

SOLUTION MANUEL

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PART 1.

CHAPTER 2.

2.7.1. Electron Energy Distribution Functions. *If electron energy distribution function is Maxwellian and the electron temperature is $T_e = 1\text{eV}$, (1) what is the mean velocity $\langle v \rangle$ of the electrons in this case?, (2) what is the mean electron energy?, (3) which electron energy $m\langle v \rangle^2/2$ corresponds to the mean velocity?, (4) how can you explain the difference between the two “average electron energies” in terms of standard deviation?*

The mean electron velocity $\langle v \rangle$ corresponding to the Maxwell velocity distribution function:

$$f(v) = 4\pi v^2 \sqrt{(m/2\pi T_e)^3} \exp(-mv^2/2T_e)$$

can be found after integration as: $\langle v \rangle = \sqrt{8T_e/\pi m}$. Numerically at $T_e = 1\text{eV}$,

$\langle v \rangle = 0.7 * 10^8 \text{ cm/sec}$. The mean electron energy in this case according to (2.1.2) is $\langle \varepsilon \rangle = 1.5 \text{ eV}$.

Electron energy corresponding to the mean velocity can be found as: $m\langle v \rangle^2/2 = 4T_e/\pi$, and numerically at $T_e = 1\text{eV}$ gives the “average” electron energy about 1.3 eV. The difference between these two “average” energies is due to the difference between mean square velocity and square of the mean velocity, which corresponds to the variance or the square of the standard deviation of the velocity distribution.

2.7.2. Ionization Potentials and Electron Affinities. *Why are most ionization potentials (Table 2.1.1) greater than electron affinities (Table 2.1.2)?*

Ionization potentials are related to the electron-ion coulomb interaction energies, which are usually greater than the electron-neutral coulomb interaction energies corresponding to electron affinities. It should be noted however that the exchange interaction energies can make significant additional contribution in both cases.

2.7.3. Positive and Negative Ions. *Why is it very doable to produce the double- or multi-charged positive ions such as A^{++} or A^{+++} in plasma, and impossible to generate in a practical gas discharge plasmas the double or multi-charged negative ions such as A^{-} or A^{----} ?*

Generation of the multi-charged positive ions such as A^{++} or A^{+++} obviously requires energies greater than conventional ionization potentials (Table 2.1.1) but can be achieved at very high plasma temperatures. Formation of the multi-charged negative ions such as A^{-} or A^{----} requires an electron attachment to a negative ion. Such processes are suppressed in gas phase because the coulomb repulsion energies (corresponding to the electron-ion interaction) are usually much stronger than the quantum mechanical affinity corresponding to the exchange interaction.

2.7.4. Mean Free Path of Electrons. *In which gases are the mean free path of electrons with electron temperature $T_e = 1\text{eV}$ longer and why? (helium, nitrogen or water vapor at the similar pressure conditions)?*

Noble gases are characterized by the lowest electron-neutral elastic-collision cross-sections (no significant long-distance polarization interaction). Therefore, at electron temperatures about $T_e = 1\text{eV}$ when the elastic collisions dominate, the longest mean free path should be expected in the noble gases (in this example, in helium) in accordance with Eq. (2.1.3).

2.7.5. Reaction Rate Coefficients. *Recalculate the Maxwellian electron energy distribution function into the electron velocity distribution function $f(v)$ and then find an expression for reaction rate coefficient Eq. (2.1.7) in the case when $\sigma = \sigma_0 = \text{const.}$*

The Maxwell velocity distribution function is related to the Maxwell energy distribution function (2.1.1) by the equation: $f(v) * dv = f(\varepsilon) * d\varepsilon$. Simple derivation results in the velocity distribution:

$$f(v) = 4\pi v^2 \sqrt{(m/2\pi T_e)^3} \exp(-mv^2/2T_e)$$

The reaction rate coefficient (2.1.7) can be found by integration:

$$k = \int \sigma_0 v f(v) dv = \sigma_0 \langle v \rangle = \sigma_0 \sqrt{8T\pi m}$$

2.7.6. Elastic Scattering. *Charged particle scattering on neutral molecules with permanent dipole momentum can be characterized by the following cross section dependence on energy: $\sigma(\varepsilon) = \text{Const} / \varepsilon$. How does the rate coefficient of the scattering depend on temperature in this case?*

The scattering rate coefficient can be calculated in this case based on the Eq. 2.1.7 as:

$$k = \int \sigma(\varepsilon) v f(v) dv = \int \frac{\text{const}}{\varepsilon} \sqrt{\varepsilon} f(\varepsilon) d\varepsilon = \frac{1}{\sqrt{\varepsilon}} > \approx \frac{1}{\sqrt{T}},$$

which reveals the required temperature dependence.

