PRIMARY ASTROPHYSICAL DUST FORMATION: LABORATORY DESIDERATA

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Abstract – The theoretical treatment of primary cosmic dust formation suggests specific laboratory experiments concerning all aspects of the molecule–solid transition along the evolution from molecules via clusters up to macroscopic grains. Basing upon the theoretical description of chemistry and dust formation processes we discuss the specific laboratory desiderata on input data like reaction coefficients, Gibbs energies of formation and sticking efficiencies for atoms and molecules involved in the primary astrophysical dust formation.

1 INTRODUCTION

Cool stellar outflows are very effective laboratories for the production of complex chemical structures (like PAHs, soot particles, silicate grains, etc.), as it is well manifested by observations, especially by large IR-excesses attributed to emission of solid particles (dust) and pronounced absorption and emission features and bands, which are assigned to vibrational and rotational transitions in molecules and clusters.

The consistent theoretical modelling of such outflows requires the simultaneous treatment of on the one hand the hydrodynamical and thermodynamical evolution consistent with the solution of the radiative transfer and on the other hand the chemical evolution, cluster formation and growth. The dust formation process consisting of the nucleation of small stable molecular clusters from the gas phase and their subsequent growth to macroscopic solid particles is closely coupled. The description of both dust formation and chemistry depends strongly on the availability and accuracy of the input data. In this context, experimental desiderata are addressed, which could help to clarify important key processes and thus lead to a better understanding of the primary cosmic dust formation for the various situations encountered.

2 PHYSICAL CONDITIONS IN COOL OUTFLOWS

In order to understand the various chemical and dust formation processes in cool outflows it is necessary to describe their physical conditions, which are illustrated by the following: a mass element moves outwards and subsequently cools (from approximately 5000K down to 50K) and dilutes (from about 10^{12} particles/cm^3 to 10^6 particles/cm^3) due to the expansion of the flow. Furthermore the matter is exposed to radiation fields. During this expansion molecules of increasing complexity evolve, which allow effective cluster formation and growth at a temperature of T $\leq$ 1000 K and a gas density of $n^g \simeq (10^{10} - 10^8)$ particles/cm^3.

The chemical situations realized in circumstellar dust shells are schematically demonstrated by Figure 1. The vertical order (star type **I**, **II**, **III**) distinguishes among the different elemental abundances and consequently among the different chemical compositions of the important dust forming objects (M–star, C–star, RCrB–star), while **A**, **B**, **C** denote the subsequent regions of each case along the flow. In contrast, **IV** shows the different cases of explosive, dust forming objects like novae or supernovae, dominated by strong UV–radiation fields and high temperatures.

Though the general physical situation in each case is sufficiently well defined, there is a particular need for specific **input data of the gas phase chemistry**, the determination of **physical properties of small clusters**, the cross sections for relevant **gas-dust surface reactions**, and for spectral data, the knowledge of necessary ingredients for a reliable modelling of dusty shells.

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Each of these topics is discussed in the following sections. According to the entries of Figure 1, important desiderata for laboratory work, necessary for improving the data base and for the clarification of key processes in the adopted theoretical description of the formation of solid particles from the gas phase, are listed below.

