RATE OF H₂ FORMATION ON AMORPHOUS GRAINS

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Abstract. The rate of formation of molecular hydrogen from hydrogen atoms adsorbed on grains is analyzed, assuming that the grains are single crystals, polycrystalline or amorphous. On polycrystalline grains, and on graphite platelets, this rate could be orders of magnitude lower than on single crystal grains. The same is true for amorphous grains because there, at low temperatures, only atoms absorbed on neighboring sites can form molecules. Suitable formulae are derived and compared with the classical results for single crystal grains. Quantitative results are given for crystalline and amorphous ice, but with small changes these should also be valid for other solids. The rates for amorphous grains can approximate, within a factor of 10 or so, those for crystalline grains if the density of H atoms is high and the density of H₂ molecules is low and only when the temperature of the grains satisfies a relation which for ice and graphite leads to a value in the proximity of 15-17 K. This maximum rate occurs only a degree or so above the temperature at which the grains are totally covered by an H₂ layer and the reaction ceases. Furthermore, for a constant number density of grains, the rates on amorphous grains are second order while those on crystalline grains are first order. Both these circumstances predict amorphous grains to lead to H₂ clouds with irregular and sharply delineated features in contrast to more uniform clouds formed on crystalline grains.

1. Introduction

Interstellar H₂ plays an important role in many astrophysical and cosmological problems, but it also poses questions concerning its origin. Although it is generally agreed that, apart from the possibility of the H⁻ + H → H₂ + e reaction in free space, the basic H + H → H₂ reaction occurs only on the surface of grains a quantitative understanding of the details of this process is not yet at hand. The main difficulty stems from the uncertainty about the true nature of the interstellar grains. One aspect concerns the various steps which permit the reaction to take place; another deals with the estimated rate of H₂ formation and its comparison with what is known about the thermal and density conditions in the dust-containing hydrogen clouds. The first detailed discussion of these problems has been made by Hollenbach and Salpeter (1970, 1971); the most recent one is that of Goodman (1978) who gives references to other pertinent papers. Without exception the authors follow the traditional assumption that the interstellar dust grains are small particles of well-known crystalline terrestrial solids such as graphite, ice, silicates, etc. Although the presence of the inevitable atomic scale imperfections, such as vacancies and interstitials, has been discussed they appear to introduce relatively small changes in the overall picture. The purpose of this paper is to estimate the rate of H₂ formation on grains which are not crystalline but truly amorphous as suggested by the recently established preference for the formation of amorphous water ice below 150 K (Narten et al.,
1976), the inability of graphite platelets to account for the 2200 Å absorption feature (Gilra, 1972; Savage, 1975), the possibility of an initial formation of carbon rather than graphite grains (Czyzak and Santiago, 1973), the possibility of the formation of an amorphous carbon layer on graphite grains (Smoluchowski, in preparation), the presence of amorphous silicate grains (Willner et al., 1979; Stephens and Russell, 1979), and the intriguing structure of grains and grain clusters observed by Brownlee et al. (1976) which are presumably of extraterrestrial, though not necessarily interstellar, origin.

Most of the discussion given below is applicable to amorphous grains of all solids but the quantitative illustration will be given only for amorphous ice grains or grains covered with an amorphous ice layer. In this sense the paper is an extension of the author’s discussion of the process of adsorption and surface mobility of hydrogen atoms on amorphous ice grains (Smoluchowski, 1979).

2. Structure and Thermodynamics of Amorphous Grains

A few words are in order to stress the often unappreciated difference between a crystalline (perfect or imperfect) solid and an amorphous solid. The first one has a structure in which the atoms or molecules are arranged with translational regularity while the other does not. As a result, the structure and most properties of the first are anisotropic while those of the other are isotropic, and this also applies to their surfaces. Since atoms, and most molecules of interest for interstellar grains, have rather well-defined effective radii and the bonds between them are almost unaffected by the degree of crystallinity, the number of nearest neighbors of a particular atom or molecule and the distances between them are usually very similar, though not identical, in crystalline and amorphous solids. The basic differences, arising primarily from altered angles between the bonds, show up in the number and distances of second, third and more distant neighbors. These differences are best described by the so-called pair-correlation function which indicates the probability that two atoms, or molecules, are at a particular distance from each other. For crystalline solids this function consists of sharp peaks determined by the translational symmetry, while for amorphous solids the peaks are broad and disappear for larger distances. In this respect an amorphous solid is fundamentally different from a solid composed of crystalline areas of the order of $10^2$–$10^3$ Å separated by narrow boundaries. Since all diffraction lines (X-ray, electrons, neutrons, etc.) become broader with decreasing crystalline size and also with strain, an experimental distinction between a fine grain crystalline solid and a truly amorphous solid is often very difficult. The best operational definition of an amorphous solid is a solid in which the structural ordering is, at most, on the order of 10 Å (Konnert and Karle, 1973).

Amorphous solids are metastable structures which, upon heating, can gradually crystallize by the usual process of nucleation and growth (Ainslie et al., 1962). This process depends exponentially on temperature and on an activation