Chapter 1

X-ray reactions involved

Primary and secondary ionization reaction from X-ray absorption are listed:

Primary Reactions (41)

$$
\begin{aligned}
H + \gamma_X &\rightarrow H^+ + e^- \\
He + \gamma_X &\rightarrow He^+ + e^- \\
C + \gamma_X &\rightarrow C^{2+} + 2e^- \\
N + \gamma_X &\rightarrow N^{2+} + 2e^- \\
O + \gamma_X &\rightarrow O^{2+} + 2e^- \\
Si + \gamma_X &\rightarrow Si^+ + e^- \\
S + \gamma_X &\rightarrow S^{2+} + 2e^- \\
Cl + \gamma_X &\rightarrow Cl^+ + e^- \\
Fe + \gamma_X &\rightarrow Fe^{2+} + 2e^- \\
C^+ + \gamma_X &\rightarrow C^{2+} + 2e^- \\
N^+ + \gamma_X &\rightarrow N^{2+} + 2e^- \\
O^+ + \gamma_X &\rightarrow O^{2+} + 2e^- \\
S^+ + \gamma_X &\rightarrow S^{2+} + 2e^- \\
Fe^+ + \gamma_X &\rightarrow Fe^{2+} + 2e^- \\
H_2 + \gamma_X &\rightarrow H^+ + H^+ + 2e^- \\
CH + \gamma_X &\rightarrow C^{2+} + H + 2e^- \\
NH + \gamma_X &\rightarrow N^{2+} + H + 2e^- \\
OH + \gamma_X &\rightarrow O^{2+} + H + 2e^- \\
CN + \gamma_X &\rightarrow C^{2+} + N + 2e^- \\
CN + \gamma_X &\rightarrow C^+ + N^+ + 2e^- \\
CN + \gamma_X &\rightarrow C + N^{2+} + 2e^-
\end{aligned}
$$

$$CO + \gamma_X \rightarrow C^{2+} + O + 2e^-$$
$$CO + \gamma_X \rightarrow C^+ + O^+ + 2e^-$$
$$CO + \gamma_X \rightarrow C + O^{2+} + 2e^-$$
$$N_2 + \gamma_X \rightarrow N^{2+} + N + 2e^-$$
$$N_2 + \gamma_X \rightarrow N^+ + N^+ + 2e^-$$
$$SiH + \gamma_X \rightarrow Si^+ + H + 2e^-$$
$$NO + \gamma_X \rightarrow N^{2+} + O + 2e^-$$
$$NO + \gamma_X \rightarrow N^+ + O^+ + 2e^-$$
$$NO + \gamma_X \rightarrow N + O^{2+} + 2e^-$$
$$O_2 + \gamma_X \rightarrow O + O^{2+} + 2e^-$$
$$O_2 + \gamma_X \rightarrow O^+ + O^+ + 2e^-$$
$$SiO + \gamma_X \rightarrow Si + O^{2+} + 2e^-$$
$$SiO + \gamma_X \rightarrow Si^+ + O^+ + 2e^-$$
$$CH_2 + \gamma_X \rightarrow C^{2+} + H_2 + 2e^-$$
$$NH_2 + \gamma_X \rightarrow N^{2+} + H_2 + 2e^-$$
$$H_2O + \gamma_X \rightarrow O^{2+} + H + 2 + 2e^-$$
$$HCN + \gamma_X \rightarrow C^{2+} + NH + 2e^-$$
$$HCN + \gamma_X \rightarrow N^{2+} + CH + 2e^-$$
$$CO_2 + \gamma_X \rightarrow C^{2+} + O_2 + 2e^-$$
$$CO_2 + \gamma_X \rightarrow O^{2+} + CO + 2e^-$$

