Advanced class – Kinetics and Reaction Dynamics

Q1. Advanced Physical Chemistry 1998, Q9

Explain each of the following concepts in collision dynamics:

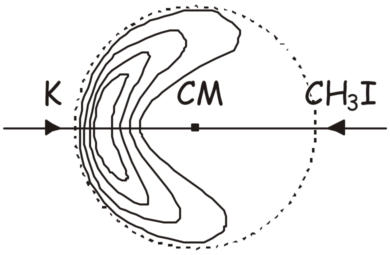
i) impact parameter
ii) centrifugal barrier
iii) total cross section
iv) differential cross section.

Answer THREE of the following parts:

a) Discuss the behaviour of the collision cross section in elastic collisions. How can such cross sections be used to provide detailed information on the intermolecular potential energy function?

b) What is meant by the harpoon mechanism of chemical reactions? How can it be used to explain the large reaction cross-section and the product angular distribution? Given that the electron affinity of Br_2 is 246 kJ mol^{-1} and the ionisation energy of Rb is 403 kJ mol^{-1}, estimate the reaction cross-section for the Rb + Br_2 reaction.

c) The following diagram shows the angle-velocity distribution of KI, produced by the collision of K atoms with CH_3I. Discuss the appearance of this diagram and comment on the fact that the majority of the energy available appears as product translational energy. How might the influence of the orientation of the CH_3I molecule on the collision dynamics be investigated?



d) How do the shape of the potential energy surface, the position of the barrier to reaction and the masses of the particles involved affect the course of a reaction between an atom and a diatomic molecule? How can measurements of the vibrational, rotational or translations distributions of the product molecules be used to provide information on reaction dynamics?

Q2. Advanced Physical Chemistry 1999, Q8

a) Explain what is meant by kinetic isotope effect and how it is related to zero point energy.

b) Consider the following gas-phase reactions:

1. $H + D_2 \xrightarrow{k_1} HD + D$
2. $D + H_2 \xrightarrow{k_2} DH + H$

Estimate the ratio of the rate constants k_2/k_1 at 300 K using the vibrational wavenumbers given below. Assume that the effect of isotopic substitution is limited to changes in the zero point energies of reactants and transition states, and that the transition states are linear.

	H_2	Reaction 1 transition state	Reaction 2 transition state
stretch / cm^{-1}	4395	1762	1773
bend (doubly degenerate) / cm^{-1}	-	694	870

($1\ cm^{-1} = 11.96\ Jmol^{-1}$)

c) For the reaction of an atom X with a diatomic molecule Y_2

$$X + Y_2 \rightarrow XY + Y$$

proceeding through a linear transition state, transition state theory gives

$$k = \frac{k_B T}{h} \frac{q_{int}^{‡}}{q_{†}\, q_{X:int}\, q_{Y2:int}} e^{-\varepsilon_0/k_B T}$$

where $q_{X:int}$ and $q_{Y2:int}$ are the partition functions for the internal modes (rotational, vibrational, electronic) of the reactants and $q_{†}$ is related to the masses of the reactants by

$$q_{†} = \left(\frac{2\pi k_B T}{h^2} \frac{m_X m_{Y2}}{m_X + m_{Y2}} \right)^{3/2}$$

Outline the origin of the expression for k (no derivations are required), comment on the assumptions involved, and explain the meaning of the symbols $q_{int}^{‡}$ and ε_0.

d) Show that the expression for k in c) leads to the following equation, stating and justifying the assumptions and approximations used.

$$\frac{k_2}{k_1} = \frac{m_D}{m_H} \frac{I_2^{‡}}{I_1^{‡}} \left(\frac{m_D + 2m_H}{m_H + 2m_D} \right)^{3/2} \exp\left[\frac{-(\varepsilon_{0:2} - \varepsilon_{0:1})}{k_B T} \right]$$

The 1,2 subscripts refer to the two reactions in b) and $I^{‡}$ denotes the moment of inertia of the transition state

e) Hence obtain a revised estimate of k_2/k_1 at 300 K. ($I_1^{‡} = 4.02 \times 10^{-47}$ kg m^2, $I_2^{‡} = 3.95 \times 10^{-47}$ kgm^2; the relative atomic masses of H and D are 1 and 2 respectively).

f) The experimental value of k_2/k_1 is 14 at 300 K. Why is this value larger than that predicted by transition state theory?

Q3. Advanced Physical Chemistry 1999, Q9

a) The RRK model for unimolecular reactions uses an energy dependent version of the Lindemann reaction scheme:

$$A + M \xrightarrow{k_1(\varepsilon)} A^*(\varepsilon) + M$$

$$A^*(\varepsilon) + M \xrightarrow{k_{-1}(\varepsilon)} A + M$$

$$A^*(\varepsilon) \xrightarrow{k_2(\varepsilon)} \text{products}$$

The rate constants are given by the following expressions.

$$\frac{k_1(\varepsilon)}{k_{-1}(\varepsilon)} = \frac{1}{(s-1)!}\left(\frac{\varepsilon}{k_B T}\right)^{s-1} e^{-\varepsilon/k_B T}$$

$$k_2(\varepsilon) = \nu \left(\frac{\varepsilon-\varepsilon_0}{\varepsilon}\right)^{s-1}$$

i) Discuss the meaning of the quantities ε, ε_0, s and ν in the theory.

ii) How can the rate constant $k_{-1}(\varepsilon)$ be estimated?

iii) Derive an expression for the overall temperature dependent rate constant $k_{uni}(T)$.

iv) How would the quantities $k_1(\varepsilon)/k_{-1}(\varepsilon)$ and $k_2(\varepsilon)$ change as s increases and as e increases? Explain the physical reasons for this behaviour.