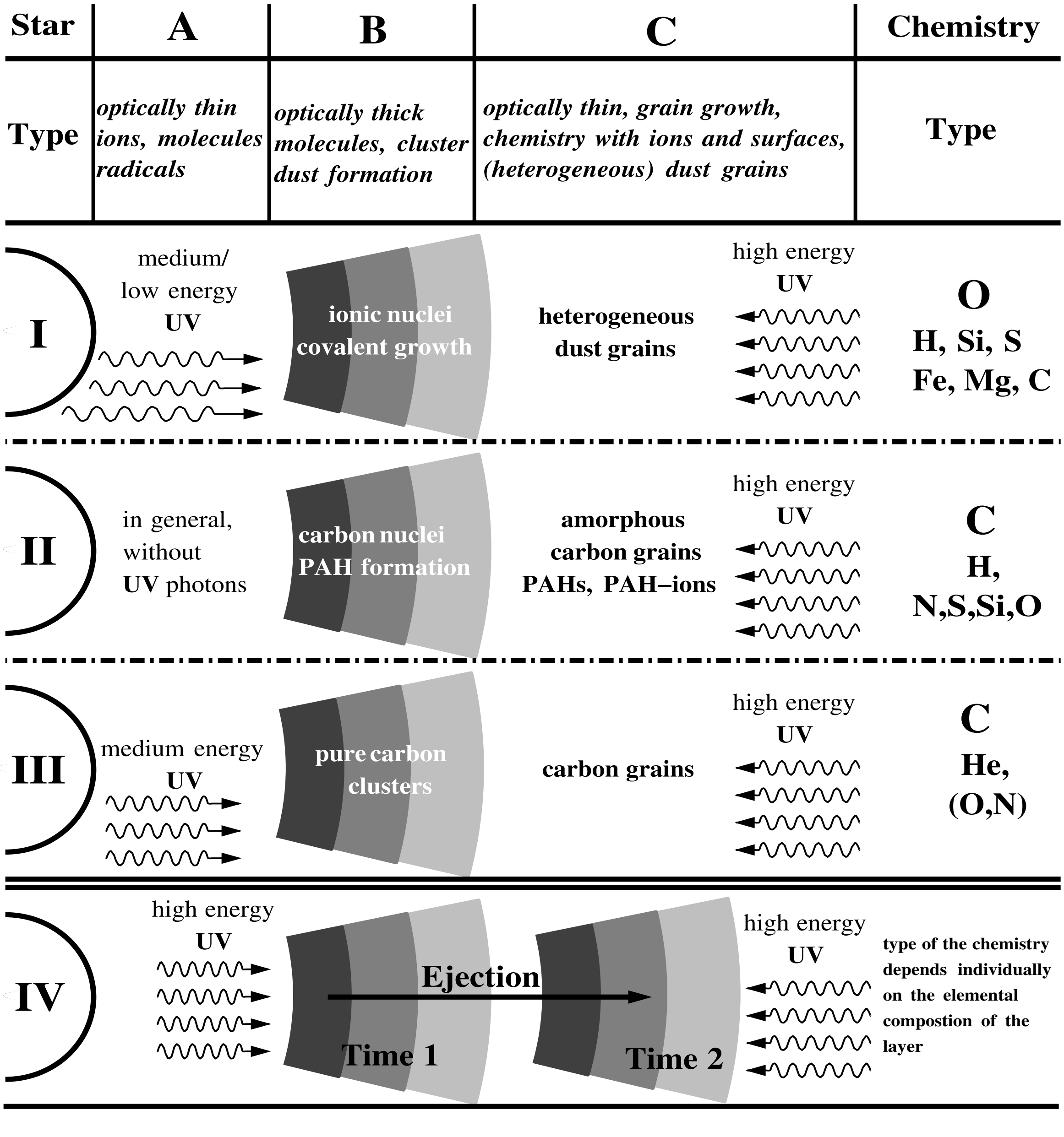


FIG. 1. THIS FIGURE DEMONSTRATES SCHEMATICALLY THE DIFFERENT BASIC SITUATIONS IN A STELLAR OUTFLOW CLASSIFIED WITH RESPECT TO THE CHEMICAL COMPOSTION. IN VERTICAL ORDER IT IS DISTINGUISHED AMONG:
I OXYGEN-RICH COMPOSITIONS (M–STAR); **II** CARBON RICH COMPOSITIONS WITH HYDROGEN (C-STAR); **III** THE SPECIAL CASE OF R CRB STARS WITH A PURE CARBON CHEMISTRY. IN EACH CASE THE SUBSEQUENT REGIONS ALONG THE FLOW ARE DENOTED BY **A**, **B** AND **C**.
IN CONTRAST, **IV** SHOWS THE DIFFERENT SITUATION OF AN EXPLOSIVE, DUST FORMING OBJECT LIKE NOVAE OR SUPERNOVAE.