Secondary Reactions (16)

$$H + e^- \rightarrow H^+ + e^- + e^-$$
$$He + e^- \rightarrow He^+ + e^- + e^-$$
$$H_2 + e^- \rightarrow H_2^+ + e^- + e^-$$
$$H_2 + e^- \rightarrow H^+ + H + e^- + e^-$$
$$C + e^- \rightarrow C^+ + e^- + e^-$$
$$N + e^- \rightarrow N^+ + e^- + e^-$$
$$O + e^- \rightarrow O^+ + e^- + e^-$$
$$Si + e^- \rightarrow Si^+ + e^- + e^-$$
$$S + e^- \rightarrow S^+ + e^- + e^-$$
$$Cl + e^- \rightarrow Cl^+ + e^- + e^-$$
$$Fe + e^- \rightarrow Fe^+ + e^- + e^-$$
$$C^+ + e^- \rightarrow C^{2+} + e^- + e^-$$
$$N^+ + e^- \rightarrow N^{2+} + e^- + e^-$$
$$O^+ + e^- \rightarrow O^{2+} + e^- + e^-$$

$$S^+ + e^- \rightarrow S^{2+} + e^- + e^-$$
$$Fe^+ + e^- \rightarrow Fe^{2+} + e^- + e^-$$

Chapter 2

Primary Ionization

For reactions of the kind:

$$\begin{aligned} A + \gamma_X &= A^{2+} + 2e^- & (2.1) \\ AB + \gamma_X &= A^{2+} + B + 2e^- & (2.2) \\ &= A + B^{2+} + 2e^- & (2.3) \\ &= A^{+} + B^{+} + 2e^- & (2.4) \end{aligned}$$

The dimensions of all the following quantities are also listed in the appendix.

2.1 Depopulating n_i

The rate of ionization for the species i is[1]:

$$\zeta_{i \to jl} = \int \sigma_{i \to jl} \frac{F}{E} e^{-\tau_X} dE \qquad [s^{-1}] \tag{2.5}$$

Where σ_i is the cross section of the ith particle, τ_X is the optical depth for X-ray photons, which is kept constant till the point where the rate is calculated. Defining F_i as $\frac{dn_i}{dt}$, and considering only the term that depopulates from n_i through primary ionization we get:

$$F_i = -\Sigma_{jl} \zeta_{i \to jl} n_i \qquad [cm^{-3} s^{-1}] \tag{2.6}$$

There is no explicit dependence of the rate on n_{el}, hence the Jacobian can be calculated as follows:

$$\begin{aligned} \frac{dF_i}{dn_k} &= -\Sigma_{jl} \zeta_{i \to jl} \frac{\partial n_i}{\partial n_k} - \frac{\partial \left(\Sigma_{jl} \zeta_{i \to jl} \right)}{\partial n_k} n_i \\ &= -\Sigma_{jl} \zeta_{i \to jl} \delta_{ik} & (2.7) \end{aligned}$$

[1]The quantities σ, τ and F are a function of energy. The explicit dependence is omitted for clear notation purposes.

2.1.1 Interpretation

- If $i \neq k$:

$$\frac{dF_i}{dn_k} = 0 \tag{2.8}$$

A small change in density for the species k does not affect the primary ionization of the ith species.

- If $i = k$:

$$\frac{dF_k}{dn_k} = -\Sigma_{jl}\zeta_{k\to jl} \tag{2.9}$$

The rate for the particle i changes with density.

2.2 POPULATING n_i

The rate of ionization for the species j that produces the species i is:

$$\zeta_{j\to il} = \int \sigma_{j\to il}\frac{F}{E}e^{-\tau x}\,dE \tag{2.10}$$

Then:

$$F_i = \Sigma_j \zeta_{j\to il} n_j \tag{2.11}$$

There is no explicit dependence of the rate on n_{el}, hence the Jacobian can be calculated as follows:

$$\begin{aligned} \frac{dF_i}{dn_k} &= \Sigma_j \zeta_{j\to il}\delta_{jk} + \frac{\partial\left(\zeta_{j\to il}\right)}{\partial n_k} n_j \\ &= \zeta_{k\to il} \end{aligned} \tag{2.12}$$

Where we repeated the same steps as in equation (2.7)

Interpretation

We point out that $i \neq k$. The only way to change F_i is changing the density of the species k.

