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CONDENSATION AND

AGGLOMERATION OF GRAINS

J. R. ARNOLD

The thermodynamics of condensation from a cooling neutral gas of solar com-position, have now been explored in great detail. Theories based on equilibrium condensation have had some striking successes, but there is still much to learn. There seems good reason to explore the condensation process experimentally, so far as it is possible to simulate the conditions usually assumed, to compare the results with what we see in the meteorites, and with the calculations. Preliminary results of this experimental investigation are being reported here.

An apparatus has been constructed and operated by J. Stephens and B. Kothari, which uses a laser system to vaporize silicates and other interesting solids in controlled atmospheres, and permits the collection and analysis of the submicron condensates formed. The target vapor apparently mixes with the ambient gas before condensation, permitting the control of redox conditions as well as other varia-bles of interest. Analysis is carried out by electron beam x-ray fluorescence in the SEM, x-ray diffraction, and other methods.

There has been a great deal of scientific work on the behavior of small par-ticles in gas streams, particularly in connection with industrial pollution prob-lems. This and the results of Stephens and Kothari, suggest that submicron and micron-scale particles in a gas adhere strongly on contact. Aggregates must form, perhaps reaching centimeter scale, under a wide variety of conditions, at rates which can be closely estimated from a general second-order rate equation. (See, for example, Fuks, N. A., The Mechanics of Aerosols, MacMillan, New York, 1964, Chapter VII). This is probably a first step in the accumulation which ultimately leads to planetesimals, under a broad range of starting conditions.

Stellar temperatures are generally too high to permit the existence of con-densed phases. Since it is believed that the material of the sun and planets had been previously incorporated in stars, it seems reasonably certain that the con-densation of grains was an essential early step in the formation of the planetary system. The time and place of this condensation step is less sure. In particular there are, broadly, two views on the conditions under which it took place. One holds that the ambient gas density was as low as those now seen in such places as the Orion nebula or at planetary distances from T Tauri stars (Alfvén and Ar-rhenius 1975). In this case the conditions were those of a low-density plasma. The other, more traditional view starts with the pressures to be expected in a disk of gas and dust massive enough to provide the raw material for the planets we see. This pressure is of the order of 10^{-3} - 10^{-4} atmospheres (Larimer and Anders 1970; Goldreich and Ward 1973). Under such conditions, at temperatures low

enough for condensation to occur, the gas must be essentially neutral, and thermodynamic equilibrium is thought to prevail.

Thermodynamics cannot, of course, tell us whether equilibrium is reached in a given case. Some gas phase reactions require milliseconds to complete at room temperature (NO_2 - N_2O_4 equilibrium), while others are incomplete after thousands of years (H_2 - O_2 reaction). In equilibria involving solids, there are two processes which may be quite slow. The first is nucleation, the formation of a cluster of atoms which can grow smoothly into the appropriate solid or liquid. The second is diffusion in the solid after it is formed.

We thought it useful to simulate (on a laboratory scale) the postulated processes for the case of a neutral gas. John Stephens and Brajesh Kothari have built a laser system which can quickly deposit several joules of energy on a small solid target in a gas cell, vaporizing tens of micrograms of material in a single "shot." The vapor mixes with the ambient gas before condensation. Thus, for example, reducing or oxidizing conditions can be achieved by filling the cell with H_2 or O_2. Particles of condensate are collected on electron microscope grids in the chamber, and analyzed later. At the pressures used, there is no significant interaction with the walls of the vessel. The time scales are of course very short compared to those expected in a solar nebula. This limitation has at least one merit: if equilibrium is reached or closely approached in the laboratory system it is reasonable to expect it to hold in the nebula.