The following data have been obtained for $k_2(\varepsilon)$ as a function of ε for isomerisation for cyclobutene. In this case ε_0 is estimated to be 139 kJ mol^{-1} and ν is determined to be equal to 5.75×10^{13} s^{-1}.

ε / kJmol^{-1}	162	170	180	187	197
$k_2(\varepsilon)$/s^{-1}	3×10^7	9×10^7	2×10^8	5×10^8	8×10^8

v) What value would be obtained for $k_2(\varepsilon)$ as $\varepsilon \rightarrow \infty$?

vi) Using your answer to v) and the data in the table above, devise a graphical procedure to test the validity of the RRK model. To what extent is it possible to determine a value for s?

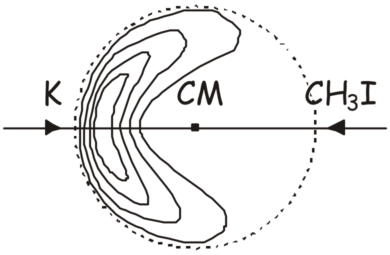
vii) What are the major deficiencies of the RRK model?

b) Explain what is meant by the potential energy surface for a reaction and illustrate your answer with respect to a reaction of the type A + BC → AB + C. What effect does the shape of the potential energy surface have on the distribution of excess energy in the reaction? What other factors are important?

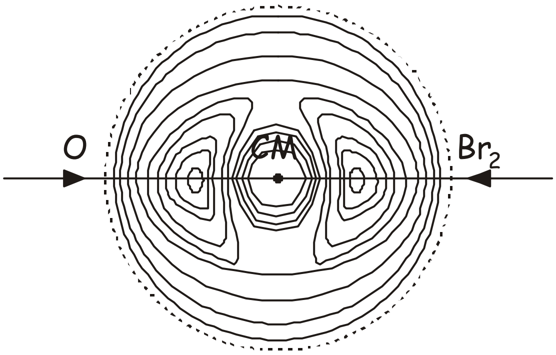
The figures below show the product flux contour plots in the centre of mass frame (CM) of three different reactions.

What can be learnt about the dynamics of these reactions from the figures? (the dashed circles show the maximum product velocity).

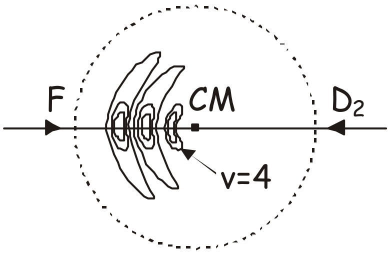
i) $K + CH_3I \rightarrow KI + CH_3$



ii) $O + Br_2 \rightarrow BrO + Br$



iii) $F + D_2 \rightarrow DF + D$



Q4. Advanced Physical Chemistry 2000, Q8

The RRK theory of unimolecular reactions predicts the rate constant for the reaction step,

$$A^+ \rightarrow \text{products},$$

to have the following dependence on internal energy, E, above the threshold, E_0.

$$k(E) = k^{\ddagger}\left(\frac{E-E_0}{E}\right)^{s-1} \qquad \text{for } E \geq E_0$$

a) What are the assumptions upon which the above RRK expression for k(E) is based? Define s and $k^{\ddagger}$ appearing in the above equation.

b) Sketch the energy dependence of the predicted rate constant, k(E), for s=1, and for two higher values of s. Provide a physical explanation for the dependence of k(E) on energy, E, and s.

c) The unimolecular dissociation of the molecule NCNO to CN and NO has been studied as a function of time using a picosecond pump and probe (flash photolysis) method. The following dissociation rate constants (in s^{-1}) were observed as a function of energy above the threshold, E_0 = 17080 cm^{-1}.

$(E-E_0)/cm^{-1}$	50	200	300	500	700
ln[k(E)]	22.1	23.9	24.4	24.9	25.3

i) Use a graphical procedure to calculate the RRK parameters $k^{\ddagger}$ and s. Comment on the value of s you obtain.

ii) Use your answer to part c)i) to estimate the limiting high pressure rate constant, k_∞, for the thermal unimolecular dissociation of NCNO at 1000 K.

iii) In reality the RRK theory estimate of k_∞ is likely to be poor, and in general the theory cannot account fo rthe wide variation in the Arrhenius A_∞-factors from one reaction to another.

What improvements could be made to the RRK model? How does the transition state theory expression for k_∞ ,

$$k_\infty = \frac{k_B T}{h}\frac{q^{\ddagger}}{q}e^{-E_0/k_B T}$$

help to rationalise the differences in A_∞-factors referred to above?

d) Pump and probe experiments have also been performed on the bimolecular reaction

$$H + CO_2 \rightarrow OH + CO$$

in which reaction was initiated by laser photolysis of HI bound to CO_2 in an OCO···HI van der Waals complex. These measurements suggest that OH is generated on a timescale of about 3×10^{-12} s at a collision energy of E_t ~170 kJ mol^{-1}.

i) Use your knowledge of the typical vibrational frequency of CO modes in molecules to determine an order-of-magnitude estimate of a CO vibrational period. What does your estimate suggest about the H + CO_2 reaction mechanism under the conditions described above?

ii) What further evidence about the reaction mechanism could be provided by a crossed-molecular beam study of the H + CO_2 bimolecular reaction?