Chapter 3

Secondary Ionization

For reactions of the kind:

$$A + e^- = A^+ + 2e^- \tag{3.1}$$

3.1 Species i with $i \neq He, H_2$

3.1.1 Depopulating n_i

The rate of collisional ionization for species i is given by:

$$\zeta_{i \to j} = r_i \frac{H_x}{W_H n_H / n_{tot}} [s^{-1}] \tag{3.2}$$

Where r_i is a parameter that takes into account the geometrical cross section of species i compared to the hydrogen cross section, n_{tot} is the total hydrogen nuclei density. H_x is the energy deposition and W_H is the mean energy per ion (Dalgarno et al., 1999).

W_H for hydrogen is given by:

$$W_H = W_{0,H} \left(1 + c_1 \left(\frac{n_{el}}{n_{tot}}\right)^\alpha\right) \left(1 + c_2 \frac{n_{H_2}}{n_H}\right) \tag{3.3}$$

W_H is the energy needed to collisionally ionize hydrogen. The values for other elements are scaled up considering the geometrical factor $r_i = \sigma_i^{coll} / \sigma_H^{coll}$. W has been calculated for He and H_2 as well, these cases will be treated separately further on. The X-ray rate of energy deposition is defined as:

$$H_x = \int \sigma_{tot} F e^{-\tau_X} dE \tag{3.4}$$

Where σ_{tot} is given by:

$$\sigma_{tot} = \sum_{j=1}^{41} \sigma_j n_j / n_{tot} \tag{3.5}$$

The rate implicitly depends on n_{el}. This must be taken into account when the Jacobian matrix is filled:

$$\frac{dF_i}{dn_k} = \frac{\partial F_i}{\partial n_k} + \frac{\partial F_i}{\partial n_{el}}\frac{\partial n_{el}}{\partial n_k} \tag{3.6}$$

Again we consider only the contribution of the secondary ionization to the statistical equilibrium of the species i. F_i is defined as:

$$F_i^{ides} = -R_{i\rightarrow j} n_i = -r_i \frac{H_x}{W_H n_H} n_{tot} n_i \tag{3.7}$$

Where the apex "ides" stands for "destruction of the species i due to secondary ionization". Deriving F_i^{ides} with respect to n_k and considering that $n_{el} = \Sigma_j n_j q_j$, where q_j is the charge of the Jth species, we obtain:

$$\frac{dF_i^{ides}}{dn_k} = -r_i n_{tot}\left[\frac{n_i}{W_H n_H}\frac{\partial H_x}{\partial n_k} - \frac{H_x n_i}{W_H^2 n_H}\frac{\partial W_H}{\partial n_k} - \frac{H_x n_i}{W_H n_H^2}\delta_{H,k} + \frac{H_x}{W_H n_H}\delta_{ik}\right] \tag{3.8}$$

Here we develop separately the partial derivative for all the involved terms:

$$\begin{aligned}\frac{\partial H_x}{\partial n_k} &= \frac{1}{n_{tot}}\frac{\partial}{\partial n_k}\int \Sigma_j n_j \sigma_j F e^{-\tau x}\, dE \\ &= \frac{1}{n_{tot}}\int \sigma_k F e^{-\tau x}\, dE \end{aligned} \tag{3.9}$$