2.7.7. Direct Ionization by Electron Impact. *Using Eq.(2.2.8) for the general ionization function $f(x)$, find the electron energy corresponding to maximum value of direct ionization cross- section. Compare this energy with the electron energy optimal for direct ionization according to the Thomson formula.*

Electron energy appears in the Eq. (2.2.6) only as $x = \frac{\varepsilon}{I}$, therefore simple differentiation of $f(x)$ in (2.2.8) gives the optimal x and therefore optimal electron energy to compare with $x=2$ for the Thompson formula.

2.7.8. Comparison of Direct and Stepwise Ionization. *Why does the direct ionization make a dominant contribution in non-thermal electric discharges while in thermal plasmas stepwise ionization is more important?*

The degree of electronic excitation in thermal plasma is usually much higher than in non-thermal plasma, which explains the high effectiveness of the stepwise ionization in this case.

2.7.9. Stepwise Ionization. *Estimate a stepwise ionization reaction rate in Ar at electron temperature 1 eV, assuming quazi-equilibrium between plasma electrons and electronic excitation of atoms, and using Eq.(2.2.19).*

Based on the Eq. (2.2.19), ratio of stepwise and direct ionization rate coefficients can be calculated as:

$$\frac{k_i^s(T_e)}{k_i(T_e)} \approx \left(\frac{I}{T_e}\right)^{7/2} = (16\text{eV}/1\text{eV})^{3.5} \approx 1.6 \cdot 10^4$$

The direct ionization rate coefficient $k_i(T_e)$ in Ar at electron temperature 1 eV can be found from the Eq. (2.2.11) as $2 \cdot 10^{-15} \text{ cm}^3 / \text{sec}$. Therefore, the stepwise ionization rate coefficient $k_i^s(T_e)$ in Ar at electron temperature 1 eV can be estimated as $3 \cdot 10^{-11} \text{ cm}^3 / \text{sec}$.

2.7.10. Electron Beam Propagation in Gases. *How does the propagation length of a high energy electron beam depend on pressure at fixed temperature? How does it depend on temperature at a fixed pressure?*

As seen from (2.2.22) and (2.2.23), the propagation length is inversely proportional to the gas density ($\propto 1/n_0$). Taking into account the equation of state ($p = n_0 T$), the electron beam propagation length decreases proportionally to pressure at fixed temperature, and increases proportionally to temperature at constant pressure.

2.7.11. Photoionization. *Why can the photoionization effect play the dominant role in propagation of both non-thermal and thermal discharges in fast flows including supersonic ones? What is the contribution of photoionization in the propagation of slow discharges?*

Propagation of the fast flow discharges, and especially supersonic flow discharges, cannot be supported by transfer of active and energetic heavy particles as well as temperature (which simplify the

ionization conditions), because the propagation of the heavy particles is limited by velocities much lower than speed of sound. Contribution of photoionization in such systems can be crucial, because it is not limited by speed of sound. Development of the relatively slow discharges (like conventional dielectric barrier discharge, DBD), which are sustained by the streamer based ionization (the spark breakdown mechanism) is also closely related to the photoionization effect. In this case, the photoionization promotes formation and propagation of streamers.

2.7.12. Massey Parameter. *Estimate the adiabatic Massey parameter for ionization of Ar-atom at rest in collision with Ar^+ -ion, having kinetic energy twice exceeding the ionization potential. Discuss the probability of ionization in this case.*

The velocity of an argon ion with energy 32 eV (corresponding to two ionization potentials) is about 10^6 cm/sec, $\alpha v \approx 10^8$ 1/sec. In accordance with the Eq. (2.2.27), the Massey parameter is about 26. Ionization probability in this case is obviously very low, about 10^{-11} (reaction rate coefficient about 10^{-21} cm³/sec).

2.7.13. Ionization in an Ion-Neutral Collision. *How large is an H^+ -ion energy supposed to be, for this ion to reach a velocity the same as an electron velocity in a hydrogen atom. Compare this energy with the H-atom ionization potential. What are your conclusions about ionization process initiated by ion impact?*

Kinetic energies are proportional to mass at the constant velocities. Taking into account that the ionization potential is 13.6 eV, and the ratio of mass is about 2,000, it is easy to estimate the H^+ -ion energy as approximately 30 keV. This level of energies is actually sufficient for the Massey parameter to become small, and to the ion-neutral ionization to become non-adiabatic and effective.

