KINETICS OF GAS-GRAIN REACTIONS IN THE SOLAR NEBULA

BRUCE FEGLEY, JR.

Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899 USA

Abstract. Thermochemical equilibrium calculations predict gas phase, gas-grain, and solid phase reactions as a function of pressure and temperature in the solar nebula. However, chemical reactions proceed at different rates, which generally decrease exponentially with decreasing temperature. At sufficiently low temperatures (which vary depending on the specific reaction) there may not have been enough time for the predicted equilibrium chemistry to have taken place before the local environment cooled significantly or before the gaseous solar nebula was dispersed. As a consequence, some of the high temperature chemistry established in sufficiently hot regions of the solar nebula may be quenched or frozen in without the production of predicted low temperature phases. Experimental studies and theoretical models of three exemplary low temperature reactions, the formation of troilite (FeS), magnetite (Fe_3O_4), and hydrous silicates, have been done to quantify these ideas. A comparison of the chemical reaction rates with the estimated nebular lifetime of 0.1-10 million years indicates that troilite formation proceeded to completion in the solar nebula. Magnetite formation was much slower and only thin magnetite rims could have formed on metal grains. Hydrous silicate formation is predicted to be even slower, and hydrous silicates in meteorites and interplanetary dust particles probably formed later on the parent bodies of these objects, instead of in the solar nebula.

1. Introduction

Starting with the pioneering work by Harold Urey in the late 1940s and early 1950s, increasingly detailed thermochemical equilibrium calculations have been done to model nebular chemistry, explain the chemistry and mineralogy of chondritic meteorites, and to model planetary bulk compositions and volatile inventories. The underlying, although often unstated, assumption of these calculations is that enough time was available for chemical equilibrium to be reached between gases, gases and grains, and between different grains. However, chemical reactions in the solar nebula and in other protoplanetary disks take place in a dynamic environment with only limited time available to reach chemical equilibrium. Furthermore, different chemical reactions proceed at different rates, which generally decrease exponentially with decreasing temperature. Hence, it is not clear that all reactions, especially low temperature reactions between gases and grains and between different solid grains, can reach equilibrium within the time available. This time may have been as long as the lifetime of the gaseous solar nebula (often taken as 0.1–10 million years), or may have been shorter and limited by radial transport of gas and grains between different temperature regions in the solar nebula.

The question of whether or not chemical reactions in the solar nebula had enough time to reach equilibrium is important because it bears upon first order questions about the origin of our solar system and about the origin of life on Earth. For example, we can ask why Earth has abundant water and is the blue planet while its neighbor and "twin planet" Venus is a hot, desiccated desert. Is this due to the accretion of hydrous minerals by Earth but not Venus or to different evolutionary paths of the two planets? What kind and how much presolar material survived destruction in the solar nebula? How efficient is chemical reprocessing in other protoplanetary disks that we can observe today? The answers to these and other equally important questions require knowledge of chemical reaction rates for gas phase, gas-grain, and solid state reactions.

The importance of kinetic factors was first realized by Urey (1953) who discussed the applications of chemical thermodynamics to nebular chemistry and noted: "Our data in this field give much information relative to possible reactions, and at higher temperatures they certainly give us practically assured knowledge of the chemical situations due to the high velocities of reactions, at least in homogeneous systems, providing the data are adequate, which is unfortunately not always the case. At lower temperatures, thermodynamic equilibrium may not be reached even in periods of time that are long compared to the age of the universe, and at these temperatures the kinetics of thermal or photochemical reactions become important." However, Urey's remarks were not acted on for almost 30 years until after the discovery of isotopic anomalies in meteorites showed that thermal processing was not 100% efficient at homogenizing the presolar gas and grains accreted by the solar nebula. It then became clear that nebular chemistry was more complex than generally believed by most cosmochemists and that it was important to consider kinetic factors as well as equilibrium chemistry (see the review by Fegley, 1993).

