Chapter 1 Problems

1. (a) Determine the collision frequency of an OH radical in 100 mTorr of Ar. Assume that the collision cross section is 50 Å^2.
   (b) Use Poisson statistics to estimate the fraction of OH radicals that have undergone zero, one, or two collisions at a time delay of 50 ns after their photolytic production (*e.g., via* the photodissociation of hydrogen peroxide).

2. The reaction

$$K + I_2 \rightarrow KI + I$$

   was studied at a mean relative velocity of 800 ms^{-1}, with I_2 in thermal equilibrium at 300 K. Use the data in the table below to estimate
   (a) the total energy available to the products,
   (b) the maximum orbital angular momentum quantum number, ℓ_{max}, and
   (c) the rotational energy of the KI product if $\boldsymbol{j}' = \ell_{max}$, where $\boldsymbol{j}'$ is the rotational angular momentum quantum number for KI.

   Identify any assumptions made in obtaining the estimate in (b).

	I_2	KI
D_0/kJ mol^{-1}	149	319
ω_e/cm^{-1}	214.5	186.5
B_e/cm^{-1}	0.037	0.061

   [The mean vibrational energy of the I_2 reactants may be calculated assuming $E_v = hc\omega_e/(e^{\theta_v/T} - 1)$ with $\theta_v = hc\omega_e/k_B$.]

3. The cross section, $\sigma_r(E_c)$, for the endothermic reaction

$$K + HCl \rightarrow KCl + H$$

   increases with the collision energy, E_c, in the following way:

E_c/kJ mol^{-1}	9	15	30	50
$\sigma_r(E_c)/10^{-20}$m^2	0.5	1.25	2.0	2.2

(a) Show that the cross section data are consistent with the line-of-centres model

$$\sigma_{\mathrm{r}}(E_{\mathrm{c}}) = \pi d^2 \left(1 - \frac{E_0}{E_{\mathrm{c}}}\right) \quad E_{\mathrm{c}} \geq E_0$$

and determine the threshold energy, E_0, and the limiting, high collision energy cross section, πd^2.

(b) In terms of the reaction cross section, the thermal rate constant can be written

$$k(T) = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} \int_{E_0}^{\infty} \frac{E_{\mathrm{c}}}{k_{\mathrm{B}}T} \sigma_{\mathrm{r}}(E_{\mathrm{c}}) e^{-(E_{\mathrm{c}}/k_{\mathrm{B}}T)} \frac{\mathrm{d}E_{\mathrm{c}}}{k_{\mathrm{B}}T}$$

Use this equation to obtain a line-of-centres expression for $k(T)$. Comment on the result you obtain. You may wish to use the following integral without proof

$$\int_{a}^{\infty} (x - a)e^{-x}\mathrm{d}x = e^{-a}$$

4. Explain how the constraints imposed by the conservation of angular momentum influence the disposal of rotational energy in the reaction

$$\mathrm{Ba} + \mathrm{HI} \rightarrow \mathrm{BaI}(v', j') + \mathrm{H}$$

This reaction has been studied under crossed molecular beam conditions, at a reactant relative velocity, v_{rel} = 976 $\mathrm{ms^{-1}}$; the rotational state distribution in the product BaI, was found to peak at the value j' = 420. Given the orbital angular momentum of the reactants in this reaction can be written $|\ell| = \mu v_{\mathrm{rel}} b$, estimate the most probable impact parameter, b, and the reaction cross section. [Take the masses to be m_{Ba} = 137.3 u, m_{H} = 1.0 u, and m_{I} = 126.9 u.]