ASTROCHEMISTRY LECTURE COURSE PROBLEMS

Q1 a) Energy of first transition in Lyman, Balmer, Paschen, Brackett, Pfund series of atomic hydrogen

$E = hcR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ Rydberg equation

$R = 109737\ \text{cm}^{-1}$

Lyman $n_1 = 1$, $n_2 = 2$ $\Rightarrow E = hcR(1 - \frac{1}{4}) = 1.635 \times 10^{-18}$ J

$\lambda = \frac{hc}{E} = 121.5$ nm

Balmer $n_1 = 2$, $n_2 = 3$ $E = hcR(\frac{1}{4} - \frac{1}{9}) = 3.028 \times 10^{-19}$ J

$\lambda = 656$ nm

Paschen $n_1 = 3$, $n_2 = 4$ $E = hcR(\frac{1}{9} - \frac{1}{16}) = 1.060 \times 10^{-19}$ J

$\lambda = 1.875\ \mu$m

Brackett $n_1 = 4$, $n_2 = 5$ $E = hcR(\frac{1}{16} - \frac{1}{25}) = 4.905 \times 10^{-20}$ J

$\lambda = 4.05\ \mu$m

Pfund $n_1 = 5$, $n_2 = 6$ $E = hcR(\frac{1}{25} - \frac{1}{36}) = 2.664 \times 10^{-20}$ J

$\lambda = 7.456\ \mu$m

b) Atmospheric windows span 300–900 nm, 1–5 μm, and 8–20 μm, so the first transitions in the Balmer, Paschen, + Brackett series could be observed using a ground-based telescope.

Q2 a) For the Hα $n = 2 \rightarrow 3$ transition, we have

$E = hcR(\frac{1}{4} - \frac{1}{9}) = 3.0275897 \times 10^{-19}$ J

$\lambda = 656.114$ nm

b) The Doppler shift is $\Delta\lambda = \left(\frac{v_{source}}{c}\right)\lambda$

The rotation speed is $43000\ \text{km hr}^{-1}$

$= 43000\,(1000\,\text{m})(3600\,\text{s})^{-1}$

$= 11944\ \text{ms}^{-1}$

The Doppler shifts of points on the left and right of Jupiter, moving towards and away from Earth at this speed, are

$$\Delta\lambda = \frac{v_{source}}{c}\lambda$$

$$= \pm\frac{11944}{c}\cdot 656.114$$

$$= \pm 0.026\,nm$$

A point observed in the centre of the planet as viewed from earth has zero velocity component along the line of sight, and $\therefore$ no Doppler shift due to rotation (there may be a small Doppler shift due to the relative motion of the two planets in their orbits)

Q3. From the Boltzmann distribution, we expect

$$\frac{n_1}{n_0} = \frac{g_1 e^{-E_1/kT}}{g_0 e^{-E_0/kT}} = 3e^{-(E_1-E_0)/kT}$$

The transition energy is (ignoring centrifugal distortion)

$$E_1 - E_0 = 2B(J+1) = 2B$$

$B = \frac{h}{8\pi^2 cI}$, and for a diatomic, $I = \mu r^2$.

The reduced mass of CO is

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{12\times 16}{12+16} = 6.857\,g\,mol^{-1}$$
$$= 1.139\times10^{-26}\,kg$$

The bond length is

$$r = 112.8\,pm = 112.8\times10^{-12}\,m$$

$$\Rightarrow I = (1.139\times10^{-26})(112.8\times10^{-12})^2$$
$$= 1.449\times10^{-46}\,kg\,m^2$$

$$\Rightarrow B = \frac{h}{8\pi^2 cI} = 1.932\,cm^{-1}$$

The transition E is $\therefore$

$$E_1 - E_0 = 2B = 3.864\,cm^{-1} = 7.676\times10^{-23}\,J$$

Rearranging the equation for $\frac{n_1}{n_0}$ gives

$$\ln\left(\frac{1}{3}\frac{n_1}{n_0}\right) = -\frac{(E_1-E_0)}{kT}$$

$$T = -\frac{(E_1-E_0)}{k\ln\left(\frac{1}{3}\frac{n_1}{n_0}\right)}$$

$$= -\frac{7.676\times10^{-23}}{k\ln\left(\frac{1.10}{3}\right)}$$

$$= 5.54\ \mathrm{K}$$

Q4. From Q 2(a), the transition energy for the $H\alpha$ line is 3.0276×10^{-19} J. The ratio of populations for $n=2$ and $n=3$ at 11000K is :.