Examination and analysis of the particles is carried out in a transmission electron microscope (TEM) with an electron diffraction system for crystal structure and in a scanning electron microscope (SEM) with an electron-beam x-ray fluorescence system for measurement of chemical composition. We are indebted to Prof. Gustaf Arrhenius and to the Scripps Analytical Facility under Mr. Ron LaBorde for making these available.
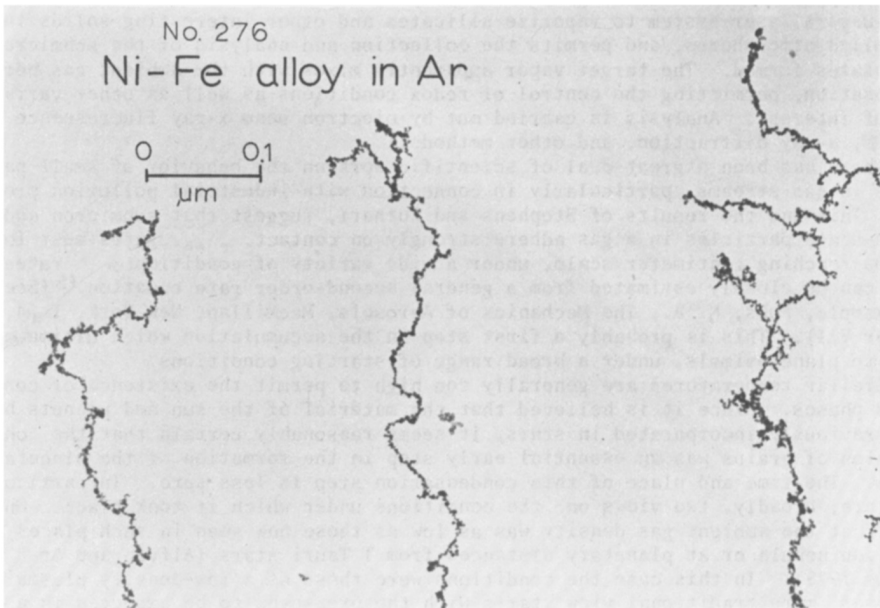

Figure 1. *TEM picture of Fe-Ni condensate. Note the extreme development of the tendency to linear agglomeration.*

The apparatus and the results obtained will be described by Kothari and Stephens at the forthcoming Meteoritical Society meeting . Their paper will include figures showing the phenomena described below, and others.

The condensate consists of particles of typically 5-100 nanometers diameter. The work on crystalline structure and composition is still in an early stage, but some tentative generalizations can be made. Chemically simply targets, such as metals and oxides like MgO and Al_2O_3, are recovered unchanged as crystalline solids, when vaporized in an inert gas atmosphere or even sometimes in reactive atmospheres. Olivine condensed as a glass, which can be devitrified with moderate heating. Reaction with the ambient gas has been observed, in some cases.

It is a familiar fact (Urey 1952) that a number of silicates, and also iron nickel-metal, have similar equilibrium temperatures of condensation out of a gas of solar composition. Especially if such a gas undergoes supercooling before condensation (an idea suggested by our observations of glass), there may be a large number of thermodynamically favorable reactions to form solids, when the temperature is finally low enough to permit nucleation. We have speculated that perhaps the first solids to form under such conditions will carry with them the memory of the most abundant (stable) gas phase molecules from which they were built, but there is no evidence either way as yet.

The fact is that the solids expected from thermodynamic calculations do form in at least some high temperature condensation experiments in the laboratory. If this holds true when we come to do the experiments which simulate the state of calculated solar nebula in nearly all ways, except for the time scale, it will be a powerful argument for the equilibrium view.

The next step after condensation is the agglomeration of grains. The behavior of grains, once they are formed, has been studied for many years by engineers concerned with industrial particulates, but (by comparison) hardly at all by physicists or chemists. The best book known to me on the subject (Fuks 1964) draws mainly on the engineering literature. In our early ignorance of its existence, we have shared with other students of the solar system the experience of rediscovering well-known phenomena.

The most striking of these is the formation of linear structures--appearing as chains, ropes, or even threads of particles--under almost all conditions of condensation. Many others (for example, Whytlaw-Gray et al. 1932, Schweckendiek 1950; and Yamijo et al. 1975) have seen this before. The explanation given by Fuks (1964) is quite reasonable. Small particles are likely to carry either one or more net electron charges, or an electric dipole, or both. When two or three particles adhere, they tend to line up in a way which accentuates the net dipole moment. The longer the chain, the stronger the dipole. The presence of a local D.C. field will cause the chain to align; increasingly the combined forces will cause an incoming particle to move to one end, depending on the sign of its charge or orientation of its dipole.

Does this behavior have any counterpart in natural systems? We do not yet know how to look. Our search, however, can be guided by some general considerations, which Fuks (1964) and others have already given in part.

