Answers

CSO 202: Atoms, Molecules and Photons
Quiz 1
3rd February 2017 – Total Marks – 15

Instructions: There are 3 questions, each carrying 5 marks. Kindly write the answer in the space provided. You have to show intermediate steps in the solution of the problems for full credit. You can use blank pages for Rough Work, but it will not be graded.

Question 1 (5 marks) Consider the reaction $K + I_2 \rightarrow KI + I$. In the reaction, the initial relative kinetic energy is 80.0 kJ/mol. Assume that the reactant I_2 is in vibrational state v=0 and in rotational states up to a maximum quantum number J_{max}=30. Further, calculate the highest possible value of vibrational state of the product v'. You are given the following information :
Bond dissociation energies: $D_e(I_2)$ = 149 kJ/mol, $D_e(KI)$ = 319 kJ/mol
Vibrational frequency: $\widetilde{v}_{I_2}=214$ cm^{-1}, $\widetilde{v}_{KI}=186$ cm^{-1}
Rotational constants: $\widetilde{B}_{I_2}=0.04$ cm^{-1}, $\widetilde{B}_{KI}=0.06$ cm^{-1}
Atomic Masses : $m_I=127.0$ u, $m_K=39.0$ u, 1 u = 1.66×10^{-27} kg
Fundamental constants: h = 6.626×10^{-34} J s, N_A = 6.023×10^{23}, c = 3.0×10^{10} cm/s

(a) Write the energy balance equation for this reaction clearly showing the different modes in which energy is stored. Simply use expressions like E_{trans} for the translational energy of the reactants, and so on.

$$E_{trans} + E_{rot} + E_{vib} + E_{elec} = E'_{trans} + E'_{rot} + E'_{vib} + E'_{elec}$$

REACTANTS PRODUCTS

(b) Substitute the appropriate expressions and values for the different terms in the above expression and derive an equality involving the rotational state of the reactant J, the vibrational state of the product v', the rotational state of the product J' and the product translational energy E'_{trans}.

$$E_{trans} + hc\tilde{B}_{I_2} J(J+1) + \frac{hc\tilde{\nu}_{I_2}}{2} - D_e(I_2) = E'_{trans} + hc\tilde{B}_{KI} J'(J'+1) + hc\tilde{\nu}_{KI}(v'+\tfrac{1}{2}) - D_e(KI)$$

$$hc = 6.626\times10^{-34}\ \text{J s} \times 3\times10^{10}\ \text{cm/s} \times 10^{-3}\ \frac{\text{kJ}}{\text{J}} \times 6.023\times10^{23}\ \frac{1}{\text{mol}}$$

$$= 0.012\ \frac{\text{kJ}}{\text{mol}}\ \text{cm}$$

Now we can write energy balance in $\frac{\text{kJ}}{\text{mol}}$

$$80.0 + 0.012\times0.04\ J(J+1) + 0.012\times\frac{214}{2} - 149 = E'_{trans} + 0.012\times0.06\ J'(J'+1) + 0.012\times186(v'+\tfrac{1}{2}) - 319$$

$$\Rightarrow 251.3 + 0.00048\ J(J+1) = E'_{trans} + 0.00072\ J'(J'+1) + 2.23(v'+\tfrac{1}{2})$$

c) Calculate the highest possible value of vibrational state of the product v'. Clearly show the reasoning used to arrive at the final value.

Since $E'_{trans} \geqslant 0$ and $J' \geqslant 0$, highest possible value of v' is when $E'_{trans} = J' = 0$ and $J = J_{max}$

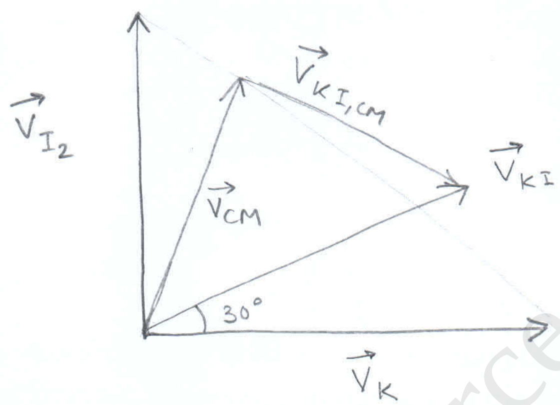
$$251.3 + 0.00048 \times 30 \times 31 = 2.23 \left(v'_{max} + \frac{1}{2} \right)$$

$$v'_{max} = 112.3$$

Hence maximum possible vibrational state is 112

Question 2 (5 marks): In a crossed molecular beam experiment involving the reaction in the first problem $K + I_2 \rightarrow KI + I$, the reactant beams were perpendicular to each other. The velocities of the reactants were both 10×10^6 cm/s. The mass spectrograph detects a signal corresponding to KI moving at 10×10^6 cm/s at an angle of 30° to the original K beam in the laboratory frame.