$$\frac{n_3}{n_2} = \frac{g_3}{g_2}e^{-\Delta E/kT}$$

$$= \frac{9}{4}\exp\left(\frac{-3.0276\times10^{-19}}{11000\,k}\right)$$

$$= 0.31$$

Q5 a) See lecture notes

b) Bond dissociation occurs when the thermal energy RT exceeds the bond dissociation energy ie

$$T > \frac{E_{bond}}{R}$$

(i) N–N $\quad T > \frac{943000}{8.314} = 1.134\times10^5\ \mathrm{K}$

(ii) C=O $\quad T > \frac{1075000}{8.314} = 1.293\times10^5\ \mathrm{K}$

(iii) C=C $\quad T > \frac{612000}{8.314} = 73,610\ \mathrm{K}$

(iv) C–C $\quad T > \frac{348000}{8.314} = 41857\ \mathrm{K}$

(v) C–H $\quad T > \frac{415000}{8.314} = 49916\ \mathrm{K}$

(c) Similarly, atoms are ionized when

$$T > \frac{I.P.}{k}$$

(i) H $\quad T > \frac{13.6e}{k_B} = 157\,809\ K$

(ii) He $\quad T > \frac{24.59e}{k_B} = 285\,333\ K$

(iii) C $\quad T > \frac{11.26e}{k_B} = 130\,657\ K$

(iv) He^+ $\quad T > \frac{54.51e}{k_B} = 632\,513\ K$

Q6. For a density of $1000\ cm^{-3} = 1\times10^{9}\ m^{-3}$, a mass of 2×10^{30} kg would take up a volume of

$$V = \frac{m}{\rho}$$

NB: Assume the cloud is made up of atomic hydrogen

$$= \frac{m}{m_H n}$$

mass of H atom; number density.

$$= \frac{2\times10^{30}}{(1.66\times10^{-27})(1\times10^{9})}$$

$$= 1.204\times10^{48}\ m^3$$

Assuming that the cloud is spherical, we have

$$V = \frac{4}{3}\pi r^3$$

$$r = \left(\frac{3}{4}\frac{V}{\pi}\right)^{\frac{1}{3}}$$

$$= \left(\frac{3}{4}\cdot\frac{1.204\times10^{48}}{\pi}\right)^{\frac{1}{3}}$$

$$= 6.600\times10^{15}\ m$$

The diameter is :

$$d = 2(6.600\times10^{15}\ m)$$

$$= 1.32\times10^{16}\ m$$

$$= 1.4 \text{ light years}$$

Q7. The collision frequency is given by

$$z = \frac{\sigma_c}{2}\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} n^2$$

For H_2, we have

$$\sigma_c = 0.27\,nm^2$$
$$= 2.7\times10^{-19}\,m^2$$

$$m = 8.303\times10^{-28}\,kg$$

(a) Using the ideal gas law, the number density at atmospheric pressure and room T

$$n = \frac{N}{V} = \frac{P}{kT} = \frac{101300}{298k} = 2.45\times10^{25}\,m^{-3}$$

$$\Rightarrow\ z = \left(\frac{2.7\times10^{-19}}{2}\right)\left(\frac{8.k.300}{8.303\times10^{-28}\pi}\right)^{\frac{1}{2}}(2.45\times10^{25})^2$$

$$= 2.89\times10^{35}\,s^{-1}m^{-3}$$

(b) when $n = 10^5\,cm^{-3} = 1\times10^{11}\,m^{-3}$, and $T = 40K$, we have

$$z = \left(\frac{2.7\times10^{-19}}{2}\right)\left(\frac{8k.40}{8.303\times10^{-28}\pi}\right)^{\frac{1}{2}}(1\times10^{11})^2$$

$$= 1.76\times10^{6}\,m^{-3}s^{-1}$$

(c) when $n = 10\,cm^{-3} = 1\times10^{7}\,m^{-3}$, and $T = 10K$, we have

$$z = \left(\frac{2.7\times10^{-19}}{2}\right)\left(\frac{8k.10}{8.303\times10^{-28}\pi}\right)^{\frac{1}{2}}(1\times10^{7})^2$$

$$= 0.0088\,m^{-3}s^{-1}$$

$$(= 32\,m^{-3}hr^{-1})$$

Q8.

$$H + H \xrightarrow{\text{dust grain}} H_2 \qquad k_1$$

$$H_2 \xrightarrow{h\nu/cr} H_2^+ + e^- \qquad k_2$$

$$H_2^+ + H_2 \longrightarrow H_3^+ + H \qquad k_3$$

$$H_3^+ + CO \longrightarrow HCO^+ + H_2 \qquad k_4$$

a) The reaction steps are:

