Chapter 12

ComChem model

This model has been developed mainly by W. Huebner and D. Boice over more than two decades, and there are a number of publications documenting this development, e.g. Giguere and Huebner [1978], Boice *et al.* [1986, 1998], Huebner *et al.* [1987], Schmidt *et al.* [1988]. The model is a multifluid, hydrodynamic model for the gas flow in the coma of a comet. Like the Haser model the ComChem model assumes isotropic radial outgassing and expansion in the coma. Using these assumption a 1-D neutral coma is modeled with a detailed treatment of the photo and gas-phase chemistry. A special focus was placed on the self-consistent description of the dynamic and chemistry in the coma. Gas dynamics and chemical reactions are coupled processes. Therefore, they have to be modeled together. The model allows a study of the changes with heliocentric distance of features within a cometary coma, e.g., spatial distributions of gas-phase species and the velocity and temperature profiles. Dust entrainment is not considered in this work, but would be part of a full modeling.

The following chapters will give a brief description of the dynamics and chemistry as used in the ComChem model. For full details see for example Huebner *et al.* [1987] and Schmidt *et al.* [1988].

12.1 Dynamics

The dynamics in the ComChem model are based on the assumption of a collision-dominated inner coma. In this case a fluid composed of four components can be assumed: fast atomic hydrogen, fast molecular hydrogen, electrons and the bulk fluid consisting of the remaining species and the thermalized fast and molecular hydrogen. This allows to solve the fluid dynamic equations for the macroscopic mass, momentum and energy of the bulk motion of an average molecule. The electrons and the fast atomic and molecular hydrogen have to be treated separately.

12.1.1 Bulk gas, fast and molecular hydrogen

The radial equations of fluid dynamics for the bulk fluid are

$$\dot{\rho} = \frac{1}{R^2}\frac{d}{dR}(R^2\rho u) \tag{12.1}$$

$$\dot{q} = \frac{1}{R^2}\frac{d}{dR}(R^2\rho u^2) + \frac{dp}{dR} \tag{12.2}$$

$$\dot{E} = \frac{1}{R^2}\frac{d}{dR}R^2[\rho\frac{u^3}{2} + (\frac{\bar{\gamma}}{\bar{\gamma}-1}pu)] \tag{12.3}$$

R   nucleocentric distance
u velocity
ρ density
p   pressure (as sum of the partial pressures of the chemical species)
q   momentum
E   Energy
$\bar{\gamma}$ adiabatic coefficient $(\sum\limits_{i=1}^{\text{species}} N_i\gamma_i / \sum\limits_{i=1}^{\text{species}} N_i)$

These equations are solved using the Lagrangian method as an initial value problem. The inhomogeneous terms for the fluid dynamics equations are the sources and sinks for mass, momentum and energy, each quantity per unit volume and time. The solution of the energy balance equation at the nucleus surface yields the initial conditions of the coma gas. Schmidt *et al.* [1988] has calculated the energy balance equation for a hemispherically illuminated nucleus:

$$\left(\frac{F_0}{r_h^2}\right)\left(\frac{\pi R_0^2}{2\pi R_0^2}\right)(1-\bar{A}) = \bar{\epsilon}\sigma_0 T_0^4 + \frac{Z_0\bar{L}}{\aleph} \tag{12.4}$$

F_0 solar flux at 1 AU
r_h heliocentric distance
R_0 radius of the nucleus
$\bar{A}$ mean visual albedo
$\bar{\epsilon}$ mean infrared emissivity
σ_0 Stefan-Boltzmann constant
T_0 surface temperature
Z_0 molecular production per unit surface
$\bar{L}$ mean latent heat of sublimation per mole $(\sum\limits_{i=1}^{\text{species}} N_i L_i / \sum\limits_{i=1}^{\text{species}} N_i))$
$\aleph$ Avogadro's number

While Schmidt *et al.* [1988] has calculated Z_0 using the Clausius-Clapeyron equation assuming an ideal gas, for this work Z_0 was used as an input parameter (see section 14).