The most serious problem for the transference of this physical situation in laboratory experiments is the scaling of the experiment from astrophysical conditions (length: 10^{13}m, particle densities of a single species: 10^2 to 10^{10} cm^{-3}, time: 10^6 to 10^8 sec) down to a laboratory situation. Besides the minor problem of theoretical scaling of the basic equations, one difficult challenge is the realization of the low pressure limit, which is essential for the behaviour of many of the activated complexes in chemistry of astrophysical objects. Many reaction products remain chemically activated up to timescales of a second affecting drastically the branching ratios of some reactions compared to a laboratory situation. Since "astrophysical experiments" need extreme low pressure and maximum timescales, the influence of the surface of the apparature may be much greater than in usual experimental setups.

3 CHEMISTRY IN THE GAS PHASE

A general consideration of the stellar outflows must take into account the effects of expansion, pulsation, UV radiation fields and variations of the thermodynamical quantities thus creating a situation which significantly deviates from chemical equilibrium. The theoretical treatment of the time dependent chemistry in circumstellar shells requires the computation of reaction networks, comprising the most abundant species and their chemical interactions. Such a chemical reaction network is defined by the set of equations of continuity ($i = 1, \ldots, N_{sp}$) for the number densities n_i of species i moving with the hydrodynamical velocity $\underline{v}(t)$. N_{sp} denotes the total number of species considered. The left hand side of Eq.(1) represents the temporal evolution of the particle density of species i in a comoving volume element.

$$\frac{\partial n_i(t)}{\partial t} + div\,(\underline{v}(t)\; n_i(t)) = \underbrace{\sum_{\mu} \left(-k^f n_i n_j + k^r n_l n_k\right)_{\mu}}_{=S_i^{kin}} + \underbrace{\sum_{\mu'} \left(-k^p n_i + k^r n_l n_k\right)_{\mu'}}_{=S_i^{photo}} \tag{1}$$

The net source terms, which describe the chemical reactions labeled by μ and μ', consist of all gain and loss rates involving the species i and including gas kinetic processes (S_i^{kin}) as well as photochemical reactions (S_i^{photo}). For simplicity, in Eq. (1) only the gas kinetic rates of 2–body collisions are depicted. The rate coefficients k^f of their forward reactions are parameterized by the empirical Arrhenius law with the pre–exponential factor A, the temperature exponent α, and the activation energy E_a as parameters.

$$k^f(T) = AT^{\alpha} \exp\left(\frac{-E_a}{R\,T}\right); \qquad k^r(T) = k^f(T) \exp\left(\frac{-\Delta_r G^{\ominus}(T)}{R\,T}\right) \tag{2}$$

k^f and the corresponding reverse reaction coefficients k^r are related by the thermodynamical expression (cf. right hand side of Eq. (2)) and therefore k^r can be calculated using the Gibbs energy of formation $\Delta_f G^{\ominus}$ of each species involved in the particular reaction. $\Delta_r G^{\ominus}$ is the change of the Gibbs energy of formation due to this reaction. The photochemical processes comprise photodissociation and photoionization reactions and their rates k^p are given by

$$k^p = 4\pi \int_{\nu_l}^{\nu_u} \mathrm{d}\nu\, \frac{J_\nu}{h\nu}\, \sigma(\nu) \tag{3}$$

where $\sigma(\nu)$ denotes the cross section of the process.

In summary, chemical networks allow us to describe the chemical evolution of circumstellar shells. For calculating these reaction networks and the determination of chemical pathways the **Arrhenius parameters** of all important reactions, the **Gibbs energy of formation** of all species of the network and the **cross sections of their photochemical processes** over the relevant wavelength range are required. In many cases the data are based on rough estimates only, or are not available at all.

