

An Introduction to Astrochemical Modelling

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Introduction

Astrochemistry is a multidisciplinary area of scientific research involving astronomers, physicists and chemists working on observations, numerical and computational models and laboratory experiments.

The main aim of astrochemistry is to take all the information that we can derive from observations of chemical species in astrophysical environments and use models and laboratory experiments to try to better understand the underlying physical conditions in and history of those environments and to deduce the types of chemical processes which are happening.

In this short introduction to astrochemical modelling we intend to demonstrate how simple astrochemical models are constructed and run. We will show you that the chemistry of astrophysical environments is coupled to the physical conditions present in that environment and how we use information from observational data to try to constrain both the physics and chemistry, in essence, we use our models as ‘virtual laboratories’. The conditions in the interstellar medium (ISM) are extreme compared with those on Earth. It is only recently that laboratories have been able to reach the very low temperatures observed in the ISM (~ 10 K) but the best vacuums we can create have densities still orders of magnitudes larger than the lowest of those observed in the ISM.

In this document we will walk through a simple model which computes the chemical evolution of a dark cloud core. These are cold (~ 10 K), relatively dense ($\sim 10^4$ cm $^{-3}$) condensations which reside in large molecular cloud complexes in the interstellar medium and which are thought to be the sites of low-mass star formation. In addition, we will explain the differences and useful similarities between dark clouds and circumstellar envelopes when calculating chemical models.

The chemical network we will use is the well-known UMIST Database for Astrochemistry (UDfA) which has been developed over the past 20 years through the continual collation of reaction rate coefficients for chemical reactions thought to be important in the interstellar medium [1]. Its web site can be found at www.udfa.net. We will be using a slightly updated version, henceforth referred to as ‘Rate13’, in which a small number of reaction rate coefficients have been updated from the most recent, official, release of UDfA, known as ‘Rate12’. In these models, we shall ignore, except in the formation of H₂, the role that grain surfaces might play in the chemistry. ‘Rate13’ contains some 6173 gas-phase reactions among 467 species with over one third of the rate coefficients experimentally determined. The one important reaction that is not included in the rate file is the grain surface formation rate of H₂ which is ‘hard-wired’ into the main programme code and the ODE file.

One of the current problems in astrochemistry is how we construct ensemble models incorporating both the gas-phase chemistry and surface chemistry as accurately as possible. The simplest approach is to consider surface chemistry in the same manner as gas-phase reactions, that is, to follow the abundances of surface species through the use of rate equations, but this approach is not always valid and as a result more complex, and computationally expensive, methods involving a stochastic approach are necessary. Such methods are not considered here but have been discussed extensively in the literature.

Astrochemical Modelling

The majority of the reactions in Rate13 are two-body reactions with the reactants being atoms, molecules, ions (positive and negative) or electrons.

Consider a simple example reaction such as



The rate of increase in abundance per unit volume of species C ($n(C)$) with time is calculated using

$$\frac{dn(C)}{dt} = k n(A)n(B) \quad \text{cm}^{-3} \text{s}^{-1}. \quad (2)$$

where the value k is called the rate coefficient of the reaction and for a two-body reaction such as this one is parameterised by the expression

$$k = \alpha (T/300)^\beta \exp(-\gamma/T) \quad \text{cm}^3 \text{s}^{-1} \quad (3)$$

where T is the gas temperature. This is the Arrhenius form for the rate coefficient with α known as the pre-exponential factor, β dictating the temperature dependence of the rate coefficient and γ the activation energy or energy barrier of the reaction in units of degrees K.

Two-body reactions fall into several sub-classes: neutral-neutral, ion-neutral, charge exchange, ion-ion neutralisation, dissociative recombination, radiative recombination, associative electron detachment and radiative association.

In addition to two-body reactions, Rate13 contains two direct photo-processes: photo-dissociation and photoionisation. The rate for these processes is given by

$$k = \alpha \exp(-\gamma A_V) \quad \text{s}^{-1} \quad (4)$$

where α is the photo-rate in the unshielded interstellar ultra-violet radiation field (ISRF), i.e., with $A_V = 0$, with A_V the extinction by interstellar dust at visible wavelengths and γ is a parameter to take into account the increased extinction at ultra-violet wavelengths compared to the visible.