The question of gas phase kinetics in the solar nebula was addressed by Lewis and Prinn (1980) who modeled kinetics of the important CO to CH_4 and N_2 to NH_3 conversions in the solar nebula (*cf.* Norris, 1980). Their work quantitatively demonstrated that reduction of CO to CH_4 and of N_2 to NH_3 was extremely slow relative to the estimated lifetime of the gaseous solar nebula. Lewis and Prinn (1980) used a nebular lifetime of 10^{13} seconds from the model of Cameron (1978), but their conclusions are also valid at much longer nebular lifetimes. As a consequence, essentially all carbon and nitrogen in the solar nebula remain as CO and N_2 instead of converting to methane and ammonia, the thermodynamically stable gases at low temperatures. Shortly thereafter Prinn and Fegley (1981) modeled gas phase kinetics in the hypothesized Jovian protoplanetary subnebula and showed that CH_4 and NH_3 formed in this environment. They also generalized their results to other giant planet subnebulae. The differences in the chemistry of carbon and nitrogen in the solar nebula and in Jovian protoplanetary subnebulae are reflected in the types of ices and in the ice/rock ratios of low temperature bodies such as icy satellites and comets formed in the two different environments (Fegley and Prinn, 1989; Prinn and Fegley, 1989).

The related question of gas-grain reaction rates in the solar nebula is also important because it affects the nature and abundance of different types of solid grains accreted by planets and other bodies and also affects the survival of different types of presolar grains (*e. g.*, diamond, graphite, organic matter, silicon carbide). Despite the broad importance of gas-grain reactions; gas-solid and solid phase kinetics are generally more difficult to measure and to model than gas phase kinetics so this area has developed slowly. Prinn and Fegley (1987) discussed the accretion of hydrous minerals by the terrestrial planets during their formation. They opined that hydrous minerals such as tremolite, serpentine and talc are difficult to form in the cold ($<400 \, \text{K}$), low density regions of the solar nebula where these phases are thermodynamically stable because solid state diffusion rates are very slow at these low temperatures. Likewise, Palme and Fegley (1990) argued that FeO-bearing silicates cannot form at the low temperatures where they are thermodynamically stable because of very slow solid state diffusion rates. Recently Gail (1998) argued that solid state diffusion in grains $0.01 \, \mu\text{m}$ in size and larger is slower than the available time for chemistry (taken as 10^{12} seconds) at temperatures below $800 \, \text{K}$.

Both Palme and Fegley (1990) and Gail (1998) used simple scaling calculations and solid state diffusion coefficients to make their points. A related approach was taken by Fegley (1988) who developed a simple collision theory (SCT) model for gas-grain kinetics. The SCT model was then used to estimate the formation rates for troilite (FeS), magnetite (Fe_3O_4), and hydrous silicates, the rate of Fe grain catalyzed CH_4 formation, and the rate of clathrate hydrate formation in the solar nebula and in Jovian protoplanetary subnebulae (Fegley, 1988; 1993; Fegley and Prinn, 1989). Subsequently, experimental work was done on troilite formation kinetics, magnetite formation kinetics, and Fe grain catalyzed CH_4 synthesis (Fegley, 1998; Fegley and Hong, 1998; Hong and Fegley, 1998; Lauretta *et al.*, 1996a-c; Lauretta *et al.*, 1997; 1998). Some of the results of this work are discussed later.

This paper reviews thermodynamics and kinetics of gas-grain reactions in the solar nebula. The equilibrium chemistry discussed is relevant to other protoplanetary disks that have solar composition. The thermochemical kinetic models are also easily applied to other protoplanetary disks. This paper does not cover kinetics of gas phase chemistry in the solar nebula because the chapter by Prinn and Fegley (1989) gives a good review of this topic. Instead the focus is on theoretical and experimental studies of gas-grain reactions thought to be important in the solar nebula and other protoplanetary disks.