For the fast and the molecular hydrogen species the inhomogeneous terms of equations (12.1-12.3) have to be obtained by solving a transport equation knowing the production rates for all species (including fast and molecular hydrogen) from the chemistry. The principles are discussed in Schmidt *et al.* [1988] and in greater detail in Huebner and Keady [1984] for the contribution of the fast hydrogen species. The numerical calculations are performed in a shell which expands with the bulk gas from the surface into the coma (see section 12.4). Here only the results are given for a shell at the nucleocentric distance R

$$\dot{\rho}(R) \; = \; -\frac{1}{R^2} \sum_{f=H}^{H_2} m_f \left(\frac{v_f}{v_f + u} \right) \frac{d}{dR} \left[R^2 j_f(R) \right] \tag{12.5}$$

$$\dot{q}(R) \; = \; -\frac{1}{R^2} \sum_{f=H}^{H_2} |m_f v_f \left(\frac{v_f}{v_f + u} \right) \frac{d}{dR} \left[R^2 j_f(R) \right] \tag{12.6}$$

$$\dot{E}(R) \; = \; \sum_{f=H}^{H_2} E_f \left\{ P_f - \frac{1}{R^2} \frac{d}{dR} \left[R^2 j_f(R) \right] \right\} \left(\frac{v_f}{v_f + u} \right) \tag{12.7}$$

$$+ E' \left\{ P - \frac{1}{R^2} \frac{d}{dR} \left[R^2 j'(R) \right] \right\} - \epsilon_{rad} \tag{12.8}$$

E_f, E'	excess energy imparted to fast hydrogens and to all other products
P_f, P	production rates of fast hydrogen and all other products
$j_f(R), j'(R)$	first-flight current density for fast hydrogen and all other species as defined in Huebner and Keady [1984]
v_f, u	speed of the fast hydrogen and of the bulk fluid
ϵ_{rad}	Radiative cooling factor (see equation 12.9)

There are several ways to cool the gas, for example endothermic reactions and radiation from collisionally excited molecular species. The major contributor to radiative cooling is water. Shimizu [1976a] published a semi-empirical equation for the cooling factor ϵ_{rad}

$$\epsilon_{rad} = \frac{8.5 \cdot 10^{-19} T^2 N^2}{N + 2.7 \cdot 10^7 T} \; [\text{erg cm}^{-3} \; s^{-1}] \tag{12.9}$$

In this equation N is the density of water and T the temperature of the bulk fluid. While close to the nucleus (within about 100 km for a Halley-type comet at 1 AU) the bulk gas is in local thermodynamical equilibrium (LTE), this is clearly not the fact at larger nucleocentric distances, where the density of the bulk gas is too low. This behavior is reflected by equation (12.9) which reduces to the value for the LTE case ($\approx 8.5 \cdot 10^{-19} N T^2$) close to the nucleus and approximates the value for the non-LTE case ($\approx 3.1 \cdot 10^{-26} N^2 T$) in the outer coma. The products of exothermic chemical reactions carry excess energy. This can be another source of energy if the products are thermalized collisionally. While slow particles are thermalized in the same shell, fast products may leave the shell and are thermalized in another shell. Molecules with a molecular weight close to the mean molecular weight of the bulk

fluid are almost thermalized in a single step. Whereas light particles, like fast hydrogen, can require 9 to 10 collisions before they are thermalized. In the photodissociation of water, hydrogen receives almost all excess energy. But following the above discussion, the hydrogen carries the energy out, instead of sharing it with the bulk fluid. This mean, while the photodissociation of water is an effective process to heat the coma globally, it has a small effect locally. Most of the energy is dissipate further out in the coma.

12.1.2   Electron gas

The requirement of charge neutrality simplifies the mass equation to

$$N_e = \sum_{i}^{ions} N_i \tag{12.10}$$

The momentum equation simplifies to

$$u_e = u \tag{12.11}$$

as charge separation is not allowed within a radial shell of the model. The charge balance is maintained by a radial electric field.