$$\begin{aligned}\frac{\partial W_H}{\partial n_k} &= \frac{\partial}{\partial n_k}\left[W_{0,H}\left(1 + c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)\left(1 + c_2\frac{n_{H_2}}{n_H}\right)\right] \\ &= W_{0,H}\alpha c_1 \frac{n_{el}^{\alpha-1}}{n_{tot}^{\alpha}} q_k \left(1 + c_2\frac{n_{H_2}}{n_H}\right) \\ &+ W_{0,H}\left(1 + c_1\frac{n_{el}^{\alpha}}{n_{tot}^{\alpha}}\right)\frac{c_2}{n_H}\delta_{H_2,k} \\ &- W_{0,H}\left(1 + c_1\frac{n_{el}^{\alpha}}{n_{tot}^{\alpha}}\right) c_2\frac{n_{H_2}}{n_H^2}\delta_{H,k}\end{aligned}$$

Where $\frac{\partial n_{el}}{\partial n_k} = q_k$.

Substituting these results in equation (3.8) we obtain:

$$\begin{aligned}\frac{dF_i^{ides}}{dn_k} &= -r_i\frac{H_x}{W_H n_H} n_{tot}\delta_{ik} + \\ &- r_i\frac{H_x}{W_H^2 n_H^2}\frac{n_{tot} n_{H_2} n_i}{n_H} c_2 W_{0,H}\left(1 + c_1\frac{n_{el}^{\alpha}}{n_{tot}^{\alpha}}\right)\delta_{H,k} \\ &+ r_i\frac{H_x}{W_H^2 n_H^2} n_{tot}\, n_i\, c_2\, W_{0,H}\left(1 + c_1\frac{n_{el}^{\alpha}}{n_{tot}^{\alpha}}\right)\delta_{H_2,k} \\ &+ r_i\frac{H_x}{W_H^2}\frac{n_i}{n_H} W_{0,H}\,\alpha\, c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha-1} q_k\left(1 + c_2\frac{n_{H_2}}{n_H}\right)\end{aligned}$$

$$
\begin{aligned}
&+ \quad r_i \frac{H_x n_i}{W_H n_H^2} n_{tot} \delta_{H,k} \\
&- \quad r_i \frac{n_i}{W_H n_H} \int \sigma_k F e^{-\tau_X} dE
\end{aligned}
\tag{3.10}
$$

Interpretation

The previous equation is composed of 6 terms, which are described as follows:

1. This is the derivative of reaction rate. It is only non–zero for the species i itself.

2. The same as the previous point, only considering H_2 instead of H.

3. This term only appears if the density of hydrogen changes, since it explicitly contains the dependence of W_H on n_H.

4. This term only appears if $k = H$, but if $i = k = H$ this term compensates with the first and the sum is zero. This is due to the fact that F_i (3.7) does not depend explicitly (but only via W_H) on n_H when $i = H$.

5. Charge effect: this term contains the dependence of n_{el} on n_k. If species k is not charged this contribute is zero, since a change of density of a neutral species does not affect the electron density.

   If we increase the density of a positively charged species the electron density increases as well. This causes W_H to increase (eq. 3.3), and then the total rate to decrease. Increasing the number of electrons in the gas phase causes an increase in the mean energy that is needed to form an ion pair, since thermal electrons also interact with fast electrons. This results in a positive contribution to F_i.

   If the density of a negative species is increased the inverse effect takes place. It means that n_{el}, and then W_H, decrease. The total rate for the ionization of species i increases and the contribution to F_i is negative. Less electrons in the gas phase decreases Coulomb interaction in favor of collisional interactions with atoms and molecules, thus causing more secondary ionization.