3.1 Kinetic reactions

The kinetic gas phase reactions comprise a large varity of different reaction types like *ion–neutral reactions* $X^+ + YZ \rightarrow XY^+ + Z$, *neutral–exchange reactions* $X + YZ \rightarrow XY + Z$, *radiative association* $X + Y \rightarrow XY + h\nu$, *radiative recombination* $XY^+ + e^- \rightarrow XY + h\nu$, *dissociative recombination* $XY^+ + e^- \rightarrow X + Y$, and *negative ion reactions*, (see e.g. Duley and Williams, 1984 for a view of the reaction types).

In the last years progress has been made in the investigation of gas phase reactions and their data by experiment as well as by theory. For example, the data of bimolecular ion–molecule reactions are given in surveys of Anicich & Huntress (Anicich, 1993; Anichich and Huntress, 1986). But there is still a lack of specific data, also concerning the atoms and molecules, which are probably involved in the primary condensation process. These species are of special interest in the theoretical modelling of circumstellar dust shells. Therefore, in the following sections the discussion of reactions and species is restricted to this point of view.

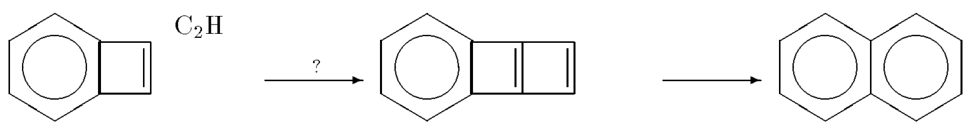
3.1.1 Kinetic reaction rates

Anorganic compounds Depending on the elemental abundances the clustering molecules have to be reactive, abundant species in the gas phase and the resulting primary seed particles must have high temperature condensates. Applying these heuristic criteria (cf. Sedlmayr, 1994; Gail & Sedlmayr, 1986) to case **I** the most important anorganic elements for dust formation in astrophysical environments are Si, Mg and Fe, which can form high temperature condensates with other abundant elements like carbon, oxygen or sulfur (see e.g. Dominik, 1992 for a list).

Compared to the Si–chemistry, the knowledge of the Fe– and Mg– chemistry is very poor. Therefore, it was impossible to investigate the formation of the monomers (e.g. FeO, FeS, MgO, MgS) in a non–equilibrium gas phase chemistry. As a basic step, the experimental determination of the main formation reactions of FeO, FeS, MgO, and MgS is needed to improve the description of dust formation in oxygen rich situations. Furthermore experimental investigation should concern other Fe- / Mg- compounds in the gas phase to provide a reliable determination of the abundances of the condensating molecules. For example, the data of the reaction $Mg + N_2O \rightarrow MgO + N_2$, which is used for the production of MgO in the laboratory (e.g. Ziemann and Castleman, 1991), are well known, but in the astrophysical context it is only of minor importance.

Reactions of organic species Concerning C-stars, we are dealing with a carbon-hydrogen chemistry where probably PAHs are formed (case **II**). Representative examples of reactions with only estimated data are for instance the reaction of chains, which is important for radical formation: $C_2H_3 + C_2H_3 \rightleftharpoons C_2H_4 + C_2H_2$ or the reaction with molecules A_i consisting of i rings: $A_i\cdot + C_2H_2 \rightarrow A_iC_2H_2$ (+ hν ?), for which in particular the temperature dependent reaction rate coefficients in low pressure limit, the activation energy and the radiative relaxation time of the product are important.

Because of the extreme low pressure, activated complexes in some cases undergo **unimolecular reactions** with high activation energy barriers. The data for such reactions are very uncertain and based only on rough theoretical arguments. The most important reactions of this type are the ring closure reactions in the PAH-chemistry. The temperature dependent ring closure rates have to be derived for the first ring closure reactions and the succeeding PAH 'growth' reactions. The following example is a second ring closure reaction.



Is such a ring closure possible and how fast is the rearrangement and the redissociation?