The equation for the electron energy conservation is given by

$$\frac{\partial}{\partial t}\left[\rho_e\left(\frac{u^2}{2} + \epsilon_e\right)\right] + \frac{1}{R^2}\frac{d}{dR}\left[R^2\rho_e u(h_e + \frac{1}{2}u^2) - R^2\kappa_e\frac{dT_e}{dR}\right]$$

$$= Q_e - Q_{en} - Q_{in} - Q_{eH} - Q_{eH^2} - m_e S_e\left[\epsilon_e(T) + \tfrac{1}{2}u^2\right] \tag{12.12}$$

$$
\begin{array}{ll}
h_e = \frac{5}{2}kT/m_e & \text{electron specific enthalpy} \\
\epsilon_e = \frac{3}{2}kT/m_e & \text{specific internal energy} \\
\kappa_e & \text{electron thermal conductivity} \\
S_e & \text{recombination rate} \\
\rho_e & \text{electron density} \\
u & \text{electron velocity} \\
R & \text{nucleocentric distance} \\
T_e & \text{electron temperature}
\end{array}
$$

The Q terms are the sources and sinks described in detail below.

The first term Q_e is the energy density source term for exothermic gas-phase chemistry and photo processes (for example photoionization)

$$Q_e = \sum_{j=1}^{q} |v_{ej}| P_j \epsilon_j \tag{12.13}$$

$$P_j \quad \text{electron production rate}$$
$$\epsilon_j \quad \text{average excess energy of the electrons produced}$$

The energy density transfer Q_{en} due to elastic collisions between the electrons and the bulk fluid can be described as

$$Q_{en} = 3\frac{m_e}{m_n}k(T_e - T)N_e N_n \sigma_{en}\left(\sqrt{\frac{8kT_e}{\pi m_e}}\right) \tag{12.14}$$

$$\begin{aligned}
m_e, m_n &\quad \text{mass of electrons and average mass of bulk gas molecules}\\
N_e, N_n &\quad \text{density of the electrons and the bulk gas}\\
\sigma_{en} &\quad \text{collision cross section for elastic collisions}
\end{aligned}$$

With $\sigma_{en} \approx 2 \cdot 10^{-15} cm^{-2}$ based on work by Shimizu [1976b].

Finally, the most important term Q_{in} accounts for energy density transfer by inelastic collision between electrons and water. Due to the fact that water is a polar molecule while CO is homopolar, the collision cross section for water is more than 4 magnitudes larger than the corresponding cross section for CO [Ashihara, 1975]. Even at 4.74 AU heliocentric distance (the largest distance studied in this work) the production rate of CO however is only by a factor of 30 larger than the water production rate.

The term for Q_{in} can be divided into two parts. The excitation of rotational transitions was studied by Ashihara [1975]. In this work the following approximation is given

$$Q_{in} \approx 1.9 \cdot 10^{-20}\left(\frac{T_e - T}{T_e^{\frac{3}{2}}}\right) \cdot \left[\ln\left(0.58\frac{T_e^2}{T} + 0.79\right)\right]N_e N_n \tag{12.15}$$

The vibrational-electronic transition was studied by Marconi and Mendis [1983].

$$Q_{in} \approx 1.1 \cdot 10^{-20}\sqrt{kT_e} \cdot N_e N_n \exp(-3.597 + 1.305\chi + 0.5917\chi^2 + 0.1213\chi^3 - 0.0359\chi^4) \tag{12.16}$$

where $\chi = \ln(kT_e)$ with kT_e given in electron volts.

This is an approximation from the integration of an empirical loss curve given by Olivera *et al.* [1972] for the energy range from $\sim$ 0.1-100 eV.

The terms Q_{eH} and Q_{eH_2} describe the energy density transfer by elastic collisions with fast atomic and molecular hydrogen. Since the probability of these collisions is negligible, this terms are not considered further.

