C/P 740 Winter Quarter 2008

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Answers To Set 4

1. $V = -\frac{C}{R^4}$ $\quad C = \frac{e^2\alpha}{2}$ $\quad V_{eff} = -\frac{C}{R^4} + E_T b^2/R^2$

$$\frac{dV_{eff}}{dR} = 0 = 4CR^{-5} - 2E_T b^2 R^{-3} \Rightarrow 4CR^{-5} = 2E_T b^2 R^{-3}$$

$$\therefore 4C = 2E_T b^2 R^2 \Rightarrow R_{max}^2 = 2C/E_T b^2$$

Orbiting Condition: $V_{eff}^{max}(R_{max}) = E_T = -\frac{C}{(2C/E_T b^2)^2} + \frac{E_T b^2}{2C/E_T b^2}$

$$E_T = -C E_T^2 b_{orb}^4 / 4C^2 + \frac{E_T^2 b_{orb}^4}{2C} = + E_T^2 b_{orb}^4 / 4C$$

$$\therefore b_{orb}^4 = 4C/E_T \qquad b_{orb}^2 = 2(C/E_T)^{1/2}$$

$$\sigma_R = \pi b_{orb}^2 = 2\pi (C/E_T)^{1/2} = 2\pi \left[\frac{e^2\alpha}{2\cdot\frac{1}{2}\mu v^2}\right]^{1/2}$$

$$\sigma_R = 2\pi\, e/v \sqrt{\alpha/\mu}$$

$$k_L = v\sigma_R = 2\pi e\sqrt{\alpha/\mu}$$

2. H_3^+ $\quad T = 10K$ $\quad n = 10^4\ cm^{-3}$

a) $k_L(H_3^+ - H_2)$ $\quad \alpha(H_2) = 0.8023 \times 10^{-24}\ cm^3$

$$\frac{1}{\mu} = \frac{1}{m(H_3^+)} + \frac{1}{m(H_2)} = 0.82686 \Rightarrow \mu = 1.20939/N_A\ gm$$

$(m(^1H) = 1.007825\ amu)$ $\quad \therefore k_L = 1.91 \times 10^{-9}\ cm^3\ s^{-1}$

$e = 4.803 \times 10^{-10}$ esu $\qquad \tau_{H_2} = \frac{1}{k_L n} = 5.24 \times 10^4$ s

$N_A = 6.022169 \times 10^{23}$ $\qquad = 14.5$ hr

b) $k_L(H_3^+ - CO)$ $\quad \alpha(CO) = 1.95 \times 10^{-24}\ cm^3$

$m(^{12}C) = 12.0000$ $\quad m(^{16}O) = 15.99491$ amu

$$\frac{1}{\mu} = \frac{1}{m(CO)} + \frac{1}{m(H_3^+)} = 0.36647 \qquad \mu = 2.729/N_A \text{ gm}$$

$$k_L(H_3^+ - CO) = 1.98 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

$$\tau_{CO} = \frac{1}{k_L [CO]} \qquad [CO]/n \sim 10^{-4}$$

$$\therefore [CO] \sim 1.0 \text{ cm}^{-3}$$

$$\tau_{CO} = \frac{1}{k_L} = 5.05 \times 10^8 \text{ s} = 16.0 \text{ yr}$$

c) $$MFP = v\tau \qquad v = \sqrt{\frac{8kT}{\pi\mu}} = 4.18 \times 10^4 \text{ cm s}^{-1}$$

$H_3^+ - H_2$

$$MFP = 4.18 \times 10^4 \text{ cm s}^{-1} (5.24 \times 10^4 \text{ s})$$

$$= 2.19 \times 10^9 \text{ cm} = 2.19 \times 10^4 \text{ km}$$

3. $HN_2^+ + e \longrightarrow ?$

<u>Heats of Formation</u>:

Species	ΔH_f° (kJ mol^{-1})
HN_2^+	1035.5
H	218.00
N	472.68
N_2	0.00
NH	376.56

$$\underset{1035.5}{N_2H^+} + e^- \xrightarrow{EXO} \underset{0.00}{N_2} + \underset{218.00}{H} \qquad \Delta H^\circ = -817.50 \text{ kJ/mol}$$

$$\xrightarrow{EXO} \underset{472.68}{N} + \underset{376.56}{NH} \qquad \Delta H^\circ = -186.26 \text{ kJ/mol}$$

$$\xrightarrow{ENDO} \underset{2(472.68)}{N + N} + \underset{218.00}{H} \qquad \Delta H^\circ = +127.86 \text{ kJ/mol}$$

Of the two exothermic channels, chemical intuition argues that $N_2 + H$ dominates, given the strong N–N chemical bond.

Nevertheless, according to Geppert et al.
[reference: Astrophys J. 609, 459(2004)],
the branching ratios are as follows:

$N_2 + H$ 36% $NH + N$ 64%

Science is often non-intuitive! Last month, the results were withdrawn!

4. $H^+ + HCN \rightarrow$ Products $\alpha(HCN) = 2.5 \times 10^{-24}\ cm^3$
$m(^{14}N) = 14.00307$ amu

$\mu = 0.9716/N_A$ gm

$\mu_D = \mu_D(HCN) = 2.984\ D = 2.984 \times 10^{-18}$ esu-cm

$k_L = 2\pi e\sqrt{\alpha/\mu} = 3.76 \times 10^{-9}\ cm^3\ s^{-1}$

$$x = \frac{\mu_D}{\sqrt{2\alpha k_B T}} \qquad k_B = 1.3807 \times 10^{-16}\ erg/K$$

$x = 113.6/\sqrt{T}$ $x(10\ K) = 35.9$

$$k_{LD}/k_L = 1 + \frac{2x}{\sqrt{\pi}} = 41.5$$

$k_{TS}/k_L = 0.62 + 0.4767x = 17.7$

$k_{LD}(10\ K) = 1.56 \times 10^{-7}\ cm^3\ s^{-1}$

$k_{TS}(10\ K) = 6.66 \times 10^{-8}\ cm^3\ s^{-1}$

Expt. data at 300K: $k_{meas} = 1.1 \times 10^{-8}\ cm^3\ s^{-1}$

$k_{TS}(300\ K) = 1.4 \times 10^{-8}\ cm^3\ s^{-1}$