2.7.14. Ionization in Collision of Excited Heavy Particles. *Why is ionization in the collisions of vibrationally excited molecules usually much less effective than in similar collisions of electronically excited molecules?*

Ionization in collisions of electronically excited molecules requires quite exact resonance. But when the electronic energy resonance is achieved, the Massey parameter becomes small and the ionization becomes effective. During such collisions, the energy is actually transferred between electrons of the collision partners. In contrast to that, the energy transfer in the ionization collisions of vibrationally excited molecules should be from the vibrational energy of heavy particles to an electronic energy. Such processes are limited not only by the Massey factors (the adiabatic nature of the processes), but also by low values of the Franck-Condon factors.

2.7.15. Ionization in Collision of Vibrationally Excited Molecules. *In principal, ionization can take place in collisions of nitrogen molecules having 32 vibrational quanta each. Is it possible to increase the probability of such ionization by increasing the vibrational energy of the collision partners?, by increasing electronic energy of the collision partners?*

The energy transfer required for ionization in collisions of vibrationally excited molecules should take place from the vibrational energy of heavy particles (molecules) to energy of light electrons, an electronic energy. Such processes are limited by the Massey factors (the adiabatic nature of the processes), and by the low values of the Franck-Condon factors. Increasing of the vibrational and electronic energy of the collision partners would obviously increase the probability of the ionization process. However, the major factors suppressing the probability of the ionization still remain in place, keeping the probability of the ionization in collision of vibrationally excited molecules quite low.

2.7.16. Dissociative Electron-Ion Recombination. *According to Eq.(2.3.4), rate coefficient of dissociative recombination is inversely proportional to gas temperature. However in reality, when the electric field is fixed, this rate coefficient is decreasing faster than the reverse proportionality. How can you explain that?*

When the electric field is fixed, increase of the gas temperature leads simultaneously to the increase of electron temperature (because of decrease of gas density and increase of the reduced electric

field E/n_0). Simultaneous increase of both gas and electron temperatures results in more significant reduction of the dissociative recombination rate coefficient.

2.7.17 . Ion-Conversion, Preceding Electron-Ion Recombination. *How large is the relative concentration of complex ions like $N_2^+(N_2)$ supposed to be to compete with conventional electron recombination with N_2^+ -ions in the same discharge conditions?*

As it is seen from the Table 2.3.1., the reaction rate coefficient of the dissociative electron attachment to N_2^+ at electron temperature 1 eV is about 10 times slower than that of the dissociative electron attachment to $N_2^+(N_2)$. It means that the relative concentration of the complex ions like $N_2^+(N_2)$ is supposed to exceed about 10% (with respect to the conventional ions) to compete with conventional electron recombination with N_2^+ .

2.7.18. Three-Body Electron-Ion Recombination. *Derive the reaction rate coefficient of the three-body recombination, using Eq.(2.2.16) for the stepwise ionization rate coefficient and the Saha thermodynamic equation for ionization/recombination balance.*

Rate coefficients of the three-body electron-ion recombination and the stepwise ionization are related by the detailed equilibrium balance between these two processes:

$$k_r^{eei} n_e n_e n_i = k_i^s n_e n_0, \quad k_r^{eei} = k_i^s \frac{n_0}{n_e n_i}$$

Taking into account the thermodynamic Saha equation (4.1.15) for the $\frac{n_0}{n_e n_i}$ ratio:

$$k_r^{eei} = k_i^s \frac{n_0}{n_e n_i} = k_i^s \frac{g_0}{g_e g_i} \left(\frac{2\pi\hbar}{mT_e} \right)^{3/2} \exp\left(\frac{I}{T_e}\right)$$

Finally, using the expression (2.2.16, 18) for the stepwise ionization rate coefficient, that of the three-body electron-ion recombination can be found as:

$$k_r^{eei} = k_i^s \frac{n_0}{n_e n_i} = k_i^s \frac{g_0}{g_e g_i} \left(\frac{2\pi\hbar}{mT_e} \right)^{3/2} \exp\left(\frac{I}{T_e}\right) \approx \frac{e^{10}}{(4\pi\epsilon_0)^5 \sqrt{mT_e^9}} .$$