a) Assuming that the reactive collision takes place in the XY plane, draw the Newton diagram corresponding to this reactive collision. You can choose the X and Y axis as you feel convenient. Try to draw all parts of the diagram approximately to scale and depict angles realistically.



$$\vec{V}_{CM} = \frac{254}{293}\vec{V}_{I_2} + \frac{39}{293}\vec{V}_K$$

b) Calculate the center of mass velocity in the laboratory frame.

$$\vec{V}_{CM} = \left(\frac{254}{293}\hat{j} + \frac{39}{293}\hat{i}\right) 10^7 \text{ cm/s}$$

$$= (1.33\,\hat{i} + 8.67\,\hat{j}) \times 10^6 \text{ cm/s}$$

c) Calculate the velocity of KI in the center of mass frame (both magnitude and direction).

$$\vec{V}_{KI,CM} = \vec{V}_{KI} - \vec{V}_{CM}$$

$$\vec{V}_{KI} = 10 \times 10^6 \times \cos 30^\circ \, \hat{i} + 10 \times 10^6 \sin 30^\circ \, \hat{j}$$

$$= 8.66 \times 10^6 \, \hat{i} + 5 \times 10^6 \, \hat{j}$$

$$\vec{V}_{KI,CM} = (7.33 \, \hat{i} - 3.67 \, \hat{j}) \times 10^6 \text{ cm/s}$$

$$|\vec{V}_{KI,CM}| = 8.20 \times 10^6 \text{ cm/s}$$

Angle with original K direction ($\hat{i}$)

$$= \cos^{-1} 0.89$$

$$= -26.6^\circ$$

Question 3. (a) What is Knudsen number? Comment on its relations with effusive and supersonic beam generation. **(1 mark)**

Knudsen number (K_n) is defined as,

$$K_n = \frac{\text{Mean free path of the gas molecules}}{\text{Diameter of the orifice}}$$

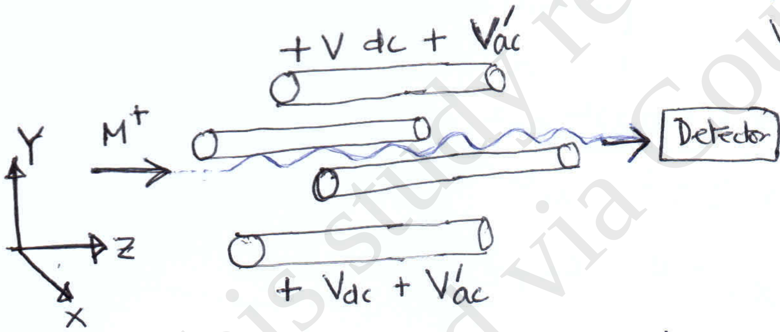
$K_n < 1$ for supersonic beam

$K_n > 1$ for effusive beam

(b) Quadrupole mass filter is used in crossed molecular beam experiment to select a particular mass of interest. However, it is possible to use the quadrupole mass filter only as a high-pass (or low-pass) mass filter by choosing proper voltage configurations. What configuration of voltages should one use so that a quadrupole mass filter acts just a high-pass mass filter? Answer schematically with brief explanation. **(2 marks)**

V_{dc} = dc voltage

$V'_{ac} = V'\cos(\omega t)$ = AC voltage



Potential is applied to the cyllinders along ~~YZ direction~~ YZ plane only. No voltage is given to the cyllinders kept in XZ plane.

M^+ will oscillate in the YZ plane and propagate along Z.

In this configuration: only high masses will be transmitted to the other end of the quadrupole; the smaller masses will be anihillated as they will strike the cyllinders (electrodes)

(c) In the $F+D_2$ crossed molecular beam experiment, Y T Lee used three stage differential pumping to reduce the partial pressure of the background DF molecules in the ionizer chamber. If the partial pressure of background DF molecules in the collision chamber is 10^{-9} torr and if all the apertures on the walls of the buffer chambers and the detector chamber have 6 mm diameter, what is the partial pressure of "straight through" molecules in the detector chamber at a distance 200 mm from the entrance aperture of the first buffer chamber?

(2marks)

If the ~~no.~~ number density of background molecules ~~at~~ at the collision chamber is n, orifice area is A, the distance from the orifice is d, then the number density of straight-through molecules n' is given by

$$n' = \frac{nA}{4\pi d^2}$$

The partial pressure is proportional to the number densities.

$$\text{So } p' = \frac{pA}{4\pi d^2}$$

where p & p' are the partial pressures corresponding to n & n'.

$$p' = \frac{10^{-9}\,\text{torr} \times \pi \times (0.3)^2\,\text{cm}^2}{4 \times \pi \times (20)^2\,\text{cm}^2}$$

$$= 5.6 \times 10^{-14}\ \text{torr}.$$

$\therefore$ The partial pressure of the straight through molecules is 5.6×10^{-14} torr