There are also two types of cosmic-ray reactions, direct cosmic-ray ionisation with a rate given by

$$k = \alpha \quad \text{s}^{-1} \quad (5)$$

and cosmic-ray induced photo-processes with a rate

$$k = \alpha (T/300)^\beta \gamma / (1 - \omega) \quad \text{s}^{-1} \quad (6)$$

where T is the gas temperature, α is the direct cosmic-ray ionisation rate, γ is the probability per cosmic-ray ionisation that the photo-reaction takes place and ω is the dust grain albedo (which measures the efficiency by which particles scatter radiation) in the far ultra-violet.

To determine the rate of change of the abundance of each species with time, we gather together all the reactions which either form or destroy each species and set up an equation for each species, i , of the form

$$\frac{dn_i}{dt} = \sum_{j,k} k_{jk} n_j n_k + \sum_l k_l n_l - n_i \left[\sum_m k_{im} n_m + \sum_n k_n \right] \quad \text{cm}^{-3} \text{s}^{-1} \quad (7)$$

The first two terms are the summation over all two-body reactions leading the formation of species i and the summation over all photo-processes and/or cosmic-ray processes leading to the formation of species i . The final two terms are the equivalent summations over processes which lead to the destruction of species i . In this way we construct an ordinary different equation (ODE) of this form for the rate of change in abundance of each species with time.

If we also consider the freeze-out onto and thermal desorption of species from dust grains, our ODE for species i needs two further terms

$$\frac{dn_i}{dt} = \sum_{j,k} k_{jk} n_j n_k + \sum_l k_l n_l - n_i \left[\sum_m k_{im} n_m + \sum_n k_n \right] + k_{des} n_{i,s} - k_{acc} n_i \quad \text{cm}^{-3} \text{s}^{-1} \quad (8)$$

where k_{des} and k_{acc} are the rates for thermal desorption and freeze-out (accretion), respectively. The value $n_{i,s}$ is the abundance of species i which is present on the grain surface. We also require ODEs for all grain surface species

$$\frac{dn_{i,s}}{dt} = k_{acc} n_i - k_{des} n_{i,s} \quad \text{cm}^{-3} \text{s}^{-1} \quad (9)$$

where we have made the implicit assumption that there are no surface processes that form or destroy species i .

The accretion rate of each species onto dust grains is given by

$$k_{acc} = \sigma_d \langle v_i \rangle n_d \quad \text{s}^{-1} \quad (10)$$

where $\langle v_i \rangle$ is the thermal velocity of species i , n_d is the number density of dust grains and σ_d is the geometrical cross-section of dust grains.

The thermal desorption rate of species i is given by

$$k_{des} = \nu_0(i) \exp(-E_{des}(i)/kT_d) \quad \text{s}^{-1} \quad (11)$$

where $\nu_0(i)$ is the characteristic vibration frequency for each adsorbed species, $E_{des}(i)$ is the binding energy of species i to the dust grain and T_d is the grain temperature.

The characteristic frequency is represented by a harmonic oscillator relation

$$\nu_0(i) = \sqrt{\frac{2N_s E_{des}(i)}{\pi^2 m_i}} \quad \text{s}^{-1} \quad (12)$$

where N_s is the number density of surface sites per dust grain and m_i is the mass of species i . This frequency is typically in the range $10^{12} - 10^{13} \text{ s}^{-1}$.

The particular models that we shall consider ignore desorption while accretion can be included or excluded in the dark cloud model through setting a flag in the main program code.

We employ numerical methods to iteratively solve our large set of 466 stiff ODEs (466 because the ODE for H_2 is replaced by a conservation equation), given a set of physical parameters and a set of initial conditions.

In this case of dark clouds, initial conditions are set by giving a set of elemental abundances while molecular abundances are used in the circumstellar calculation.

