C/P 740 Winter Quarter 2008

Answers To Set # 5

1. $A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{+*} \qquad AB^{+*} + C \xrightarrow{k_2} AB^+ + C$

$$\frac{d[AB^{+*}]}{dt} = 0 = k_1[A^+][B] - k_{-1}[AB^{+*}] - k_2[AB^{+*}][C]$$

$$\therefore \quad [AB^{+*}] = \frac{k_1[A^+][B]}{k_{-1} + k_2[C]}$$

$$\frac{d[AB^+]}{dt} = k_2[AB^{+*}][C] = \frac{k_1 k_2}{k_{-1} + k_2[C]}[A^+][B][C]$$

<u>High C Density</u>

$k_{-1} < k_2[C] \qquad \frac{d[AB^+]}{dt} \approx \frac{k_1 k_2}{k_2[C]}[A^+][B][C] = k_1[A^+][B]$ "saturation"

all complexes are collisionally stabilized.

<u>Low C Density</u>

$k_{-1} > k_2[C] \qquad \frac{d[AB^+]}{dt} = \underbrace{\frac{k_1 k_2}{k_{-1}}}_{k_{3-B}}[A^+][B][C]$ third-order

2. $A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{+*} \qquad AB^{+*} \xrightarrow{k_r} AB^+ + h\nu$

$AB^{+*} + C \xrightarrow{k_2} AB^+ + C$

$$\frac{d[AB^{+*}]}{dt} = 0 = k_1[A^+][B] - k_{-1}[AB^{+*}] - k_r[AB^{+*}] - k_2[AB^{+*}][C]$$

$$\therefore \quad [AB^{+*}] = \frac{k_1[A^+][B]}{k_{-1} + k_r + k_2[C]}$$

$$\frac{d[AB^+]}{dt} = k_r[AB^{+*}] + k_2[AB^{+*}][C]$$

$$\frac{d[AB^+]}{dt} = [AB^{+*}](k_r + k_2[C])$$

$$= \frac{k_1[A^+][B]}{k_{-1} + k_r + k_2[C]}(k_r + k_2[C])$$

$$= \frac{k_1(k_r + k_2[C])}{k_{-1} + k_2[C]}[A^+][B] \qquad k_{-1} \gg k_r$$

$$k_{eff} = \frac{k_1(k_r + k_2[C])}{k_{-1} + k_2[C]}$$

<u>Very high density</u>: $k_2[C] > k_{-1} > k_r$

$$k_{eff} \to \frac{k_1 k_2[C]}{k_2[C]} = k_1 \quad \text{"saturation"}$$

<u>Very low density</u>: $k_{-1} > k_r > k_2[C]$

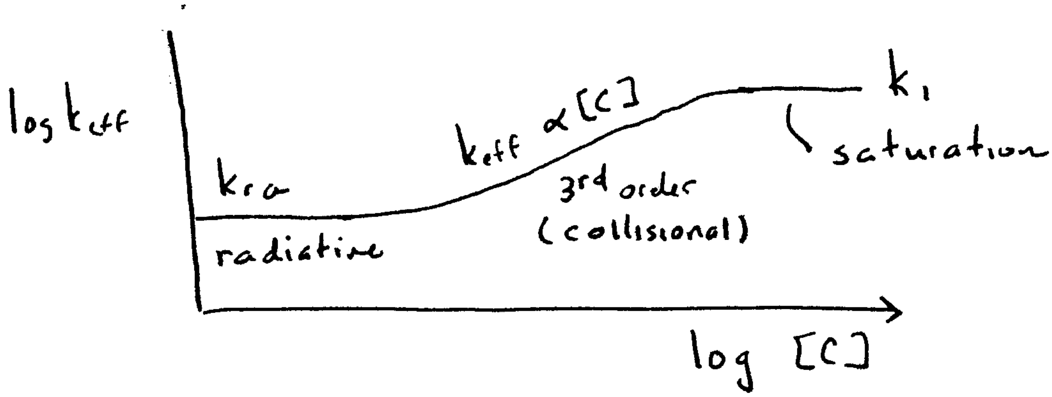
$$k_{eff} \to \frac{k_1 k_r}{k_{-1}}$$ radiative association; $k_{eff} = k_{ra}$