3.2 Thermodynamical data

To calculate the reverse reaction rates k^r Eq. (2) the thermodynamical data of many molecules are required in the temperature range from about 3000K to 100K. Many data are provided by compilations like e.g. Chase *et al.*, 1985, but the Gibbs energy of formation especially for molecular cations and radicals is absent. Most of the Gibbs energies of formation of organic species can be derived by group additivity rules. However, this approach fails in the case of radicals, ions and especially for curved PAHs including one or more pentagons. Therefore, the experimental determination of $\Delta_f G^{\ominus}$ of these organic and anorganic species is necessary.

Another problem is the uncertainty of the available data. For example, the values for $\Delta_f H^{\ominus}$ of MgO and MgS are very uncertain. The dissociation energies of MgO (MgS) available in the literature vary from 2.6eV to 3.9eV ($<$ 2.4eV to 3.0eV). The exact determination of these energies is also important for theoretical cluster calculations (cf. section 4.1).

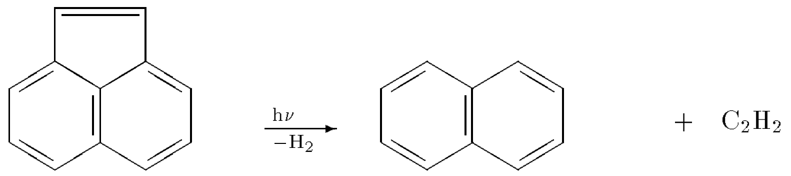
3.3 Cross sections of photoreactions

In astrophysical environments atoms and molecules are subject to various processes which may alter their state of energy, momentum and their composition. One class of such processes are interactions of radiation with matter, which lead to a change in the charge (e.g. photoionization) as well as in the structure of the particle (e.g. photodissociation). In some objects strong UV–radiation fields dominate the chemical situation (e.g. in the inner shells of oxygen rich envelopes (case **I A**) or in the outer optically thin region of any dust shell (case **C**)).

Anorganic compounds In the case of an oxygen rich shell (case **I A**), many of the photoreactions have a key position in the chemical network. Information about the photoionization cross section can be obtained from both, theory and experiment. Many experimental techniques have been applied to obtain total and partial photoionization cross sections. For example Gallagher *et al.*, 1988 provide a compilation of ionization cross sections of some di– and triatomic molecules. Besides the requirement of photoionization data there is a strong need for information of photodissociation cross sections of molecules and molecular ions. A brief overview of the current knowledge of cross sections for photodissociation is given e.g. in van Dishoeck, 1994, 1988, and references therein. But the still rather poor knowledge about the ionization and dissociation processes of silicon bearing species like SiO, SiO_2, SiH, SiH_2 or SiOH, which are important in the chemistry of M–stars, has to be improved.

Organic species Though PAHs are probably formed in the optically thick region of the dust shell (case **II B**), the observed spectra of dust envelopes are generated in the outer, optically thin region, where PAHs are modified by the interstellar radiation field (case **II C**). A typical photon intensity in interstellar space is given by $1.7 \cdot 10^6$ (E/eV) - $2.2 \cdot 10^5$ (E/eV)^2 + $7 \cdot 10^3$ (E/eV)^3 [photons $cm^{-2}\ s^{-1}\ sr^{-1}\ eV^{-1}$]. To calculate the spectra of such objects, the photochemistry of large PAHs has to be considered in the selfconsistent models of the dust shells. Although some work on standard type PAHs has already been addressed to this question (e.g. Jochims *et al.*, 1994; Verstraete *et al.*, 1990), there is still a lack of information, especially concerning PAH molecules containing pentagons and acetylenic groups.