2. Evolution and Thermal Structure of the Solar Nebula

A model of the physical conditions in the solar nebula and of how these conditions varied with time is necessary for any discussion of nebular chemistry. A general picture can be obtained from astronomical observations of protoplanetary disks and young stars, from geochemical analyses and geochronological dating of meteorites, and from astrophysical modeling. This type of synthesis has been done

by Cameron (1995) who divides nebular evolution into four stages. Below I give a brief summary of Cameron's model taken from my earlier discussion of chemistry in the outer solar nebula (Fegley, 1999).

Stage 1: Molecular cloud collapse. During this stage, the nebular disk is assembled of infalling material from the collapsing molecular cloud core. This stage lasts for a few times 10^5 years. Most (if not all) of the matter in the disk during this stage ultimately goes into the proto-Sun.

Stage 2: Disk dissipation. The Sun forms during this stage, which lasts for about 50,000 years (*i. e.*, the Sun accretes at a rate of about 2×10^{-5} solar masses per year). The disk mass is less than the mass of the proto-Sun. Most matter falling onto the accretion disk is transported through the disk into the proto-Sun and angular momentum is transported outward in the disk. The major dissipation (*i.e.*, transport) mechanisms include spiral density waves, disk-driven bipolar outflows, and the Balbus-Hawley magnetic instability. Cameron (1995) discusses why turbulent viscosity driven by thermal convection is less important than these other dissipative mechanisms, but some other modelers continue to rely on turbulent viscosity as the main dissipative mechanism. The amount of outward mass transport, that would tend to "contaminate" the outer nebula with products from thermochemical processing in the innermost few AU of the nebula, is controversial and uncertain. Near the end of stage 2, some disk material survived and is preserved in meteorites (*e. g.*, ^{26}Al-bearing minerals).

Stage 3: Terminal accumulation of the Sun. The final accumulation of the Sun occurs during this stage, which lasts for about $(1–2) \times 10^6$ years and the accumulation rate decreases from about 10^{-7} to 10^{-8} solar masses per year. The proto-Sun becomes a classical T Tauri star in this phase. Planetary accretion (almost complete for Jupiter and Saturn, and less advanced for the other planets) occurs during this stage.

Stage 4: Loss of nebular gas. The Sun becomes a weak line T Tauri star in this stage, which lasts $(3–30) \times 10^6$ years, and is no longer accreting material from the disk. The T Tauri wind removes gas in the inner nebula and photoevaporation due mainly to UV radiation from the T Tauri wind removes gas in the outer nebula. Ultraviolet photochemistry and ion-molecule chemistry may be important disequilibrating processes in the outer nebula, but their importance depends on the poorly constrained and time dependent nebular column density. Gas-grain chemistry throughout the nebula ceases sometime (although not necessarily at the same time everywhere) during this stage.

In this model of nebular evolution, accumulation of the Sun consumed essentially all of the material accreted by the nebular disk during the early stages of its history. Planets and all the other bodies in the solar system were then assembled from material accreted after the Sun had formed (*i. e.*, during the time from the end of stage 2 into stage 4). I think the conclusion that most of the material in solar system bodies dates from the latter part of nebular history is robust, whether or not one accepts all details of Cameron's (1995) synthesis or prefers a somewhat diffe-
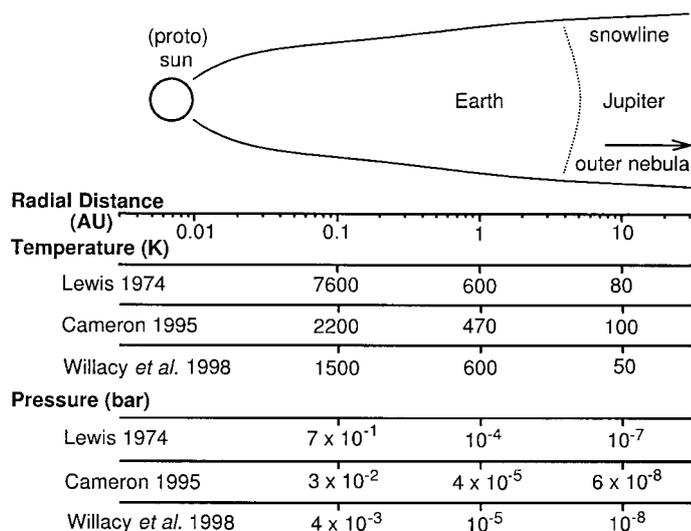
Figure 1. A schematic diagram comparing the radial variation of temperature and pressure for the solar nebula models of Lewis (1974), Cameron (1995), and Willacy et al. (1998). In the cartoon at the top the calculated snowline, where water vapor condenses to water ice, divides the solar nebula into an inner (<5.2 AU) and an outer (≥5.2 AU) region. Most of the latter region is not shown here. Modified from Fegley (1999).