1. Surface catalysed reaction of 2 H atoms on a dust grain to form H_2

2. Photoionisation or electron-impact ionization (an e^- or photon knocks an e^- out of H_2 to make H_2^+.)

3. Ion-molecule reaction (H atom abstraction from H_2 by H_2^+) to form H_3^+.

4. Ion-molecule reaction (proton transfer from H_3^+ to CO) to form HCO^+.

b) Apply SSA to $[H_2^+]$ and $[H_3^+]$

$$\frac{d[H_2^+]}{dt} = 0 = k_2[H_2] - k_3[H_2^+][H_2]$$

$$\Rightarrow [H_2^+] = \frac{k_2}{k_3}$$

$$\frac{d[H_3^+]}{dt} = 0 = k_3[H_2^+][H_2] - k_4[H_3^+][CO]$$

$$[H_3^+] = \frac{k_3[H_2^+][H_2]}{k_4[CO]}$$

$$= \frac{k_2[H_2]}{k_4[CO]} \quad \text{since } [H_2^+] = \frac{k_2}{k_3}$$

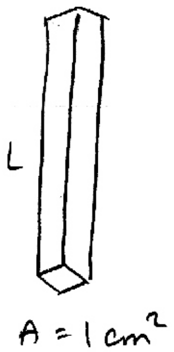
$$\therefore \frac{d[HCO^+]}{dt} = k_4[H_3O^+][CO]$$

$$= k_4 \cdot \frac{k_2[H_2]}{k_4[CO]} \cdot [CO]$$

$$= k_2[H_2]$$

Ionisation of $[H_2]$ is the rate limiting step in the mechanism.

c)



The no. of molecules in a column of cross section 1 cm^2 and length L is 3×10^{24}.

The length of the column is :.

$$L = \frac{3\times10^{24}}{2\times10^{4}} = 1.5\times10^{20}\ \text{cm} = 1.5\times10^{18}\ \text{m}$$

This is about 160 light years
(1 light year = 9.46×10^{15} m).

Q9

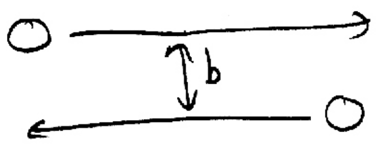
$$C + H_2 \rightarrow CH^+ + H \qquad k_1$$
$$CH^+ + N \rightarrow CN^+ + H \qquad k_2$$
$$CH_2^+ + H \rightarrow CH^+ + H_2 \qquad k_3$$
$$C + CH^+ \rightarrow C_2^+ + H \qquad k_4$$

a) Treating the CH^+ ion as a reactive intermediate, we have

$$\frac{d[CH^+]}{dt} = 0 = k_1[C][H_2] - k_2[CH^+][N] + k_3[CH_2^+][H] - k_4[C][CH^+]$$

$$[CH^+] = \frac{k_1[C][H_2]}{k_2[N] - k_3[H] + k_4[C]}$$

b)



The impact parameter is the distance by which two particles would miss each other in the absence of attractive or repulsive interactions. It gives a measure of how "direct" a collision is. ie very small b corresponds to a "head on" collision, larger b corresponds to a "glancing" collision, and much larger b will eventually lead to no collision. The reaction cross section can be defined in terms of the maximum b leading to reaction i.e. $\sigma = \pi b_{max}^2$

c) The orbital angular momentum is

$$L = \mu v b$$

Taking v as the mean relative velocity,

$$v = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}$$

we have

$$L = \mu\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} b$$

ie for a given b and T, $L \propto \mu^{\frac{1}{2}}$

$$= \left(\frac{8kT\mu}{\pi}\right)^{\frac{1}{2}} b$$

For the four reactions, we have

1. $\mu(C^+ + H_2) = \frac{12\times2}{12+2} = 1.714\,g\,mol^{-1} = 2.847\times10^{-27}\,kg$

$$L = \left(\frac{8k.50.2.847\times10^{-27}}{\pi}\right)^{\frac{1}{2}} b$$

$$= (3.94\times10^{-24})\,b$$

2. $\mu(CH^+ + N) = \frac{13\times14}{13+14} = 6.74\,g\,mol^{-1} = 1.119\times10^{-26}\,kg$

$$L = \left(\frac{8k.50.1.119\times10^{-26}}{\pi}\right)^{\frac{1}{2}} b$$

$$= (4.44\times10^{-24})\,b$$

3. $\mu(CH_2^+ + H) = \frac{14\times1}{14+1} = 0.933\,g\,mol^{-1} = 1.550\times10^{-27}\,kg$