6. If the species k contributes in building the cross section for X-ray absorption, then H_x changes as well.

3.1.2 Populating n_i, with $i \neq He, H_2$

The rate of collisional ionization for species j that leads to the formation of species i is given by:

$$
\zeta_{j \to i} = r_j \frac{H_x}{W_H n_H / n_{tot}} [s^{-1}] \tag{3.11}
$$

The analytical expression for the element ik of the Jacobian matrix is exactly the same as in the previous case, but with a sign inversion since we are now considering the formation process for the products. Taking into account the correct indexes we obtain:

$$
\begin{aligned}
\frac{dF_i^{ifor}}{dn_k} &= r_j \frac{H_x}{W_H n_H} n_{tot} \delta_{jk} + \\
&+ r_j \frac{H_x}{W_H^2 n_H^2} \frac{n_{tot} n_{H_2} n_j}{n_H} c_2 W_{0,H} \left(1 + c_1 \frac{n_{el}^\alpha}{n_{tot}^\alpha}\right) \delta_{H,k} \\
&- r_j \frac{H_x}{W_H^2 n_H^2} n_{tot}\, n_j\, c_2\, W_{0,H} \left(1 + c_1 \frac{n_{el}^\alpha}{n_{tot}^\alpha}\right) \delta_{H_2,k} \\
&- r_j \frac{H_x}{W_H^2} \frac{n_j}{n_H} W_{0,H}\, \alpha\, c_1 \left(\frac{n_{el}}{n_{tot}}\right)^{\alpha-1} q_k \left(1 + c_2 \frac{n_{H_2}}{n_H}\right) \\
&- r_j \frac{H_x n_j}{W_H n_H^2} n_{tot} \delta_{H,k} \\
&+ r_j \frac{n_j}{W_H n_H} \int \sigma_k F e^{-\tau x}\, dE
\end{aligned}
\qquad (3.12)
$$

Where the apex "ifor" stands for "formation of the species i via ionization of species j".

3.2 H_2

3.2.1 Depopulating n_{H_2}

The rate for H_2 collisional ionization is given by:

$$\zeta_{H_2}^{sec} = \frac{H_x}{W_{H_2} n_{H_2}} n_{tot} \qquad (3.13)$$

Where W_{H_2} is given by:

$$W_{H_2} = W_{0,H_2} \left(1 + c_1 \left(\frac{n_{el}}{n_{tot}}\right)^\alpha\right) \left(1 + c_2 \frac{n_H}{n_{H_2}}\right) \qquad (3.14)$$

Then $F_{H_2}^{des}$ for the depopulating case is:

$$F_{H_2}^{des} = -\zeta_{H_2}^{sec} n_{H_2} \qquad (3.15)$$

Substituting (3.13) in (3.15) we obtain:

$$F_{H_2}^{des} = -\frac{H_x}{W_{H_2}} n_{tot} \qquad (3.16)$$

Deriving $F_{H_2}^{des}$ with respect to n_k we get:

$$\frac{dF_{H_2}^{des}}{dn_k} = -n_{tot} \left[\frac{1}{W_{H_2}} \frac{\partial Hx}{\partial n_k} - \frac{H_x}{W_{H_2}^2} \frac{\partial W_{H_2}}{\partial n_k}\right] \qquad (3.17)$$

Here we compute the terms listed above:

$$
\begin{aligned}
\frac{\partial W_{H_2}}{\partial n_k} &= W_{0,H_2}\left(1+c_2\frac{n_H}{n_{H_2}}\right)\alpha c_1\frac{n_{el}^{\alpha-1}}{n_{tot}^{\alpha}}q_k \\
&+ W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)c_2\frac{1}{n_{H_2}}\delta_{H,k} \\
&- W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)c_2\frac{n_H}{n_{H_2}^2}\delta_{H_2,k}
\end{aligned} \tag{3.18}
$$

Using (3.9) we obtain:

$$
\begin{aligned}
\frac{dF_{H_2}^{des}}{dn_k} &= \frac{H_x}{W_{H_2}^2}\frac{n_{tot}}{n_{H_2}}c_2\,W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)\delta_{H,k} \\
&- \frac{H_x}{W_{H_2}^2}\frac{n_{tot}n_H}{n_{H_2}^2}c_2\,W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)\delta_{H_2,k} \\
&+ \frac{H_x}{W_{H_2}^2}W_{0,H_2}\alpha c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha-1}q_k\left(1+c_2\frac{n_H}{n_{H_2}}\right) \\
&- \frac{1}{W_{H_2}}\int\sigma_k(E)F(E,r)dE
\end{aligned}
$$