The complexity of chemical models varies from simple static homogenous models to fully 3-D dynamical models which evolve in both space and time. The computation time required is strongly dependent on the complexity of the model being run. For a simple model which has a set of constant physical conditions and evolves only chemical abundances in time, the computation of the abundances of 467 species involved in about 6200 reactions takes about 30 seconds to run for a model time of 10^8 years, with computational time scaling more steeply with the number of species than the number of reactions. More complex models take much much longer, on the order of days to weeks. Often, sacrifices in chemical complexity are made to reduce computation time and models are run with severely reduced networks. Here we are running a chemically complex network using two simplified physical models.

Circumstellar Chemistry

Chemistry also occurs in the expanding, circumstellar envelopes (CSEs) around late-type, Asymptotic Giant Branch (AGB) stars. These objects, which are too cool to generate stellar UV photons, lose mass to the interstellar medium through a wind that moves dust and molecules from just above the stellar photosphere. For the simple case of a steady spherically symmetric flow at constant mass-loss rate, the number density decreases as r^{-2} , and the extinction as r^{-1} . Thus, as these *parent* molecules flow out they eventually interact with the external, interstellar UV radiation and are broken down to form reactive radicals and ions. If densities are large enough, collisions among these reactive species can synthesise new species in the CSE. The final fate of these molecules is that they are degraded into atoms and atomic ions as they enter the general interstellar medium.

Although the divergence of the flow adds a term to the ODE describing the change of molecular abundances with time, the ODEs can be cast in the same form as those for dark interstellar clouds for a flow in which the expansion velocity of the envelope, v_e , and the mass-loss rate, \dot{M} , are constant in time. If we solve for the *fractional* abundance, $f(r)$, as a function of radius - rather than $n(t)$ as a function of time - the ODE can be written, in analogy to Eqn. (7), as:

$$\frac{df_i}{dr} = \frac{1}{v_e} \left[\sum_{j,k} k_{jk} f_j f_k n(r) + \sum_l k_{li} f_l - f_i \left[\sum_m k_{im} f_m n(r) + \sum_n k_n \right] \right] \quad \text{cm}^{-1} \quad (13)$$

where $f_i(r) = n_i(r)/n(r)$ and $n(r)$ is the hydrogen nucleon density, or equivalently the H_2 abundance, at radius r . The power of this approach is that essentially the same equation writer can be used for both interstellar clouds and CSEs - the CSE equations reduce to the interstellar case if we set $v_e = 1$, and $n(r) = 1$. For the CSE case, we solve for fractional abundances as a function of radius; for the interstellar case, we solve for number densities as a function of time.

There are, of course, a number of differences in running the CSE molecule compared to the dark cloud model. Once the choice of mass-loss rate and expansion velocity are set, which determine the density distribution, $n(r)$, one has to specify the temperature distribution, $T(r)$, often taken to be a power-law, $T(r) = T_i(r/r_i)^{-n}$, where T_i = the temperature at initial (inner) radius r_i and $n = 0.6 - 0.7$, typically. To these are added the initial, parent fractional molecular abundances, i.e. the abundances that reflect photospheric chemistry, dust formation and the pulsational shock waves that affect the chemistry in the inner envelope. The chemical model is calculated from an initial radius, r_i , usually where the effects of external photons begin to photodissociate the parent species - a useful rule of thumb is that the inner radius is chosen such that the radial visual extinction to infinity is around 10 mag.

Because the model assumes that the CSE is spherically symmetric, UV photons can reach a particular radial point from any direction and the code takes this into account when calculating the photo-rates at each point.

One other major difference between the CSE code and the dark cloud code is that because density, extinction and temperature vary as a function of radius, the rate coefficients must be calculated at every internal radial point during the integration, unlike the isothermal dark cloud model where the rate coefficients are calculated once only. In the CSE code, this is performed by a call from within the ODE subroutine to the subroutines that calculate the rate coefficients. In this case, the rate coefficients can be calculated tens of thousands of times per integration. For more information on modelling CSE chemistry see [2], [3] and [4].

In the following, we describe how these codes can be run through describing in some detail the case of a dark cloud chemical model, a so-called pseudo-time dependent, 'one-point' model in which physical conditions remain constant over time. File names refer to those in the download from the UDfA web site.

