C/P 740

Winter 2008
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Answers To Homework Set #6

1. $N + OH \rightarrow NO + H$
$NO + N \rightarrow N_2 + O$
$N_2 + He^+ \rightarrow N^+ + N + He$
$N^+ + H_2 \rightarrow NH^+ + H$
$NH^+ + H_2 \rightarrow NH_2^+ + H$
$NH_2^+ + H_2 \rightarrow NH_3^+ + H$
$NH_3^+ + H_2 \rightarrow NH_4^+ + H$
$NH_4^+ + e^- \rightarrow \boxed{NH_3} + H$

$HCNH^+ + e^- \rightarrow CN + H + H$
$C + H_3^+ \rightarrow CH^+ + H_2$
$CH^+ + H_2 \rightarrow CH_2^+ + H$
$CH_2^+ + H_2 \rightarrow CH_3^+ + H$
$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$
$CH_5^+ + e^- \rightarrow CH_4 + H$

$C^+ + NH_3 \rightarrow HCNH^+ + H$
$N + CH \rightarrow CN + H$
$CN + H_3^+ \rightarrow HCN^+ + H_2$
$HCN^+ + H_2 \rightarrow HCNH^+ + H$
$HCNH^+ + e^- \rightarrow \boxed{HCN} + H$

Both NH_3 & HCN (as well as HCCCN) are destroyed by a variety of ions: H_3^+, He^+, H^+, etc.

$C^+ + CH_4 \rightarrow C_2H_3^+ + H$
$C_2H_3^+ + e^- \rightarrow C_2H_2 + H$
$CN + C_2H_2 \rightarrow \boxed{HCCCN} + H$

2. First consider H_3^+: as shown in class

$$[H_3^+] = \zeta [H_2]/k_1[CO] \qquad \zeta = 1.3 \times 10^{-17}\ s^{-1}$$

where $H_3^+ + CO \xrightarrow{k_1} HCO^+ + H_2$; $k_1 = 1.6 \times 10^{-9}\ cm^3\ s^{-1}$

$$[H_3^+] = \zeta / k_1 f_{CO} \qquad f_{CO} = 10^{-4}$$

$$\therefore\ [H_3^+] = 8.1 \times 10^{-5}$$

$$\frac{d[HCO^+]}{dt} = k_1[H_3^+][CO] - k_2[HCO^+][e^-] = 0$$

$HCO^+ + e^- \xrightarrow{k_2} CO + H$ (etc.) $\qquad k_2 = 2.6 \times 10^{-7} (T/300)^{-0.69}$

$$k_2(10\ K) = 2.7 \times 10^{-6}\ cm^3\ s^{-1}$$

$$[HCO^+] = \frac{k_1[H_3^+][CO]}{k_2[e^-]} = \frac{k_1[H_3^+] f_{CO}}{k_2 f_{e^-}}$$

$[HCO^+] = 5 \times 10^{-5}\ cm^{-3}$ $\quad f_{HCO^+} = 5 \times 10^{-9}$

3. $H_3^+ + HD \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2D^+ + H_2$

$H_2D^+ + CO \xrightarrow{k_2} DCO^+ + H_2$ (1/3) ; $HCO^+ + HD$ (2/3)

$DCO^+ + e^- \xrightarrow{k_3} CO + D$ (etc.)

Also: $H_3^+ + CO \xrightarrow{k_4} HCO^+ + H_2$

$HCO^+ + e \xrightarrow{k_5} CO + H$ (etc)

$f_{HD} = 2 \times 10^{-5}$

$$[H_2D^+] = \frac{k_1[H_3^+][HD]}{k_{-1}[H_2] + k_2[CO]}$$

$$[DCO^+] = \frac{1}{3}\frac{k_2[H_2D^+][CO]}{k_3[e^-]}$$

$$[HCO^+] = \frac{k_4[H_3^+][CO]}{k_5[e^-]}$$

$$\frac{[DCO^+]}{[HCO^+]} = \frac{1}{3}\frac{[H_2D^+]}{[H_3^+]} \qquad k_2 \approx k_4 \quad k_3 \approx k_5$$

$$\frac{[H_2D^+]}{[H_3^+]} = \frac{k_1[HD]}{k_{-1}[H_2] + k_2[CO]} = \frac{k_1 f_{HD}}{k_{-1} + k_2 f_{CO}}$$

$K = k_1/k_{-1} \cong e^{230/T}$ $\quad k_1 \sim 10^{-9}\ cm^3\ s^{-1}$

$k_2 \cong 1.6 \times 10^{-9}\ cm^3\ s^{-1}$

$T = 10\,K$ $\quad K = 9.7 \times 10^9 \Rightarrow k_{-1} = 1.0 \times 10^{-19}\ cm^3\ s^{-1}$

$T = 20\,K$ $\quad K = 9.9 \times 10^4 \Rightarrow k_{-1} = 1.0 \times 10^{-14}\ cm^3\ s^{-1}$

$T = 10\,K$ $\quad \dfrac{[H_2D^+]}{[H_3^+]} = \dfrac{k_1 f_{HD}}{k_{-1} + k_2 f_{CO}} = \dfrac{k_1 f_{HD}}{k_2 f_{CO}} = 0.13$

tiny $\longrightarrow 10^{-19}\ cm^3 s^{-1}$

$$\frac{[DCO^+]}{[HCO^+]} = \frac{1}{3}\frac{[H_2D^+]}{[H_3^+]} = 0.043$$

$T = 20\,K$ $\quad \dfrac{[H_2D^+]}{[H_3^+]} = \dfrac{k_1 f_{HD}}{1\times10^{-14} + 1.6\times10^{-13}} = 0.12$

$$\frac{[DCO^+]}{[HCO^+]} = 0.040 \quad \text{small effect}$$

4. $H_3O^+ + e^- \longrightarrow H_2O + H$ $\quad 30\%$ $\quad 0.3\,k_{dr}$

$\longrightarrow OH + 2H/H_2$ $\quad 70\%$ $\quad 0.7\,k_{dr}$

$H_2O + H_3^+ \xrightarrow{k_a} H_3O^+ + H_2$ (neglect reformation of H_2O)

$OH + O \xrightarrow{k_b} O_2 + H$

$$[H_2O] = 0.3\,k_{dr}\,[H_3O^+][e^-] / k_a [H_3^+]$$

$$[OH] = 0.7\,k_{dr}\,[H_3O^+][e^-] / k_b [O]$$

$$\frac{[H_2O]}{[OH]} = \frac{3}{7}\frac{k_b[O]}{k_a[H_3^+]} = \frac{3}{7}\frac{k_b f_O}{k_a f_{H_3^+}}$$

$f_O \sim 10^{-4}$ $\quad f_{H_3^+} \sim 8\times10^{-9}$

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$O + OH$ $\quad k_b = 7.5\times10^{-11}\,(T/300)^{-0.25} = 1.76\times10^{-10}\ cm^3 s^{-1}$

$H_2O + H_3^+$ $\quad k_a = 4.5\times10^{-9}\,(T/300)^{-0.5} = 2.46\times10^{-8}\ cm^3 s^{-1}$

$$\frac{[H_2O]}{[OH]} = \frac{3}{7}\,\frac{1.76\times10^{-10}\ \ 10^{-4}}{2.46\times10^{-8}\ \ 8\times10^{-9}} = 38$$