The cooling of electrons by inelastic collisions exciting the rotational levels of water is sufficiently effective to maintain $T \approx T_e$ close to the nucleus. At larger nucleocentric distances the electrons thermally decouple from the coma gas and their temperature, T_e, rises rapidly (see figure 12.1). This occurs at about 1000 km from the nucleus and is not very sensitive to chemical composition or heliocentric distance r_h for heliocentric distances smaller than 3 AU. This has been shown by Huebner *et al.* [1987] and using a different approach by Marconi and
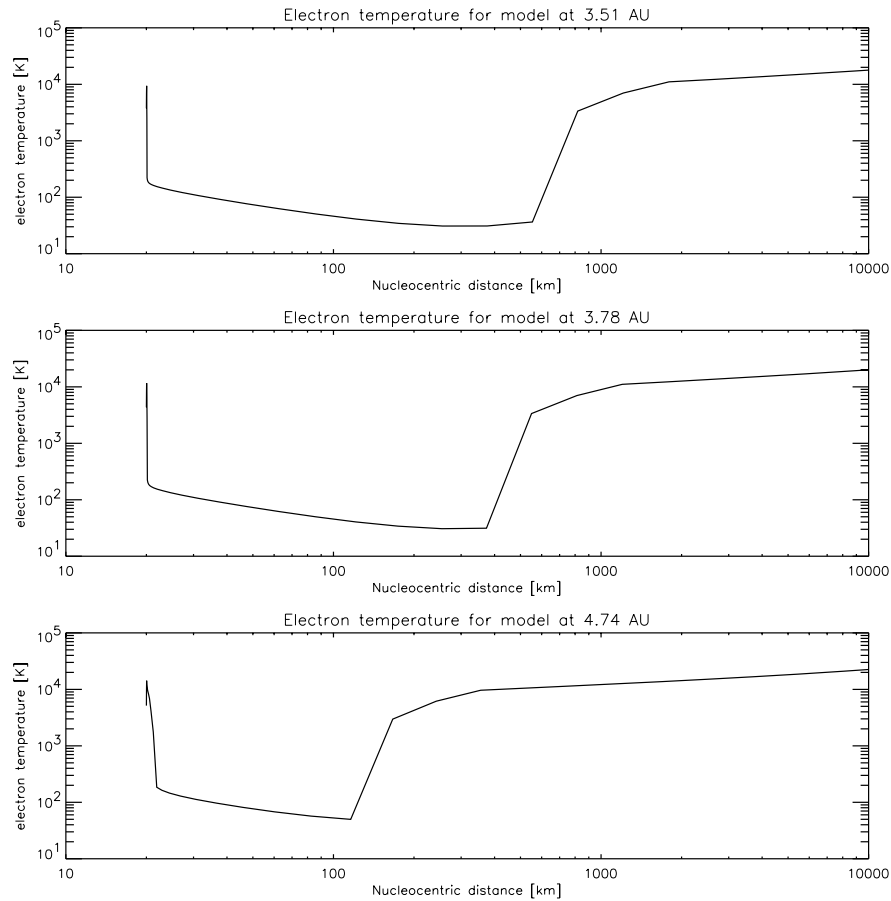
Figure 12.1: Electron temperature T_e aas calculated by the ComChem model for 3.51 AU, 3.78 AU and 4.74 AU

Mendis [1983]. Boice *et al.* [1986] and Zwickl *et al.* [1986] showed that the modeled electron temperature was in good agreement with the measurements for comet Giacobini-Zinner.

For heliocentric distances larger than 3 AU the water sublimation rate decreases rapidly. As shown above water is the main molecule cooling the electrons. A decrease in the density of water molecules in the coma should lead to less efficient cooling of the electrons. Figure 12.1 is a display of the electron temperature versus nucleocentric distance, calculated with the ComChem model for three heliocentric distances. The plots show exactly the expected effect. With increasing heliocentric distance the nucleocentric distance at which the electron temperature starts to rise moves closer to the nucleus, because cooling by collisions with water molecules becomes less efficient. For large nucleocentric distances however the profile of the electron temperature remains virtually unaffected.

12.2 Chemistry

The chemistry of the coma is modeled by a large network containing all collisional and photolytic gas-phase reactions. Table 4.2 on page 40 gives an overview of the reaction categories included in the model.