Dark Cloud Chemical Model

If you are not familiar with using the Unix operating system, spend some time reading through 'A Short Guide to Unix' to familiarise yourself with how the terminal and command line operate. Practise using all the commands listed as well as changing directories, creating new directories and files, moving and copying directories and files and viewing and editing the contents of files.

Use the command `ls` to list the contents of this directory. You will see a list of files. The files with the extension `.f` are FORTRAN programs. The files are compiled and linked together (using commands in the makefile) into one executable called `'model'` by running the make command.

The reactions from Rate13 are listed in the colon-separated file `'rate13.rates'` and the species in the file `'dc.specs'`. There are also two files with the extension `.pl` which are Perl scripts. You will also find a recent publication [1] which describes the format and content of the UDfA database in detail, as well as two pdf files - this document and 'A Short Guide to Unix'.

We will first have a look through the species file.

```
% emacs dc.specs &
```

Recall that the ampersand following the command opens the application in the background of the terminal allowing the command prompt to remain available for further commands.

This file has four aligned columns.

Column	Entry
1	Species number
2	Species name
3	Initial abundance
4	Species mass

Each species is referred to by its chemical formula e.g. carbon monoxide is CO and formaldehyde is H₂CO.

The third column contains the list of initial fractional abundances of each species, relative to the total number of H nuclei, and the fourth contains the mass of the species in atomic units (au).

We will next have a look at the rates file.

```
% emacs rate13.rates &
```

This file has a number of colon-separated items columns. In its simplest format, each line contains the following information:

Column	Entry
1	Reaction number
2	Reaction type
3	Reactant 1
4	Reactant 2
5	Product 1
6	Product 2
7	Product 3
8	Product 4
9	No. of T fields
10	α
11	β
12	γ
13	Minimum temperature
14	Maximum temperature
15	Source type
16	Accuracy
17	Reference

Note the strict format of the file and the fact that not all fields have entries. The following table lists the types (column 2) and number of reactions in UDfA.

Code	Reaction type	Count
AD	Associative Detachment	132
CD	Collisional Dissociation	14
CE	Charge Exchange	579
CP	Cosmic-Ray Proton (CRP)	11
CR	Cosmic-Ray Photon (CRPHOT)	249
DR	Dissociative Recombination	531
IN	Ion-Neutral	2589
MN	Mutual Neutralisation	981
NN	Neutral-Neutral	619
PH	Photoprocess	336
RA	Radiative Association	92
REA	Radiative Electron Attachment	24
RR	Radiative Recombination	16

Each row represents a chemical reaction with the reactants in fields 3-4 and the products in columns 5-8. In some cases, the behaviour of the rate coefficient has a complex dependence on temperature and more than one set of parameters are needed to describe this behaviour. Column 9 indicates the number of temperature fields and columns 10-17 are repeated the appropriate number of times. Our FORTRAN codes contain a subroutine that can read the correct set of parameters for any given temperature.

The entries in columns 10-12, α , β and γ , are values for computation of the reaction rate coefficient for each reaction. How this is computed depends on the type of reaction as described in the preceding section. Scrolling through the file you will see that photo-processes (type PH), direct cosmic-ray ionisation (type CP) and cosmic-ray induced photo-processes (type CR) are identified by having PHOTON, CRP and CRPHOT as the second reactant, respectively.

Finally, columns 12 and 13 contain the minimum and maximum temperatures, respectively, in which the rate coefficient, and the specific values of α , β and γ , applies. References to the source of the data, either papers or DOIs, are given for each reaction in column 17.

Take some time to scroll through the file and identify examples of all the reactions which are mentioned in the preceding section. Radiative processes (types RA, REA and RR) involve the emission of a photon and dissociative recombination (type DR) is the reaction between a cation (a positively charged ion) and an

electron that leads to fragmentation of the cation.

Finally we will have a look at the file containing the ordinary differential equations (ODEs) describing the rate of change of species abundance with time.

```
% emacs dcodes.f &
```

This file is different in that it is essentially a FORTRAN program. Don't worry too much about the preamble, instead scroll down to have a look at the format of each ODE. The rate of change of each species' abundance is represented by YDOT(*) with the rate coefficients given by K(*) and each species' current abundance by Y(*) with the '*' replaced by either the species number or reaction number as given in the species and rates files respectively.