2.7.19. Radiative Electron- Ion Recombination. *Give an example of discharge parameters (type of gas, range of pressures, plasma densities etc.), when the radiative electron-ion recombination dominates between other mechanisms of losses of charged particles.*

According to the Eq. (2.3.8), the reaction rate coefficient of the radiative electron-ion recombination is about $10^{-13} \text{ cm}^3/\text{sec}$ at electron temperatures 1-3 eV. This recombination process is obviously suppressed by dissociative electron-ion recombination in molecular gases. In noble gases, it competes with three-body recombination characterized by the coefficient about $10^{-27} \text{ cm}^6/\text{sec}$. Thus at the electron densities below 10^{14} cm^{-3} , the radiative electron-ion recombination can dominate in noble gases (see 2.3.9).

2.7.20. Dissociative Attachment. *Calculate the dissociative attachment rate coefficients for molecular hydrogen and molecular oxygen at electron temperatures 1 eV and 5eV. Compare the results and give your comments.*

The numerical calculation of the dissociative attachment rate coefficient can be simply accomplished using the practical formula Eq. (2.4.3). The necessary parameters in the formula for the gases of interest ϵ_{\max} , $\sigma_{\text{d.a.}}^{\max}$ and $\Delta\epsilon$ are provided in the Table 2.4.1.

2.7.21. Negative Ions in Oxygen. *What are the discharge and gas parameters supposed to be if the negative oxygen ions are mostly generated by three-body attachment processes, and not by dissociative attachment?*

When $T_e=1\text{eV}$, $T_0=300\text{K}$, a good estimation for the three-body attachment rate coefficient is $k_{3M} \approx 10^{-30} \text{ cm}^6/\text{sec}$. The rate of three-body process is greater than dissociative attachment (k_a) when the gas number density exceeds a critical value $n_0 > k_a(T_e) / k_{3M}$. Numerically in oxygen with $T_e=1\text{eV}$, $T_0=300\text{K}$, this means $n_0 > 10^{18} \text{ cm}^{-3}$, or in pressure units at room temperature: $p > 30 \text{ Torr}$.

2.7.22. Associative Detachment. *Calculate the relative concentration of CO in CO₂-discharge plasma if the main associative detachment process in this discharge dominates over dissociative attachment. Suppose that the electron temperature is 1eV, and the concentration of negative ions is 10 times less than positive ions.*

The associative detachment from the negative oxygen ions dominates over formation of these ions in the dissociative attachment when:

$$k_{ad}[CO][O^-] > k_a n_e [CO_2]$$

Assuming $[O^-]/n_e = 0.1$, $k_a = 10^{-12} \text{ cm}^3/\text{sec}$, $k_{ad} = 5 \cdot 10^{-10} \text{ cm}^3/\text{sec}$ (see Table 2.4.3), the required fraction of CO in carbon dioxide should exceed 2%.

2.7.23. Detachment by Electron Impact. *Detachment of an electron from negative ion by electron impact can be considered as “ionization” of the negative ion by electron impact. Why can’t the Thomson formula be used in this case instead of Eq.(2.4.15)?*

The electron impact detachment is similar to the direct ionization of neutrals by an electron impact following the Thomson mechanism. The main difference is related to significant repulsive Coulomb force acting between the incident electron and the negative ion.

2.7.24. Negative Ions in Thermal Plasma. *Why is concentration of negative ions in thermal plasmas usually very low even in electro-negative gases? Which specific features of thermal plasmas with respect to non-thermal plasmas are responsible for that?*

Ionization potentials are usually much greater than electron affinities responsible for keeping the negative ions stable (see Tables 2.1.1 and 2.1.2). Ionization in thermal plasma follows the thermal ionization mechanism, which is controlled by gas temperature. Therefore, temperature in thermal plasma should be sufficient for ionization. As a result, this temperature is significantly higher than that one required for thermal destruction of the negative ions.

2.7.25. Ion-Ion Recombination in Binary Collisions. *Determine how the ion-ion recombination rate coefficient depends on temperature. Use Eq.(2.5.5) for the cross section of the binary collision recombination rate and assume the Maxwellian distribution function with temperature T_0 for both positive and negative ions.*

The cross-section of the recombination is inversely proportional to the collision energy:

$$\sigma_{rec}^{ii}(\varepsilon) \approx \sigma_0 \frac{I}{E A_A} \frac{I}{\varepsilon}.$$

Integration of the recombination cross-section over the Maxwellian distribution function, obviously gives the inverse proportionality of the rate coefficient of the ion-ion recombination process on the temperature T_0 .

