction of fluorine atoms with bromine follows the stoichiometric equation



The following concentrations of Br_2 were observed as a function of time at 298 K when the initial fluorine atom concentration was $[\text{F}] = 4 \times 10^{-9} \text{ mol dm}^{-3}$.

time / ms	0	0.7	1.3	2.7	3.9
$[\text{Br}_2] / 10^{-9} \text{ mol dm}^{-3}$	0.100	0.066	0.048	0.022	0.011

- i) Show that the reaction is first order with respect to Br_2 .
- ii) Given that the reaction is also first order with respect to F atoms, calculate the overall second-order rate constant.

Question 2

- a) Under what conditions can a reaction with rate law

$$\frac{d[\text{P}]}{dt} = \frac{k[\text{A}][\text{B}]^{1/2}}{1+k'[\text{A}]}$$

be said to have a definite classification by order and molecularity?

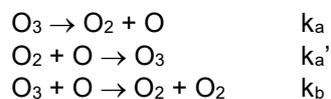
- b) Deduce the relation between the rate constant and the half-life of a species for a first-order reaction.
- c) The following data were obtained for the concentration of product in a reaction of the form $\text{A} \rightarrow \text{P}$:

t / s	10	20	40	60	80	∞
$[\text{P}] / \text{mol L}^{-1}$	0.90	1.13	1.29	1.35	1.39	1.50

Determine the (integer) order and rate constant of the reaction.

Question 3

- a) Explain what is meant by the *steady-state approximation* in chemical kinetics. Why is it useful, and under what conditions is it valid?
- b) The following mechanism has been proposed for the thermal decomposition of ozone:



- i) Derive an expression for the rate of decomposition of O_3 in terms of the concentrations of O_3 and O_2 and of the three rate constants k_a , k_a' and k_b .

- ii) Discuss the conditions under which the overall reaction will exhibit kinetics that are a) first order with respect to O₃ and b) second order with respect to O₃.
- iii) Interpret the rate equation you have derived, and in particular explain the role of O₂.

Question 4

- a) Why does the rate of most chemical reactions increase when the temperature is raised?
- b) The rate constant for the decomposition of HI into H₂+I₂ shows the following temperature dependence:

k / dm ³ mol ⁻¹ s ⁻¹	3.13x10 ⁻⁶	7.90x10 ⁻⁵	3.20x10 ⁻³	0.10
T / K	550	625	700	830

Determine the activation energy for the reaction, and the pre-exponential factor A in the Arrhenius equation.

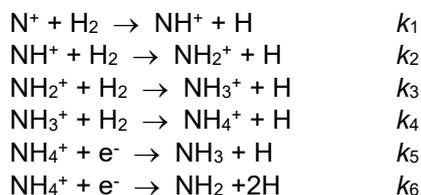
- c) What is the overall reaction order for the decomposition? What justification does information in the table above give for the form of the rate equation?
- d) The reaction between hydrogen and iodine to form hydrogen iodide is believed to proceed via a chain mechanism. Using this reaction as an example, explain the meanings of the terms *initiation*, *propagation* and *termination*.
- e) For the reaction between nitric oxide and oxygen, 2NO(g) + O₂(g) → 2NO₂(g), the rate law is

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

The rate of reaction is found to fall as the temperature is increased. Propose a mechanism for the reaction, and show how it explains both the rate law and the temperature dependence of the reaction.

Question 5

- a) A possible ion-molecule reaction mechanism for synthesis of ammonia in interstellar gas clouds is shown below.



Use the steady state approximation to derive equations for the concentrations of the intermediates NH⁺, NH₂⁺, NH₃⁺ and NH₄⁺ in terms of the reactant concentrations [N⁺], [H₂] and [e⁻]. Treat the electrons as you would any other reactant.

- (b) Show that the overall rate of production of NH₃ is given by

$$\frac{d[\text{NH}_3]}{dt} = \frac{k_1 k_5}{k_5 + k_6} [\text{N}^+][\text{H}_2]$$

- (c) What is the origin of the *activation energy* in a chemical reaction?
- (d) The rates of many ion-molecule reactions show virtually no dependence on temperature.

- (i) What does this imply about their activation energy?
- (ii) What relevance does this have to reactions occurring in the interstellar medium?

Question 6

- a) For the elementary gas phase reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$, the second-order rate constant varies with temperature in the following way:

T / K	198	298	400	511	604
$10^{12} k / (\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})$	0.20	1.13	2.83	4.27	7.69

Use the data to calculate the activation energy, E_a , and the pre-exponential factor, A , for the reaction.

- b) The simple collision theory of bimolecular reactions yields the following expression for the rate constant:

$$k = \left(\frac{8kT}{\pi \mu} \right)^{1/2} \sigma \exp(-E_a/RT)$$

where μ is the reduced mass of the reactants and σ is the reaction cross section.

- i) Interpret the role of the three factors in this expression.
- ii) Use the answer to part a) to estimate σ for the reaction at 400 K.
- iii) Compare the value obtained with an estimate of $4.0 \times 10^{-19} \text{ m}^2$ for the collision cross section.

[Take the atomic masses of H and C to be 1.0 amu and 12 amu, respectively.]