The term HNR is included in every term describing a two-body reaction and is set to 1.0 in dark cloud/interstellar models. Despite its redundant nature here, it is included because the same form of ODE can be used to describe the flow in a uniformly expanding gas, such as the circumstellar envelope around late-type stars. In this case, Y(*) is defined to be the fractional abundance and HNR is defined as the number density at radial distance r .

You can also have a look at the program main source code which is located in the file 'rate13main.f'. Near the beginning of the file you will see where the input and output files are defined. Physical parameters for the cloud - density, temperature, visual extinction, etc - and for the grains are defined around lines 60-80.

The rate coefficients are calculated in a separate file called 'dcrates.f'. Open this and scroll through to find the region in the code where the reaction rate coefficients are calculated.

If you have not already done so, run the make command to compile and link the object files into one executable file 'model'. This may be slow the first time because the dcodes.f file is large. To run the model, at the command prompt type:

```
% ./model
```

The model will begin to run and as it executes it will write data, including its initial data, to the screen to show how it is progressing. The program will take less than a minute to run depending on the speed of the computer you are using. The program writes three files in the course of its execution. One is a more readable set of chemical reactions, called rates.txt - have a look to convince yourself that this statement is true! A second file, rate13steady.state, contains the initial conditions as well as the fractional abundances of all species at the last time step (10^8 years), by which time the models should have reached steady-state. This file is very useful for getting a feel as to whether the detailed output can be trusted. At steady-state, which should be reached in all dark cloud calculations in which freeze-out is ignored, $dn(i)/dt = 0$ and the abundances are given by the solution of algebraic rather than ordinary differential equations and some, such as H_2^+ and H_3^+ , can be checked by a simple 'back-of-the-envelope' calculation.

Now open the main output file, dc.out, and scroll through it.

The bulk of the file is a table which lists the fractional abundance (with respect to H_2 density) of each species as a function of time. The one exception is H_2 itself, for which its number density per cm^3 is listed. The reason for this is that the number density can show up instances where the calculation is incorrect, for example, a calculation in which conservation didn't hold could give a H_2 number density greater than the initial hydrogen abundance. This would be shown up in this output file whereas normalising everything to the H_2 density would have every fractional abundance of H_2 equal to one and one wouldn't pick up the non-conservation.

To create a graph displaying the abundances of selected species with time, we use the Perl script, 'dc.pl' and generate the graphical output using the Xmgrace software using the instructions as described in 'A Short Guide to Unix'.

Make sure you save your plot with some appropriate name.

Run the model again, except this time, switch on the freeze-out of molecules onto the dust grains by setting `IFREEZE = 1` in the main programme `rate13main.f`. Change the name of the output file to ensure that you don't write over it. Since you have edited one of the FORTRAN programmes you must run the `make` command again. This time you will notice that it compiles and links almost instantly because the other files have not been amended. Run the model by typing `% ./model`.

Again, generate a graph of the species listed above making sure to give it a different name and compare with the graph generated previously.

To open a graph already generated use:

```
% gv graph_name.ps
```

To see the effects of density on freeze-out, increase the density in the main program by an order of magnitude. What difference does this make to the abundances as a function of time? (You may need to reduce the time over which the chemical evolution is being calculated by changing the value of `TFINAL` in the main program).

Now go back to the original choice of density, $DN = 2e4$, and set `IFREEZE = 0`. Our 'standard model' uses oxygen-rich initial elemental abundances. The initial abundances adopted are listed in the file 'dc.specs'. Open up this file and scroll through the list of species to see which species are initialised - they are listed below as Set 1. You can see that several elements are listed in their ionic form.

We can vary these abundances to account for changes in the elemental composition of different astrophysical environments. Most environments can be classed as oxygen-rich ($O/C > 1$) or carbon-rich ($O/C < 1$). To vary the initial abundances, we edit the species file. As the abundances are read in from this file, the code does not need to be recompiled and the model is run as described previously - type `% ./model`.