As has been discussed above already, the dynamic time scale of expansion can be much faster than the time scale of some of the reactions. Therefore time-dependent reactions have to be considered. For each species a particle conservation equation can be written in the form

$$\frac{dN_i}{dt} = \sum_{j=1}^{q} v_{ij} k_j \prod_{l=1}^{s} N_l^{m_{ij}} \quad i = 1, \ldots, s \tag{12.17}$$

s	number of species
N_i	number density of species i
q	number of the chemical reaction
v_{ij}	stoichiometric coefficient of species i in reaction j
m_{ij}	reaction order
k_j	rate coefficient

The stoichiometric coefficient v_{ij} is positive for products and negative for reactants. The reaction order m_{ij} is equivalent to the absolute value of v_{ij} when it is negative, zero otherwise. The rate coefficients k_j for collision processes are given in the Arrhenius form (see equation (4.4))

$$k_j = A_j \left(\frac{T}{300}\right)^B_j \exp{-\frac{C_j}{T}} \tag{12.18}$$

T	gas or electron temperature, depending on the reaction
A_j, B_j, C_j	Arrhenius coefficients for reaction j

For reactions with known cross sections, the rate coefficients for photolytic reactions are obtained directly by the following relation

$$k_j = r_h^{-2} \cdot \int_0^{\lambda_0} \sigma_j(\lambda) F_\odot(\lambda) d\lambda \tag{12.19}$$

r_h	heliocentric distance [AU]
$\sigma_j(\lambda)$	cross section for dissociation or ionization
$F_\odot(\lambda)$	solar flux
λ_0	threshold wavelength for dissociation or ionization

For the numerical integration of equation (12.19) about 120 wavelength bins in the UV spectrum have been used. For details on the numerical integration and the solar flux used see [Huebner *et al.*, 1992]. For reactions where the cross sections are unknown rate coefficients are entered directly. These rate coefficients have been either obtained from the literature or are determined in this work. For details see section 14.2.

Different reactions dominate at different heliocentric and nucleocentric distances. The importance of a reactions can also be altered by the initial composition of the nucleus. Several processes can lead to the same product or can destroy the same reactant. These competing processes can change the relative importance of a species while at the same time minimizing the effects from uncertainties in a reaction rate for a single process on the whole network (see discussions in chapter 19). The network used for this work contains over 1000 reactions and 21 species in the initial composition.

12.3   Sublimation

The ComChem model as used for this work does not contain a sublimation model. The values for the surface productionrate Z_0 and the surface temperature T_0 are entered as input parameter (see section 14). The initial composition is the composition of the gas coma in a shell only a few centimeter above the nucleus surface. This might be different from the composition of the nucleus itself. The reason for not using a nucleus composition is simply that the composition of the ices in the nucleus is unknown. All existing measurements describe production rates of gaseous species in the coma. Strictly, without a sublimation model this can not be converted into abundance ratios for cometary ices. Including a sublimation model into ComChem is one of the future tasks for a further development of the model.

12.4   The numerical approach

The model calculations are based on the processes occurring in a thin shell of coma gas as it expands and moves outward. Therefore, chemical reactions take place in a continually diluting gas exposed to solar ultraviolet radiation flux. The practical details are illustrated in figure 12.2. The time step for the chemical reaction is much smaller than the fluid dynamic time step at which the density is calculated. As an example for a model run at 3.78AU close to the nucleus chemical time steps are of the order of 0.01sec. This translates to a spatial resolution of approximately 2m. Fluid dynamic time steps are approximately logarithmically spaced. Close to the nucleus they are about 0.1sec, translating to about 20m spatial scale. Only at large distances from the nucleus does the chemical time step approach the fluid dynamic time step, with an approximate time step of $5 \cdot 10^5$sec. This translates to a spatial scale of about $1 \cdot 10^5$km.