In particular the photoionization cross sections in the range 5eV up to 20eV are required for phenylacetylene, acenaphtylene, fluoranthene, corannulene, etc. The photodissociation rates of these molecules according to the following reactions are also of fundamental importance :



4 CLUSTER

The formation process of dust particles from the gas phase is controlled by the reaction with the slowest net growth rate in the whole reaction chain, leading from a single atom via small and subsequently larger molecules (cluster!) up to macroscopic grains. The educt of this bottleneck reaction is called the critical cluster of size N_* and its net growth rate is called the nucleation rate J_*, which gives the number of seed particles formed per second and unit volume. The nucleation rate is the most important quantity in the description of the dust formation process. In astrophysical problems the size of the critical cluster is very small ($N_* < 10$), and the reaction rates in this cluster size regime depend strongly on the individual chemical and thermodynamical properties of the clusters. The most common form of the net transition rate $J_{N,i}$ between two clusters of size $(N-i)$ and N is given in Gail and Sedlmayr, 1988. Considering equal gas and dust temperature T, one gets for the transition rate

$$\begin{aligned} J_{N,i} &= A_{N-i} v_{i,N-i} \alpha\,(N-i,i)\, f\,(i,t)\, \overset{\circ}{f}\,(N-i) \\ & \left\{ \frac{f\,(N-i,t)}{\overset{\circ}{f}\,(N-i)} - \frac{f\,(N,t)\;\; \overset{\circ}{\alpha}\,(N-i,i)\;\; f\,(i,t)}{\overset{\circ}{f}\,(N)\;\; \alpha\,(N-i,i)\;\; \overset{\circ}{f}\,(i)} \right\} \end{aligned} \tag{4}$$

where A_{N-i} denotes the surface of the $(N-i)$-cluster and $v_{i,N-i}$ the relative thermal velocity between an $(N-i)$ and an i cluster. The number densities of the clusters are given by $f(N,t)$, and $\alpha(N,i)$ is the average sticking efficiency of an i-cluster on the surface of an N-cluster. The quantities with a circle refer to the case of thermodynamical equilibrium (TE). The cluster densities $\overset{\circ}{f}\,(N)$ in TE can be derived from the law of mass action

$$\frac{p(N)}{p(1)^N} = \frac{1}{p_0^{N-1}} \exp\left[\frac{\Delta_f G^{\ominus}(N,T) - N\Delta_f G^{\ominus}(1,T)}{RT}\right] \tag{5}$$

and the ideal gas law $f(N) = p(N)/kT$. All relevant cluster–forming reactions (with the net reaction rates $J_{N,i}$) together build up a rate network for the determination of the actual cluster densities $f(N,t)$. The approaches for the solution of such systems are comparable to the methods used by the non–equilibrium gas phase chemistry. It can easily be seen from Eqs. (4) and (5), that the network of the clusters is controlled by the two material and temperature dependent quantities $\alpha(N,i)$ and $\Delta G^{\ominus}(N)$. Therefore, these physical quantities are definitely necessary for theoretical investigations of dust formation processes in any astrophysical environment. It is a subject of experiments and theoretical considerations to provide reasonable values for the **sticking efficiency** α and the **Gibbs energy of formation of the cluster** as a function of cluster size.

4.1 Ionic clusters

Ionic clusters like the II-VI-compounds MgO and MgS are possible candidates for the formation of seed particles in an oxygen-rich chemistry (case **I A**). These nuclei are assumed to be formed from the gas phase by a homogeneous nucleation of MgO or MgS molecules.

As an example for a **theoretical approach** determining the quantities required for the dust formation process we present the theoretical results of a model for the interaction potential of the ions (Mg^{++}, O^{--} and S^{--}) in small MgO and MgS clusters, developed for the description of the formation of these clusters. Details of the model and the calculation method are given in Köhler *et al.*, 1994. The model allows for the calculations of the clusters total bond energies, eigenfrequencies, moments of inertia, and the Gibbs energy of the MgO clusters. Figure 2 shows the temperature dependence of the minimum of the equilibrium distribution function $\overset{\circ}{f}(N)/\overset{\circ}{f}(1)$, which corresponds to the critical cluster N_*.

Nevertheless to prove the quality of the model results and to adjust empirical parameters, experimental studies on the dissociation energies, IR spectra and the dipole moments of the clusters would be helpful.

