

REACTION DYNAMICS

Section A

1. Explain what is meant by the following terms relating to molecular dynamics.
 - a) Elastic, inelastic and reactive collisions.
 - b) Differential cross section
 - c) Orbital angular momentum L
 - d) Impact parameter b
 - e) Centrifugal barrier
 - f) Excitation function
 - g) Potential energy surface
2.
 - a) What information can infra-red chemiluminescence provide on the energetics and/or dynamics of a chemical reaction? What other experimental methods can be used to obtain similar information?
 - b) Why do beam experiments represent an improvement over bulk gas phase experiments? What are the advantages and disadvantages of effusive and supersonic molecular beams? Give an example of their application in chemical reaction dynamics.
 - c) What is the relationship between the potential energy surface for a chemical system and its reaction dynamics? How can quasi-classical trajectory (QCT) calculations be used in conjunction with experimental results to test the accuracy of a calculated potential energy surface?

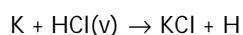
Section B

QUESTION 1. 1994 General physical chemistry II, Question 4

- a) How does the form of the potential energy surface linking products with reactants influence the distribution of excess energy in the products of an exothermic reaction?
- b) What is meant by i) a collision cross section, σ_c ; and ii) a reaction cross section, σ_r ? How, *in principle*, is a thermal rate constant k for a reaction at a specific temperature obtained from the reaction cross section?
- c) One theory suggests that σ_r varies with reactant translational kinetic energy E_t according to the equation

$$\sigma_r = \sigma_r(0) \frac{E_t - E^0}{E_t},$$

where $\sigma_r(0)$ is a constant, and E^0 is the threshold energy for reaction. The reaction



is slightly endothermic for $v=0$. The following data were obtained for the reaction cross section σ_r at different energies E_t .

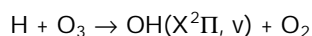
E_t / kJmol^{-1}	8	12	20	30
$10^{16} \sigma_r / \text{cm}^2$	0.33	1.08	1.7	2.0

Estimate the threshold energy for reaction from the data.

- d) Vibrational excitation to $v=1$ in HCl increases σ_r much more than the equivalent amount of energy in translational excitation. What qualitative conclusion can you draw about the shape of the potential energy surface?

QUESTION 2. 1995 General physical chemistry I, Q7 (second part)

The reaction



takes place in the stratosphere, and produces OH in its ground electronic state with a population inversion in its vibrational levels v : the vibrational population distribution peaks at the highest energetically accessible level $v=9$. The reaction results in the emission of the Meinel bands in the night sky, an example of which is the transition from $v=9$ to $v=4$ in the visible region.

- Describe features of the potential energy surface which will give rise to the vibrational distribution observed in reaction (1).
- Describe the radiative processes which can occur in emission from OH($v=9$) formed in the reaction. Include in your answer an explanation of why transitions in which $|\Delta v| > 1$ take place.

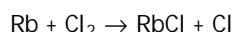
QUESTION 3. 1996 General physical chemistry II, Question 4

The reaction cross section, σ_r , can be expressed by the equation

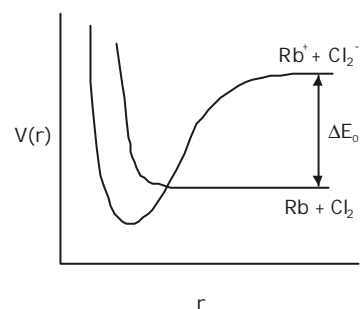
$$\sigma_r = \int_0^{\infty} 2\pi b \text{Pr}(b) db$$

where b is the impact parameter and $\text{Pr}(b)$ is the probability of reaction for impact parameter b .

- How is σ_r related to the collision cross section σ_c ?
- Discuss briefly reasons why σ_r might be i) smaller; ii) larger than σ_c .
- The reaction between R and Cl_2 ,



proceeds extremely rapidly. Use the potential energy diagram to suggest a possible mechanism for the reaction that would explain the kinetics of the process.



- Estimate the reaction cross section by assuming that the potential curve leading to $\text{Rb} + \text{Cl}_2$ is independent of r ($V(r) = 0$) at large r , and that the curve leading to $\text{Rb}^+ + \text{Cl}_2^-$ is dominated by electrostatic attraction for r beyond the potential minimum. Comment on your result.

[$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} = \frac{-1.44}{r}$ for $V(r)$ in eV and r in nm. The ionization potential of R is 4.2 eV and the electron affinity of Cl_2 is 2.4 eV.]