Radial Distance (AU)	0.01	0.1	1	10
Temperature (K)				
Lewis 1974		7600	600	80
Cameron 1995		2200	470	100
Willacy et al. 1998		1500	600	50
Pressure (bar)				
Lewis 1974		7×10^{-1}	10^{-4}	10^{-7}
Cameron 1995		3×10^{-2}	4×10^{-5}	6×10^{-8}
Willacy et al. 1998		4×10^{-3}	10^{-5}	10^{-8}

rent model (e. g., see the review by Boss, 1998). If this conclusion is adopted, as done in this paper, it is clear that the temperature and pressure in the nebula during its latter history are important for discussions of nebular chemistry because the material accreted by planets and other bodies was chemically reprocessed (to a greater or lesser extent) during this time.

Figure 1 contrasts three models (Lewis, 1974; Cameron, 1995; Willacy et al., 1998) of temperature and pressure as a function of radial distance in the solar nebula. These three models are derived using different assumptions and differ in detail. Lewis' (1974) thermal profile gives higher temperatures and pressures at a given radial distance in the inner solar nebula than the other two models. But all three models predict temperatures that agree within a factor of two and pressures that agree within an order of magnitude throughout most of the solar nebula. These three models are snapshots at one moment in time when the snowline, where water ice condenses, was at Jupiter's present orbit (5.2 AU). This is also the time when Jupiter started to form because water ice was the "glue" needed for its runaway accretion (Stevenson and Lunine, 1988), and falls into stage 3 of Cameron's (1995) model. Observations of asteroids with hydrous spectral features (Jones et al., 1990) suggest that the snowline moved inward to the asteroid belt. Presumably this occurred during Cameron's stage 4 when nebular gas was dissipated.

3. Thermodynamic Predictions for Gas-Grain Chemistry of Solar Composition Material

Figure 2 illustrates several important gas-grain reactions that are predicted by thermochemical equilibrium modeling of the chemistry of solar composition material. Comprehensive summaries of nebular condensation calculations, including listings for all natural elements of their major gases, condensates, condensation tempera-

tures, and of the computational methods used are given by Larimer (1988), Fegley (1997), and Lodders and Fegley (1998). The discussion in this paper focuses on the key reactions involved in the temperature-dependent equilibrium chemistry of Mg, Si, Fe, and S, which are the four major rock-forming elements. The solids formed by combination of these four elements with each other and with oxygen (*e. g.*, Fe, FeS, $MgSiO_3$, and Mg_2SiO_4) constitute about 91% by mass of the material accreted by the terrestrial planets.

Let's start by considering the cosmochemistry of iron, the most abundant metal in solar composition material. Iron initially condenses as Fe alloy (containing smaller amounts of Ni, Co, and other siderophile elements dictated by their elemental abundances and volatility). The net thermochemical reaction describing iron condensation is

$$Fe \ (gas) \ = \ Fe \ (alloy), \tag{1}$$
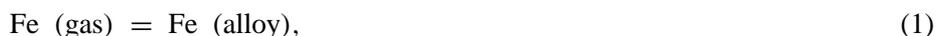
which is shown by the line labeled "Fe" in Fig. 2. Thermodynamically, this line shows the highest temperature at which Fe alloy is stable at any pressure in solar composition material. Traditionally, cosmochemists also interpreted this line as the Fe alloy condensation curve, which shows the temperatures where Fe alloy first starts to condense from the gas as a function of total pressure in the solar nebula. Because of the exponential dependence of vapor pressure with temperature, essentially no iron is present in the gas at temperatures about 100 degrees below this line. All chemistry involving iron at lower temperatures takes place by the reaction of Fe-rich metallic alloy with nebular gas.