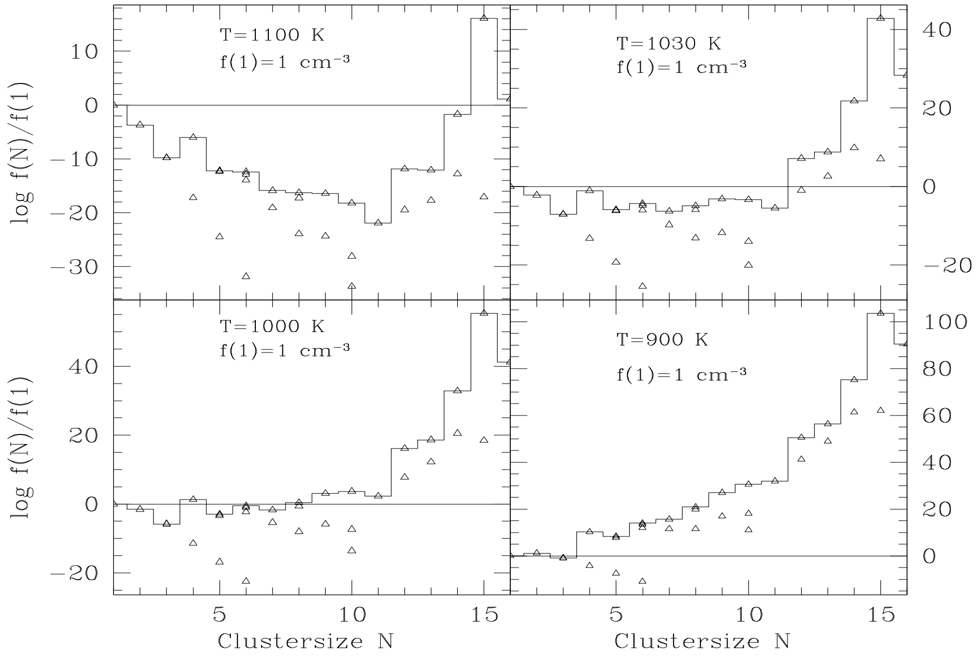


FIG. 2. SIZE DEPENDENT EQUILIBRIUM DISTRIBUTION FUNCTION AT DIFFERENT TEMPERATURES AND CONSTANT MONOMER DENSITY 1 [cm^{-3}] ACCORDING TO THE LAW OF MASS ACTION (Eq. 5) [From Köhler *et al.*, 1994]

4.2 Covalent clusters

In an oxygen-rich situation (case **I**), the primary nuclei are small ionic clusters (see last section) or small clusters of for example Fe or SiO. Compared with the ionic clusters, the knowledge of these covalent clusters in the size regime between 2 and 20 atoms is relatively poor. Nevertheless Hale *et al.*, 1989 have investigated the nucleation of SiO by experiment. They derived values for a stationary nucleation rate, which cannot be applied to the low particle densities of astrophysical environments without problems.

In the case of a pure carbon chemistry (case **III**), the dehydrogenized polyaromatic carbon-molecules (PACs) are expected to be the most relevant clusters. These PACs are formed by the most effective chain of radical reactions leading from C-atoms to subsequently larger molecules and clusters. This reaction chain probably involves those gas species which are the most abundant. On the basis of an equilibrium chemistry these species are (besides the neutral C-atom): small linear carbon chains ($C_2, \ldots, C_{14}$, especially the C_3−radical), monocyclic rings ($C_6, \ldots, C_{22}$) and larger flat or curved PAC-clusters ($C_{20}, \ldots$) (cf. Palmer and Shelef, 1968; Broyer *et al.*, 1993).

Is this general picture of the pure carbon chemistry correct or not? What are the most abundant dehydrogenized carbon species in equilibrium at extremely low pressures? Which isomeric structures are realized?

