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

$$F + Br_2 \rightarrow FBr + Br$$

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

time / ms	0	0.7	1.3	2.7	3.9
$[Br_2]$ / 10^{-9} 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

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

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 $A \rightarrow P$:

t / s	10	20	40	60	80	∞
[P] / 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:

$O_3 \rightarrow O_2 + O$	k_a
$O_2 + O \rightarrow O_3$	k_a'
$O_3 + O \rightarrow O_2 + O_2$	k_b

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 O_3 and b) second order with respect to O_3.

iii) Interpret the rate equation you have derived, and in particular explain the role of O_2.

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 H_2+I_2 shows the following temperature dependence:

k / dm^{3}mol^{-1}s^{-1}	3.13×10^{-6}	7.90×10^{-5}	3.20×10^{-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, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, the rate law is

$$\text{rate} = k[NO]^2[O_2]$$

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.

$$N^+ + H_2 \rightarrow NH^+ + H \qquad k_1$$
$$NH^+ + H_2 \rightarrow NH_2^+ + H \qquad k_2$$
$$NH_2^+ + H_2 \rightarrow NH_3^+ + H \qquad k_3$$
$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad k_4$$
$$NH_4^+ + e^- \rightarrow NH_3 + H \qquad k_5$$
$$NH_4^+ + e^- \rightarrow NH_2 + 2H \qquad k_6$$

Use the steady state approximation to derive equations for the concentrations of the intermediates NH^+, NH_2^+, NH_3^+ and NH_4^+ in terms of the reactant concentrations $[N^+]$, $[H_2]$ and $[e^-]$. Treat the electrons as you would any other reactant.

(b) Show that the overall rate of production of NH_3 is given by

$$\frac{d[NH_3]}{dt} = \frac{k_1 k_5}{k_5 + k_6}[N^+][H_2]$$

(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 $H + C_2H_4 \rightarrow C_2H_5$, the second-order rate constant varies with temperature in the following way:

T / K	198	298	400	511	604
10^{12} k/ ($cm^3 molecule^{-1} s^{-1}$)	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 4.0×10^{-19} m^2 for the collision cross section.

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