## **Chemical Engineering**

## Principles of Plasma Processing UCLA, Spring 2004

## Due: May 13, 2004

## From HW#3

- 4. Use Fig. 20 on page 149 in the textbook, identify and discuss the dissociative electron attachment, and polar dissociation processes. Label the pertinent energies on the diagram and discuss the energy of the dissociated atoms, whenever possible.
- 5. Problem 8. 7, part (d) in LL.
- 1. Stepwise ionization can occur in the plasma involving excited species:

$$A + e^{-} \xrightarrow{K_{ex}} A^{*} + e^{-}$$
$$A^{*} + e^{-} \xrightarrow{K_{iz^{*}}} A^{+} + 2e^{-}$$

Assume there are two competing mechanisms for the loss of A\*:

- (a) collisional de-excitation:  $A^* + e^- \xrightarrow{K_{dex}} A^+ e^-$
- (b) first order losses due to radiative emission and de-excitation at the wall:  $A^* \xrightarrow{K_1} A$

Let the ionization potentials of A and  $A^*$  to be  $E_{iz}$  and  $E_{iz^*}$ . Assume that the statistical weights of A and  $A^*$  are the same, and  $T_e \ll E_{iz}$ ,  $E_{iz^*}$ , and  $K_{iz^*} \ll K_{dex}$ .

(1) From the detailed balance, show that:

- (2) Show  $n_{A*}$  as a function of  $n_e$ ,  $n_A$ , and the rate constants.
- (3) Use the Thomson ionization rate constants, show that the ratio of two-step

$$K_{ex} = K_{dex} \cdot exp\left(-\frac{E_{iz} - E_{iz^*}}{T_e}\right) \text{to single-step ionization rates is:}$$
$$\frac{R_{iz^*}}{R_{iz}} = \frac{n_e K_{dex}}{n_e K_{dex} + K_1} \frac{E_{iz}^2}{E_{iz^*}^2}$$

(4) Finally, is two-step ionization important or not? If so, under what conditions?

2. To use optical spectroscopy to determine the plasma chemistry, you need to determine the number of photons at various wavelengths accurately. Assume that you have a plasma in that the electron and neutral density are  $10^{11}$  cm<sup>-3</sup> and  $5x10^{13}$  cm<sup>-3</sup>, respectively, with a mean electron temperature of 2.5 eV. Use the model shown on the next page to describe the most important transitions, where  $E_0$ ,  $E_1$ ,  $E_2$ , and  $E_i$  are ground state, excited state 1, excited state 2, and ionized state,  $R_1$ , and  $R_2$  are rate of collisional excitation from the ground state (cross-section of both processes are shown below), and  $A_{10}=4x10^8$  s<sup>-1</sup>,  $A_{20}=2x10^7$  s<sup>-1</sup>, and  $A_{21}=3x10^7$  s<sup>-1</sup> are rates of spontaneous emission. Calculate the number of photons and their wavelength using a plasma volume of 100 cm<sup>3</sup>.



- 3. Actinometry is widely used to aid the quantification of the optical emission spectra from plasmas and determine the concentration of various excited species. You have developed a silicon etching process using chlorine gas at a pressure of 10 mtorr. Your preliminary experimental results with a pure chlorine plasma indicate that you have a strong emission line at 837.6 nm and another line at 251.7 nm towards the etching end-point. What electronic transition state are these lines corresponding to? Which noble gas and its corresponding emission line will you choose for actinometry and why? With 1 at.% of the noble gas of your choice mixed in your chlorine plasma, the integrated intensity ratio of the 837.6nm line to the line of your choice is 10:1. Determine the concentration of chlorine atoms in your plasma. If your chlorine plasma is very weakly dissociated, which wavelength(s) of light would you expect to see with your OES setup? (list two dominant lines for Cl<sub>2</sub>).
- 4. Explain what is the appearance mass spectrometry? For a high density chlorine BCl<sub>3</sub> plasma, if you scan the filament energy from 0 to 70 eV, how many features do you expect to see and at what energies? Please justify your answers. (Hint: Find the dissociation and ionization energies for important atomic and simple molecular species).