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EE 239

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Problem Set 8 Solution

1. Problem 9.1a

(1) $$\frac{dn_{O_2}}{dt} = K_2' n_{O_3} n_{O_2} - K_3 n_O n_{O_2}^2 + 2K_2 n_O n_{O_3} + G = 0$$

(2) $$\frac{dn_O}{dt} = K_2' n_{O_3} n_{O_2} - K_2 n_O n_{O_3} - K_3 n_O n_{O_2}^2 = 0$$

(3) $$\frac{dn_{O_3}}{dt} = -K_2 n_O n_{O_3} - K_2' n_{O_3} n_{O_2} + K_3 n_O n_{O_2}^2 - \frac{2}{3} G = 0$$

Here $R = -\frac{2}{3} G$ is the rate of conversion of O_3 to O_2.

From (2),

$$n_O = \frac{K_2' n_{O_3} n_{O_2}}{K_2 n_{O_3} + K_3 n_{O_2}^2}.$$

Combining (2) and (3),

$$R = 2 K_2 n_O n_{O_3}$$

$$R = \frac{2 K_2 K_2' n_{O_3}^2 n_{O_2}}{K_2 n_{O_3} + K_3 n_{O_2}^2}$$

Using $K_2 = 1.8 \times 10^{-11} e^{-2300/298} = 8.00 \times 10^{-15}$ cm³/s

$K_2' = 1.78 \times 10^{-26}$ cm³/s

$K_3 = 6.84 \times 10^{-34}$ cm⁶/s

$\Rightarrow R = 3.03 \times 10^{5}$ cm^{-3}-s^{-1} //

2. Problem 9.4. (a) There are six metastable states and one ground state. Hence using (8.5.14)

$$\frac{K_1}{K_2} = \frac{6}{1} e^{-11.58/T_e}$$

$$K_2 = \frac{1}{6} K_1 e^{+11.58/T_e} = 8.67 \times 10^{-16}\, T_e^{0.74} \quad //$$

(b)

$$K_1 n_e n_{Ar} = K_2 n_e n_{Ar}^*$$

$$\frac{n_{Ar}^*}{n_{Ar}} = \frac{K_1}{K_2} = 6 e^{-11.58/T_e} \approx 0.126 \quad \text{at } T_e = 3\text{ V} \quad //$$

(c)

$$\frac{dn_{Ar}^*}{dt} = K_1 n_e n_{Ar} - K_2 n_e n_{Ar}^* - K_4 n_e n_{Ar}^* = 0$$

$$n_{Ar}^* = n_{Ar} \frac{K_1}{K_2 + K_4}$$

$$\frac{\text{meta. ioniz}}{\text{sec}-\text{m}^3} = K_4 n_e n_{Ar}^* = n_e n_{Ar} \frac{K_4 K_1}{K_2 + K_4}$$

$$\frac{\text{gnd. ioniz}}{\text{sec}-\text{m}^3} = n_e n_{Ar} K_3$$

$$\text{Fraction due to metastables} = \frac{\overbrace{\left(\frac{K_4 K_1}{K_2 + K_4}\right)}^{2.34 \times 10^{-16}\ \text{m}^3/\text{s}}}{K_3 + \frac{K_4 K_1}{K_2 + K_4}} = 0.51 \quad ///$$

$$\left(\begin{aligned} &K_4 = 3.54 \times 10^{-14}\ \text{m}^3/\text{s}; \quad K_3 = 2.45 \times 10^{-16}\ \text{m}^3/\text{s} \\ &K_2 = 1.95 \times 10^{-15}\ \text{m}^3/\text{s}, \quad K_1 = 2.47 \times 10^{-16}\ \text{m}^3/\text{s} \end{aligned} \right)$$

3. Problem 9.11 (a, b)

$$n_0' \frac{d\theta}{dt} = n_0' K_a n_{AS}(1-\theta) - K_d n_0' \theta - 2K_{d2} n_0'^2 \theta^2 = 0$$

$$n_0' K_a n_{AS}(1-\theta) = K_d n_0' \theta + 2K_{d2} n_0'^2 \theta^2$$

Note $n_0' K_a n_{AS} = \frac{1}{4} \bar{v}_A n_{AS} \sim 2 \times 10^{17} \frac{1}{cm^2\text{-}s}$

$K_d n_0' \sim 10^{14} e^{-3/.026} 10^{15} \sim 7.7 \times 10^{-22} \frac{1}{cm^2\text{-}s}$

$K_{d2} n_0'^2 \sim (0.1) e^{-1/.026} (10^{15})^2 \sim 2.0 \times 10^{12} \frac{1}{cm^2\text{-}s}$

Clearly associative desorption dominates normal desorption and $\theta \approx 1$ because

$$n_0' K_a n_{AS} \gg 2K_{d2} n_0'^2 \gg K_d n_0'$$

(c) From above, $\Gamma_{A2} \sim 2.0 \times 10^{12} \frac{1}{cm^2\text{-}s}$

$\Gamma_A = \frac{1}{4} n_{AS} \bar{v}_A = 2 \times 10^{17} \frac{1}{cm^2\text{-}s}$

$\Gamma_{A2} / \Gamma_A = 10^{-5}$ //

(d) Now $K_d n_0' \sim 10^{15} e^{-\frac{0.2}{0.026}} 10^{15} \sim 4.6 \times 10^{26} \frac{1}{cm^2\text{-}s}$

$K_{d2} n_0'^2 \sim (0.1) 10^{30} \sim 10^{29} \frac{1}{cm^2\text{-}s}$

Hence $n_0' K_a n_{AS} \ll K_d n_0'$ and thus $\theta \ll 1$.

In this case $K_{d2} n_0'^2 \theta^2 \ll K_d n_0' \theta$

To find θ, ignore associative desorption

$$n_0' K_a n_{AS} = (n_0' K_a n_{AS} + K_d n_0')\theta \approx K_d n_0' \theta$$

$$\theta \approx \frac{n_0' K_a n_{AS}}{K_d n_0'} = \frac{2 \times 10^{17}}{4.6 \times 10^{26}} = 4.4 \times 10^{-10} \ll 1$$

(e) $K_d n_0' \theta \gg K_{d2} n_0'^2 \theta^2$, so almost all atoms desorb as atoms

(f) $$\frac{\Gamma_{A2}}{\Gamma_A} = \frac{K_{d2} n_0'^2 \theta^2}{\frac{1}{4} n_{AS} \bar{v}_A} = \frac{10^{29} (4.4 \times 10^{-10})^2}{2 \times 10^{17}}$$

$$\frac{\Gamma_{A2}}{\Gamma_A} = 9.6 \times 10^{-8} \ll 1$$