In order to determine the efficiency of the possible reaction chains leading to PACs, that is to determine the major reaction chain and the nucleation rate, it would be very useful to derive the size – and temperature–dependence of the **Arrhenius parameters** (Eq.(2)) experimentally in the low pressure limit and further results of some representative examples of the following types of chemical reactions (case **III** A, B) like chain-chain-reactions, ring closure reactions, which seem to be the major step from one- to two-dimensional clusters, ring-chain-reactions and ring-ring-reactions. The last reaction type appears to represent the key reaction type from two- to three-dimensional clusters and might be the bottleneck reaction of the PAC-formation. For the PAC growth reactions the size and temperature dependent sticking efficiencies should be investigated.

For a time–dependent chemical model of the PAC–formation process, the **thermodynamical data** of the various species are needed in order to calculate the rates of the reverse reactions k^r (cf. Eq. (2)). Especially for the larger molecules ($C_{10}, \ldots$), no experimental data are available by now. Another open question is the **number of isomers** which can be realized by a cluster consisting of N C-atoms and their relative abundances at a given temperature. These numbers are also needed for the reaction network.

5 DUST

One of the main properties of dust grains in a stellar atmosphere is that these grains introduce a surface into the physical system. The presence of a surface allows completely new possibilities for chemical reactions to proceed. On the one hand this is important for the gas phase chemistry since many molecules may form on the grain surface (e.g. formation of H_2). On the other hand, the reactions may alter the properties of the dust grain itself, and this is the type of surface reactions, which are important for the dust formation process.

Grain growth In this context reactions leading to grain growth are the most important grain surface processes. With the exception of pure carbon grains, usually the so-called "nominal molecule" of the grain material does not exist in the gas phase or only in small concentrations. One of the most important examples are the silicates formed in the envelopes of M type stars (case **I**). There are several gas molecules contributing to the formation of this material like SiO_2, MgOH, FeS, etc.. The reaction probabilities of these molecules with silicate grains of mixed composition have to be known and consequently the measurement of these sticking efficiencies is required.

Since in some special cases the coexistence of carbon- and oxygen-chemistry is expected (cf. Beck *et al.*, 1992), it would be also of interest to investigate the growth reactions of silicate molecules on a carbon grain surface and of carbon bearing species on silicates. Due to the heterogeneous formation of these solids, the structure of the condensates will not be crystalline, but rather amorphous, with different composition at different sites in the grain. What is the real structure formed under astrophysical conditions?

Charged dust particles The work function of typical grain materials is of the order of several electron Volts. Therefore, if UV-photons are present, grains are ionized and become positively charged. This is preferentially the case at the innermost region of the dust shell, where the clusters are small (case **B**). If the grains move outwards and become larger, their electron affinity becomes dominant and the grains accumulate electrons resulting in a grain charge up to $Z \approx -100 \cdots -500$. Because of the high concentration of cations in the outer part of the shell, this process dramatically increases the growth-rate and also changes the final chemical composition of the emerging dust particles (case **C**).

To describe the influence of the dust charge quantitatively, experimental data are required for the photoelectric yield for photoionization and the electron sticking probability of dust grains as a function of particle size, particle charge (positive and negative) and dust temperature for various materials like amorphous carbon (with hydrogenated surface), different microscopic structures of graphite or anorganic grains (e.g. FeO, SiO_2, MgO, Mg_2SiO_4). Moreover, the influence of the charge on the reaction proabilities (sticking efficiencies) has to be investigated by experiment.

Structure As mentioned above, the chemical composition and structure of the dust grains are expected to vary inside the grains. Since the newly formed dust grains have an amorphous, heterogeneous structure, they are not in the energetically most favourable state. Therefore, we expect an internal rearrangement of the material in the grains with time. The following questions concern these points: Is it experimentally possible to observe such internal rearrangements? How fast do these processes proceed under the various astrophysical conditions?

6 CONCLUDING REMARK

With the experimental clarification of these problems the quantitative, theoretical description of dust formation of both organic and anorganic grains will be substantially improved and will be put on a reliable basis.

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