Grains in a neutral, reasonably quiet gas are subject to significant forces of three kinds: electrical, gravitational and the variety of short-range chemical interactions which non-chemists lump as "contact" forces. (Magnetic forces must also be considered for Fe-Ni and Fe_3O_4). In a solar nebula the gravitational acceleration is of the same order as solar gravity at the earth (about 6×10^{-4} g). It will have little direct influence on the short-term behavior of a small grain in a gas at 10^{-4} atmospheres pressure.

The electrical forces act on the net charge of the particle. In a neutral gas there is always a small concentration of molecular ions and electrons, produced by cosmic rays, radioactive decay, and other mechanisms. The grain's charge comes to equilibrium with these. Since the kinetic energy of each gaseous ion is of the order of kT, this limits the charge which can be brought to

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a grain to a value such that the grain's electrostatic self-energy (q^2/r) is of the same order. For a micron-size grain this is typically one electron charge; the smaller the grain the more likely it is to be neutral. Hence the mutual attractive or repulsive energy of two grains of radius r $(q^2/2r)$ is also at most of the order of kT. Electrostatic repulsion cannot therefore serve as a significant barrier to mutual collisions, and attraction of opposite charges also should not play a large role.

Large scale D.C. electric fields would doubtless exist in a solar nebula. Air at atmospheric pressure can sustain fields of the order of kilovolts/cm and these could induce significant drift of grains, with velocities up to one meter per second and direction depending on sign. This could only increase the rate of grain-grain collision over that to be expected from Brownian motion alone (the same is true for Fuks' model of chain formation, discussed above). However, a pressure of 10^{-3} - 10^{-4} atmospheres is that used in gas discharge tubes. The sustainable large scale D.C. field is much less, and the drift velocities cannot be very large.

When two grains do collide, their mutual kinetic energy may be of the order of kT (Brownian motion) or somewhat more. This energy must be compared to the "contact" energy, which is always attractive, corresponding to a decrease of total surface energy, whatever the nature of the two surfaces. That is, the surface energy (surface tension) of any condensed phase is always a positive quantity.

The surface energy may be estimated in various ways. If we think of a solid as having a surface energy on the order of 300 ergs/cm^2, not an especially high value, and of an atom's area as 10^{-15} cm^2, we deduce an attractive energy of about 0.2 electron volts per atom pair in contact, or 5 kT at room temperature. But of course when grains touch there must be many atoms in contact. If there are as few as ten, the sum is 50 kT. If the bonds formed are of "chemical" rather than "van der Waals" strength, the energy rises to a few electron volts per atom pair, an order of magnitude higher. These attractive energies dominate the energy balance.

The conclusion is that when small grains collide they will stick together.

It remains to estimate the rate of growth of aggregates, that is, the rate at which grain-grain or grain-aggregate collisions occur. Here the generally applicable equation is

$$\frac{dn}{dt} = -Kn^2$$

where n is the number density of grains per cm^3, and K is a constant which in principle depends on particle size and shape, and on the gas density. However, as explained in detail by Fuks (1964), it is in fact roughly independent of these factors over very broad ranges of grain size. The value of K in c.g.s units (cm^3/sec) is not far from 3 x 10^{-10} throughout the region of interest. If we think of (Kn) as a mean collision lifetime for a grain, it is on the order of half a day for n = 10^5/cm^3, or one year for n = 10^2/cm^3. These values fit the qualitative behavior of clouds and smokes in air.

Some special circumstances, such as a high degree of (non-equilibrium) grain charging, or a high density of acoustic energy, can speed this process up, but I know of no likely mechanism for slowing it down.

For the composition usually assumed for a solar nebula the mass density of solids μ_s would be about 5 x 10^{-3} of that of the gas -- about 5 x 10^{-11} g/cm^3 at a pressure of 10^{-4} atm. The number density is related to the mass density by

$$n \approx 0.7 \ \mu_s d^{-3}$$

if $\rho s \sim 3$. This gives n ~ 30/cm^3 for d = 1 μm, or 3 x 10^7 for d = 10 nm. One sees that the agglomeration must reach the 0.1-1 μm range quickly, before the grains can move far relative to the gas. As the grains move to the mid-plane of the

cloud (Goldreich and Ward 1973) the concentration will tend to rise, and the aggregates will grow further.

What will bring this agglomeration to an end? Gravitational instability (Goldreich and Ward 1973) may simply supersede it, and produce much larger planetesimals. If such a process is much slower than agglomeration the limits will probably depend most of all on temperature.