3.2.2 Populating H_2

It can be easily shown that:

$$
F_{H_2}^{form} = -F_{H_2}^{des} \tag{3.19}
$$

Then:

$$
\begin{aligned}
\frac{dF_{H_2}^{form}}{dn_k} &= -\frac{H_x}{W_{H_2}^2}\frac{n_{tot}}{n_{H_2}}c_2\,W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)\delta_{H,k} \\
&+ \frac{H_x}{W_{H_2}^2}\frac{n_{tot}n_H}{n_{H_2}^2}c_2\,W_{0,H_2}\left(1+c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha}\right)\delta_{H_2,k} \\
&- \frac{H_x}{W_{H_2}^2}W_{0,H_2}\alpha c_1\left(\frac{n_{el}}{n_{tot}}\right)^{\alpha-1}q_k\left(1+c_2\frac{n_H}{n_{H_2}}\right) \\
&+ \frac{1}{W_{H_2}}\int\sigma_k(E)F(E,r)dE
\end{aligned}
$$

3.3 He

3.3.1 Depopulating He

The only reaction involved is:

$$
He + e^- \rightarrow He^+ + 2e^- \tag{3.20}
$$

The rate is:

$$\zeta_{He}^{sec} = \frac{H_x}{W_{He} n_{He}} n_{tot} \tag{3.21}$$

Then:

$$F_{He}^{des} = -\frac{H_x}{W_{He}} n_{tot} \tag{3.22}$$

W_{He} is given by:

$$W_{He} = W_{0,He} \left(1 + c_1 \left(\frac{n_{el}}{n_{tot}} \right)^{\alpha} \right) \tag{3.23}$$

The Jacobian term can be written as:

$$\frac{dF_{He}^{des}}{dn_k} = -n_{tot} \left[\frac{1}{W_{He}} \frac{\partial H_x}{\partial n_k} - \frac{H_x}{W_{He}^2} \frac{\partial W_{He}}{\partial n_k} \right] \tag{3.24}$$

Where:

$$\frac{\partial W_{He}}{\partial n_k} \quad = \quad W_{0,He}\, \alpha\, c_1 \frac{n_{el}^{\alpha-1}}{n_{tot}^{\alpha}} q_k \tag{3.25}$$

Using again (3.9) we obtain:

$$\begin{aligned} \frac{dF_{He}^{des}}{dn_k} &= \frac{H_x}{W_{He}^2} W_{0,He}\, \alpha\, c_1 \left(\frac{n_{el}}{n_{tot}} \right)^{\alpha-1} q_k \\ &- \frac{1}{W_{He}} \int \sigma_k(E) F(E,r) dE \end{aligned}$$

3.3.2 Populating He

Given that:

$$F_{He}^{form} = -F_{He}^{des} \tag{3.26}$$

We obtain:

$$\begin{aligned} \frac{dF_{He}^{form}}{dn_k} &= -\frac{H_x}{W_{He}^2} W_{0,He}\, \alpha\, c_1 \left(\frac{n_{el}}{n_{tot}} \right)^{\alpha-1} q_k \\ &+ \frac{1}{W_{He}} \int \sigma_k(E) F(E,r) dE \end{aligned}$$

Appendix

Dimensions:

$$
\begin{aligned}
\sigma &= [cm^2] \\
F &= [erg\, s^{-1} cm^{-2} erg^{-1}] \\
N_H &= [cm^{-2}] \\
H_x &= [ergs^{-1} H^{-1}] \\
F_i &= [cm^{-3} s^{-1}] \\
W_H &= [erg] \\
n_i &= [cm^{-3}] \\
W_{0,H} &= [erg]
\end{aligned}
$$

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