2.7.26. Three-Body Ion-Ion Recombination. *Comparing Thomson's and Langevin's approaches for the three-body ion-ion recombination and correspondent rate coefficients Eqs.(2.5.9) and (2.5.13), find a typical value of pressure when the recombination reaches the maximum rate. Consider oxygen plasma with heavy particle temperature 1 eV as an example.*

Comparing the Thomson and Langevin models (2.5.9) and (2.5.13), it is seen that at lower pressures, the recombination rate coefficients grows with pressure $k_{r2}^{ii} = k_{r3}^{ii} n_0$ (see Eq. (2.5.9)), and then at high pressures the recombination rate coefficients begin to decrease as $1/p$ together with ion mobility Eq.(2.5.13). The highest recombination coefficient according to Eq.(2.5.10) corresponds to the concentration of neutrals:

$$n_0 \approx \frac{4\pi\varepsilon_0 T_0}{\sigma e^2}$$

At room temperature this gas concentration is about $3 \cdot 10^{19} \text{ cm}^{-3}$, which corresponds to the atmospheric pressure.

2.7.27. Langevin Cross Section. *Calculate the Langevin cross section for Ar^+ -ion collision with an argon atom and with water molecule. Comment on your result. Compare the contribution of the*

polarization term and the charge-dipole interaction term in the case of Ar^+ -ion collision with a water molecule.

For molecules like H_2O , having a large permanent dipole moment, the ratio of the second to the first terms in Eq.(2.6.5) characterizing the Langevin capture is about $\sqrt{I/T_0}$, where I is ionization potential. It means that the Langevin cross section and rate coefficient for water molecules exceed by a factor of 10 the numerical values obtained for pure polarization collisions Eq.(2.6.4), which can be applied in the case of argon.

2.7.28. Resonant Charge Transfer Process. *Is it possible to observe the resonant charge transfer process during an ion-neutral interaction with only a slight perturbation of trajectories of the collision partners?*

The resonant charge exchange process can significantly involve the electron tunneling, and therefore can be characterized by cross section hundred times exceeding the gas-kinetic one. Therefore, the resonant charge transfer process during an ion-neutral interaction can be observed with only a slight perturbation of trajectories of the collision partners.

2.7.29. Tunneling Effect in Charge Transfer. *Estimate how strong the tunneling effect can be in resonant charge transfer in ion-neutral collision. For two different velocities compare the cross section of charge exchange between an argon atom and argon positive ion calculated with and without taking into account the tunneling effect.*

The calculation is easy to carry out based on formulas (2.6.12) and (2.6.14). The first one doesn't take into account tunneling, and the second one does. Even easier the comparison can be done using numerical formula (2.6.15), and taking into account that classical formula gives the charge transfer cross section close to the gas-kinetic one. The tunneling effect can increase the cross section of the resonant charge exchange more than two orders of magnitude.

2.7.30. Non-Resonant Charge Exchange. *Most negative ions in non-thermal atmospheric pressure air discharges are in form of O_2^- . What will happen to the negative ion distribution if even a very small amount of fluorine compounds is added to air?*

Strongly electronegative fluorine containing compounds added in air plasma will form significant amount of negative ions by means of both electron attachment and exothermic non-resonant charge exchange processes.

2.7.31. Plasma Catalytic Effect. *Compare the catalytic effect of plasma provided by negative ions, positive ions, active atoms and radicals. All these species are usually quite active, but which one is the most generally relevant to the plasma catalysis.*

Ions are the most relevant active plasma species for the effect of plasma catalysis. However, other active plasma species, and even the “local heating effects” can also contribute to the general effect of plasma catalysis.

2.7.32. Winchester Mechanism. *Why is the ion mechanism of cluster growth usually less effective in combustion plasma during soot formation than in similar situations in electrical discharge plasma?*

The ion mechanism of cluster growth is less effective in combustion systems during the soot formation than in similar situations in electrical discharges because ion density in the plasma discharges is usually much greater than in flames.

CHAPTER 3.

3.8.1. Lifetime of Metastable Atoms. *Compare the relatively long radiative lifetime of a metastable helium atom $\text{He} (2s^1 \ ^3S_1)$ with the time interval between collisions of the atom with other neutrals and with a wall of a discharge chamber (radius 3 cm) in a room temperature discharge at low pressure of 10 Torr. Comment on the result.*