

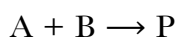
Dynamics and Kinetics. Exercise 9

Problem 1: Molecular beams

In a molecular-beam experiment measuring effective cross sections of collisions, it was found that the intensity of a CsCl beam was reduced by 40% during a passage across a chamber containing CH_2F_2 at 10 mTorr and 85 K. When the target was argon at the same temperature and pressure, the intensity was reduced only by 10%. What is the ratio of the effective cross sections for the two types of collisions and why is one larger than the other?

Problem 2: Steric factor

Consider the gas phase reaction

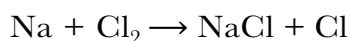


The experimental effective cross section for this reaction, deduced from the pre-exponential factor in the rate equation, was found to be $9.2 \times 10^{-22} \text{ m}^2$. A different method yielded collision cross sections 0.95 nm^2 for A and 0.65 nm^2 for B.

Compute the steric factor for this reaction.

Problem 3: Harpoon mechanism

Reactions involving electron transfer can proceed by the so-called harpoon mechanism, for example:



Since electron transfer can occur over a distance that is larger than the collision cross sections of the reaction partners would suggest, this leads to a steric factor that is larger than one.

Determine the distance over which the electron transfer occurs if the reaction proceeds by the harpoon mechanism. Also compute the steric factor.

The ionization potential $E_I(\text{Na}) = 5.1 \text{ eV}$, electron affinity $E_{\text{ea}}(\text{Cl}_2) = 2.38 \text{ eV}$, and the distance of nearest approach of neutral Na and Cl_2 is $d = 350 \text{ pm}$.