<u>Intermediate density</u>

$$k_{-1} > k_2[C] > k_r$$

$$k_{eff} \to \frac{k_1 k_2[C]}{k_{-1}}$$ 3rd order-kinetics

$$k_{3\text{-}B} = k_1 k_2 / k_{-1}$$



<u>Example</u>: $k_1 = 10^{-9}\ cm^3\ s^{-1}$ $k_2 = 10^{-10}\ cm^3\ s^{-1}$
$k_r = 10^2\ s^{-1}$ $k_{-1} = 10^8\ s^{-1}$

$$k_{eff} = \frac{k_1(k_r + k_2[C])}{k_{-1} + k_2[C]}$$

[C]	k_{eff} ($cm^3\ s^{-1}$)	
$10^4\ cm^{-3}$	1×10^{-15}	radiative regime
$10^6\ cm^{-3}$	1×10^{-15}	
$10^9\ cm^{-3}$	1×10^{-15}	
$10^{12}\ cm^{-3}$	2×10^{-15}	third-order $k_{eff} \propto [C]$
$10^{14}\ cm^{-3}$	1×10^{-13}	
$10^{16}\ cm^{-3}$	1×10^{-11}	
$10^{18}\ cm^{-3}$	5×10^{-10}	
$10^{20}\ cm^{-3}$	1×10^{-9}	saturation

3. Use quantum RRK theory.

$$k_{ra} = \frac{k_1}{k_{-1}} k_r \qquad k_1 = k_L = 2\pi e\sqrt{\frac{\alpha}{\mu}} = 1.6 \times 10^{-9}\ cm^3 s^{-1}$$

$$\alpha = 0.8\ \mathring{A}^3 \qquad \mu = 1.73/N_A\ \text{gm}$$

$$k_r = 10^6\ s^{-1}$$

$$E = E_c = j h\nu \qquad k_{-1} = \bar{\nu}\,\frac{j!\,(s-1)!}{(j+s-1)!}$$

$$E/hc = j\tilde{\nu} = 4.3 \times 8065\ cm^{-1}$$

$$\tilde{\nu} = 2000\ cm^{-1} \qquad \therefore\ j = \frac{34{,}680\ cm^{-1}}{2{,}000\ cm^{-1}} \sim 17 \qquad s = 3$$
(non-linear)

$$k_{-1} = \bar{\nu}\,\frac{17!\,2!}{19!} = \frac{\bar{\nu}\cdot 2}{19 \times 18} = \frac{\bar{\nu}}{9 \times 19} \qquad \bar{\nu} = c\tilde{\nu} = 6.0 \times 10^{13}\ s^{-1}$$

$$k_{-1} = 3.5 \times 10^{11}\ s^{-1} \qquad k_{ra} = \frac{1.6 \times 10^{-9}\ cm^3 s^{-1}}{3.5 \times 10^{11}\ s^{-1}}\ 10^6 s^{-1} = 4.6 \times 10^{-15}\ cm^3 s^{-1}$$

(high by an order of magnitude)

4. $dN_H/dt = k_{acc}[H] - k_{des} N_H$ per grain

$$\frac{dN_H}{dt} = 0 \Rightarrow N_H = k_{acc}[H]/k_{des}$$

$$k_{acc} = \langle v_H \rangle \sigma_{gr} \qquad a = 0.1\mu = 10^{-5}\ cm$$

$$\sigma_{gr} = \pi a^2 = \pi \times 10^{-10}\ cm^2$$

$$\langle v_H \rangle = \sqrt{\frac{8 k_B T}{\pi m_H}} = 1.449 \times 10^4\ T^{1/2}\ cm\ s^{-1}$$

$$k_{acc} = 4.553 \times 10^{-6}\ T^{1/2}\ cm^3\ s^{-1}$$

$$k_{des} = 10^{12} e^{-373/T}\ s^{-1} \qquad [H] = 1\ cm^{-3}$$

<u>T = 10K</u>

$$k_{acc} = 1.44 \times 10^{-5}\ cm^3\ s^{-1} \qquad k_{des} = 10^{12} e^{-37.3} = 6.32 \times 10^{-5}\ s^{-1}$$

$N_H = 0.2278$ atoms reaction can occur but with less than unit efficiency

<u>T = 20K</u>

$$k_{acc} = 2.04 \times 10^{-5}\ cm^3\ s^{-1} \qquad k_{des} = 10^{12} e^{-18.65} = 7.95 \times 10^3\ s^{-1}$$

$N_H = 2.56 \times 10^{-9}$ atoms reaction unlikely