The problem is to solve s rate equations in the closed chemical network. Conservation of charge and mass for each element for the s unknown number densities N_i of the species have to be guaranteed. This means the system is overdetermined and therefore some of the equations are redundant. For the practical approach, the complete set of rate equations is
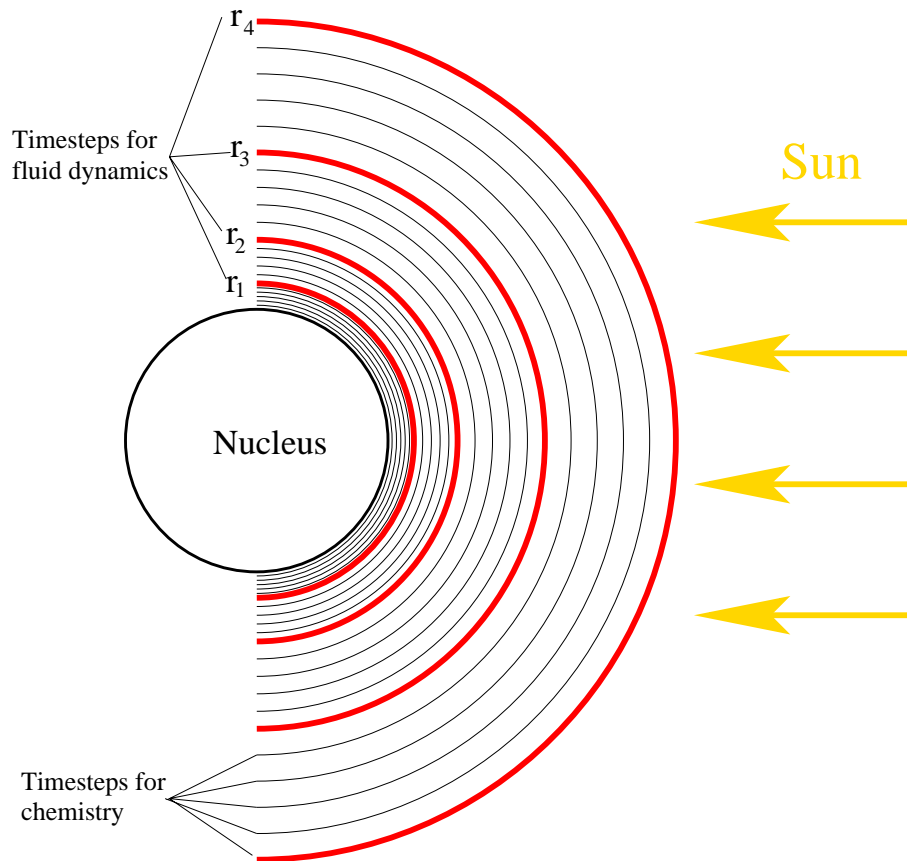
Figure 12.2: Combination of physics and chemistry: While the time steps for the chemistry are small, the fluid dynamics are recalculated in larger steps (r_1, r_2, ..., logarithmically spaced)

solved and the conversation equations are used to check the accuracy of the solution. The system is solved using the Gear method [Gear, 1971] for stiff differential equations, where time constants can vary by many orders of magnitudes. The method uses variable time steps to preserve the accuracy during the integration and checks this using several error control techniques as described in Gear [1971]. For a detailed description of the numerical approach see Giguere and Huebner [1978], Boice *et al.* [1986, 1998], Huebner *et al.* [1987], Schmidt *et al.* [1988].

As stated already, the ComChem model is a one dimensional model. The modeling follows the expansion of a shell through the coma, but only radial velocity components are taken into account. Only under the assumption of isotropic radial outgassing and expansion the one dimensional results can be used to modeled the whole coma. Based on this it is straightforward to convert from the modeled number densities $n(\rho)$ to column densities $N(\rho^*)$ (where ρ^* is the projected nucleocentric distance on the sky plane). The same numerical line-of-sight (LOS) integration routine is used as for the Haser model. For details on the LOS integration routine see section 10.2. The tests for numerical accuracy described in that section have

been repeated for this modeling and yield the same results for the number of integration steps and the radial extension of the coma. In fact the safety margins described in section 10.2 are partly based on the test performed for the ComChem model.