$$L = \left(\frac{8.k.50.1.550\times10^{-27}}{\pi}\right)^{\frac{1}{2}} b$$

$$= (1.65\times10^{-24})\,b$$

4. $\mu(C + CH^+) = \frac{12\times13}{12+13} = 6.24\,g\,mol^{-1} = 1.036\times10^{-26}\,kg$

$$L = \left(\frac{8.k.50.1.036\times10^{-26}}{\pi}\right)^{\frac{1}{2}} b$$

$$= (4.27\times10^{-24})\,b$$

The orbital angular momentum is highest for $CH^+ + N$

d) The orbital angular momentum leads to a centrifugal barrier $\frac{L^2}{2I}$ on the PES. The barrier height increases with b and with the reduced mass of the collision partners, so the second step is likely to be the rate determining step.

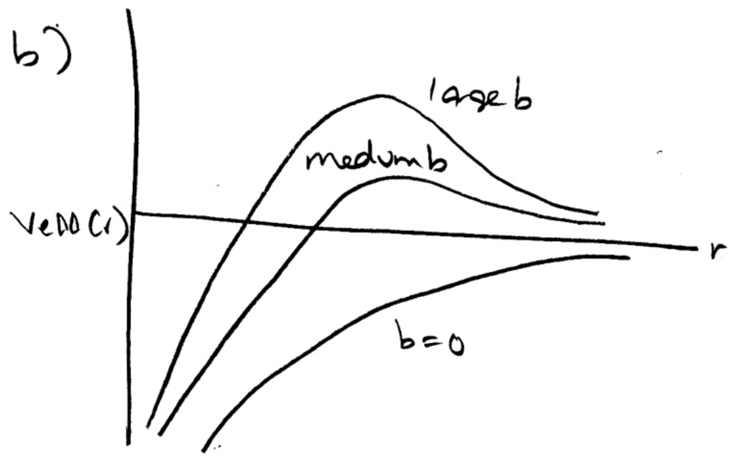
Q10. $V_{eff} = -\frac{\alpha q^2}{8\pi\varepsilon_0 r^4} - \frac{\mu_D q}{4\pi\varepsilon_0 r^2} + \frac{\mu v_{rel}^2 b^2}{2r^2}$

a) ion-induced dipole term: The ionic charge induces a dipole in the neutral, leading to an attractive interaction

ion-dipole term: The ionic charge interacts with a permanent dipole on the neutral molecule.

centrifugal barrier term: Angular momentum associated with the orbital motion of the reactants must be conserved. The kinetic E associated with this motion is not available for reaction + is often treated in terms of an effective barrier on the PES.

b)



c) To find the maximum, we differentiate $V_{eff}(r)$ w.r.t. r, set the result equal to zero, and solve for r, to find r_0

$$\frac{dV_{eff}}{dr} = 0 = \frac{d}{dr}\left[-\frac{\alpha q^2}{8\pi\epsilon_0} r^{-4} - \frac{\mu_D q}{4\pi\epsilon_0} r^{-2} + \frac{\mu v_{rel}^2 b^2}{2} r^{-2}\right]$$

$$= \frac{\cancel{4}\alpha q^2}{\cancel{8}_2 \pi\epsilon_0 r^5} + \frac{\cancel{2}\mu_D q}{\cancel{4}_2 \pi\epsilon_0 r^3} - \frac{\cancel{2}\mu v_{rel}^2 b^2}{\cancel{2} r^3}$$

$$= \frac{\alpha q^2}{r^2} + \mu_D q - 2\pi\epsilon_0 \mu v_{rel}^2 b^2$$

$$r = \left[\frac{\alpha q^2}{2\pi\epsilon_0 \mu v_{rel}^2 b^2 - \mu_D q}\right]^{\frac{1}{2}}$$

d) As the impact parameter b increases, the height of the centrifugal barrier increases (see figure in b)). At some value of b the barrier will exceed the collision energy E_{coll}, we can find this maximum impact parameter by setting the barrier height equal to E_{coll}, solving for b. ie

$$V_{eff}(r_0) = E_{coll}$$

The reaction cross section is then

$$\sigma_r(E_{coll}) = \pi b_{max}^2$$

e) From simple collision theory, the rate constant for a given relative velocity is

$$k(v_{rel}) = \sigma_r(v_{rel})\, v_{rel}$$

The thermal rate constant is found by integrating $k(v_{rel})$ over the Maxwell-Boltzmann velocity distn of temperature T, $f(v_{rel})$.

$$k(T) = \int \underbrace{\sigma_r(v_{rel})\, v_{rel}}_{k(v_{rel})} f(v_{rel})\, dv_{rel}$$