Run the standard physical model without freeze-out using the sets of initial elemental abundances relative to total H nuclei listed in the table below. Remember to give each of your model results files a new name, preferably something sensible which will easily identify it. At this point you may wish to create new directories in which to save your sets of results and graphs.

Species	Set 1	Set 2	Set 3	Set 4
He	9.0×10^{-2}	9.0×10^{-2}	9.0×10^{-2}	9.0×10^{-2}
C ⁺	1.4×10^{-4}	1.4×10^{-4}	1.2×10^{-4}	1.4×10^{-4}
N	7.5×10^{-5}	7.5×10^{-5}	7.6×10^{-5}	7.5×10^{-5}
O	3.2×10^{-4}	1.0×10^{-4}	2.6×10^{-4}	3.2×10^{-4}
S ⁺	8.0×10^{-8}	8.0×10^{-8}	1.5×10^{-5}	2.0×10^{-7}
Si ⁺	8.0×10^{-9}	8.0×10^{-9}	1.7×10^{-6}	8.0×10^{-9}
Na ⁺	2.0×10^{-9}	2.0×10^{-9}	2.0×10^{-7}	2.0×10^{-9}
Mg ⁺	7.0×10^{-9}	7.0×10^{-9}	2.4×10^{-6}	7.0×10^{-9}
Fe ⁺	2.0×10^{-9}	2.0×10^{-9}	2.0×10^{-7}	2.0×10^{-9}
P ⁺	3.0×10^{-9}	3.0×10^{-9}	1.2×10^{-7}	3.0×10^{-9}
F	2.0×10^{-8}	2.0×10^{-8}	1.8×10^{-8}	2.0×10^{-8}
Cl ⁺	4.0×10^{-9}	4.0×10^{-9}	1.8×10^{-7}	4.0×10^{-9}

Abundance sets 1 and 2 vary our elemental C/O ratio. Abundance sets 3 and 4 vary metallicity which here we are defining as all elements which are not H or He. Abundance set 3 uses 'high-metal' abundances as observed towards the ζ Oph diffuse cloud [5]. Abundance set 4 is different from Set 1 only in that it has an increased abundance of sulfur [6]. For each set of model results think about which types of species are going to be affected by the difference in the initial elemental abundances. Produce graphs of species where you see a dramatic change in the abundance and/or evolutionary behaviour compared with our 'standard model', Set 1. As a hint, the change in C/O ratio will probably affect C and O bearing species and the change in metallicity will affect the abundance of charged species including the electron abundance. If you so wish you can run these models again switching on freeze out to see the effects.

So far we have used the physical conditions typical for a cold, dense molecular cloud, however, we can

use our model to probe a range of different environments, from the hot, diffuse interstellar medium to the warm, dense envelopes surrounding young stellar objects. We can use this simple model for any extended environment which has relatively constant physical conditions.

Model	Density	Temperature	Visual Extinction	Type of Source
1	10^5	5	15	Dense core
2	10^5	70	10	Orion extended ridge: enhanced S abundance
3	10^6	30	10	L1527: C-rich protostellar envelope
4	10^3	50	5	Diffuse cloud
5	10^2	100	2	Diffuse interstellar medium

Run each of the physical models listed choosing a set of initial elemental abundances from the table above. Produce graphs of species which trace the chemical nature of the model run e.g. atomic or molecular, ionisation fraction, photon-dominated, C-rich or O-rich, and so on. This will hopefully illustrate to you how astronomers chose different types of species to trace the physical conditions in different astrophysical environments.

Summary

Hopefully by now you will have gained some insight into astrochemical modelling of dark clouds and will be confident about investigating the CSE model at your own leisure. Of course, carrying out astrochemical models is not just about running models, it is more about developing an understanding of the basic chemical processes and the complex interactions that determine molecular abundances. Don't believe everything the computer tells you - check that total elemental abundances are conserved and that the abundances of species with very simple chemistries, for example H_2^+ and H_3^+ , agree with those calculated analytically.

My e-mail address is `tom.millar@qub.ac.uk` if you have any further questions concerning the model and/or running and modifying the code.

References

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