At temperatures where the solid state diffusion constant reaches 10^{-10} (c.g.s) or more, perhaps 800° K or so, recrystallization and grain growth will proceed. The chains and puff-balls will become stronger, and finally tend to become pebbles. The resulting solid grains of 100 μ or more will no longer stick so well, because the kinetic energy at the very modest velocity expected from gravitational forces (Whipple 1973; Goldreich and Ward 1973) is large compared to reasonable contact energies. At temperatures of the order of 300° K, the agglomerates will not change their structure. The loose ropes and puff-balls will collide quite inelastically, tending to stick or even tangle until a larger size is reached, where the energy of impact causes the weak clusters to break up. At still lower temperatures, perhaps 200° K, ices may condense and again grow by diffusion.

In the above discussion, we have assumed throughout that the individual grains, grown directly over long periods from the gas, would be small. This may be wrong. However, the direct growth from the gas of large grains or droplets is very difficult, under any conditions familiar to us. It is a practical rule of thumb at ordinary pressures that the partial pressure of condensible materials cannot exceed a small factor, at most 10, above the equilibrium vapor pressure without abundant spontaneous nucleation of very small grains, which then rapidly take up the excess. Since the vapor pressure depends exponentially on the temperature, the region of T and p in which growth of a crystal from the gas is possible, but nucleation is inhibited, is a narrow one. Undoubtedly there are astrophysical situations, as there are terrestrial ones, where these special conditions are met and large masses can grow directly by condensation from the vapor. It is hardly imaginable, however, that they could extend widely through the solar system. Donn and Sears (1963) have discussed this question in detail. The elongated crystals (whiskers) they discuss are not observed in our experiments because of the short time scale, but they may well occur in space. If so, they provide another mechanism for formation of linear structures on a micron scale.

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DISCUSSION

WILLIAMS: At what pressures did you carry out your experiments and are there any obvious pressure dependences?

ARNOLD: At one atmosphere or below. We have not seen a steep pressure variation, but this is at an early stage.

LIPSCHUTZ: At what temperature were these experiments carried out?

ARNOLD: The vaporization occurs at a fairly low temperature, on the order of the thermodynamic "boiling point," in the region of 2000° C.

WASSON: I found your evidence for reaction of vaporized materials with the fill gas quite convincing, but I failed to understand the basis for your statement that chemical equilibrium had been attained.

ARNOLD: The statement was insufficiently precise. One can only say that in many cases the solid phase expected on thermodynamic arguments is in fact produced.

SONETT: I am intrigued by your photograph of Fe grains showing long chains. If these particles are single domain as seems likely, the usual quantum mechanical exchange forces (which are very important) would not clearly permit long chains to form--rather a generalized multi-domain structure.

ARNOLD: I must defer to experts on magnetics on this question. I only point to the striking difference in the form of the chains between Fe-Ni and non-magnetic materials.

GOLD: There are three different reasons for grains to attach to each other: firstly, the chemical surface adhesion; secondly, the attraction between electric dipoles, which the small particles frequently are; thirdly, the attraction between magnetic dipoles. They each have a different effect for organizing the infall of each further particle. In the first case, there is essentially no effect on an approaching particle. In the electrostatic case, the organizing force extends, with an inverse cube law, over dimensions characteristic of the particle size. In the third case, the magnetic one, the organizing dimension is of the order of the length of the chain already formed, because of the high value of the permeability that makes a dipole as long as the chain. In the electrical case, the dielectric constant is not high enough to do the same.

BRECHER: I have discussed some related aspects of laboratory grain condensation and aggregation five years ago at IAU Coll. No. 13 (Brecher, page 311). Magnetic interactions cannot be invoked to explain chain formations for silicates, although they adequately account for ferromagnetic particle aggregates. However, the magnetic energy of cohesion for submicron iron grains is only one order of magnitude greater than for larger iron grains. Other mechanisms leading to chain formation (e.g., electrostatic polarization) must be called upon. The second comment regards the apparent chemical equilibrium between gas and condensed grains at much lower temperatures and much faster than expected in the equilibrium condensation model. I obtained similar results by condensing two-phase Ni-Fe directly from a plasma-gas phase (Brecher, 1972 Ph.D. Thesis, U. Calif.).

ARNOLD: My missing your earlier work is an embarrassing example of the fragmentary and unsatisfactory state of the literature in this field. Some of the things Stephens and Kothari "discovered" have been seen as early as 1932. Most of the relevant papers are in engineering journals.

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