About 200 degrees below the "Fe" line in Fig. 2, some of the condensed iron reacts with phosphorus gases to form the mineral schreibersite (mainly Fe_3P but also containing some Ni and Co). Both the gas phase chemistry of phosphorus, which determines the major phosphorus gas and the formation of schreibersite are pressure dependent (*e. g.*, see Fegley and Lewis, 1980). Schreibersite formation only consumes a few percent of all the iron because the solar abundance of iron is much larger than the solar abundance of phosphorus (the atomic Fe/P ratio in solar material is about 110).

A much more significant reaction takes place at 710 K when hydrogen sulfide (H_2S) starts to corrode the Fe alloy grains to form troilite (FeS). This occurs via the net thermochemical reaction

$$Fe \ (alloy) + H_2S \ (gas) \ = \ FeS \ (troilite) + H_2 \ (gas) \tag{2}$$

and consumes about 50% of all iron. Because there is no change in the number of gas molecules in reaction (2), it is pressure independent unlike many of the other curves in Fig. 2.

Thermodynamic modeling predicts that two other reactions take place at lower temperatures and consume the remaining Fe metal. One reaction, which continually proceeds and becomes increasingly important with decreasing temperature, is incorporation of ferrous iron (Fe^{2+}) into magnesian silicates. This occurs via the
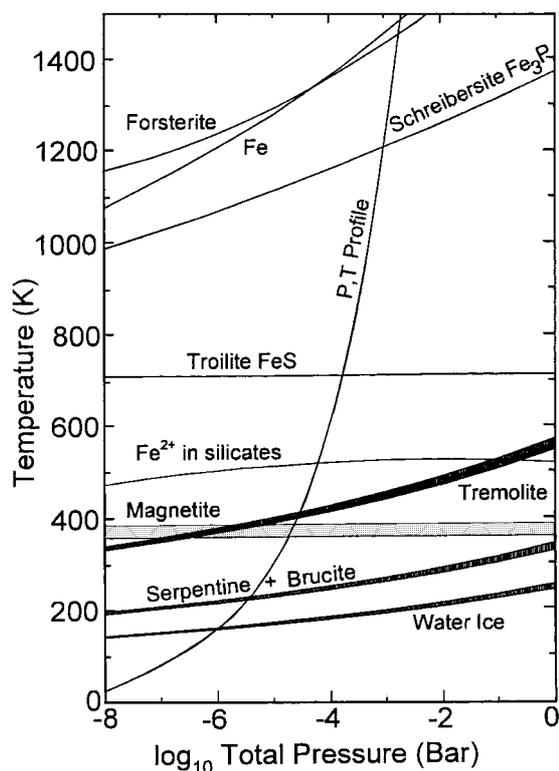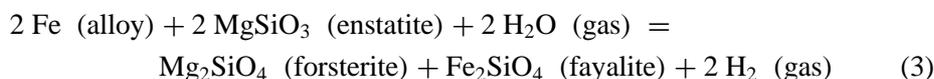
Figure 2. Thermodynamic predictions for the nebular chemistry of the four most abundant rock-forming elements (Mg, Si, Fe, and S) in solar composition material. Iron metal and magnesian silicates (*e. g.*, forsterite) initially condense from the gas at high temperatures and are stable on and below the curves. With decreasing temperature, gas-grain reactions between a pre-existing condensate such as Fe metal and different gases form new solids. For example, phosphorus gases consume some Fe to form schreibersite (Fe_3P), H_2S reacts with metal to form troilite (FeS), and the remaining Fe reacts with water vapor to make magnetite (Fe_3O_4). Curves for the formation of hydrous minerals and the condensation of water ice are also shown. The magnetite, hydrous mineral, and water ice curves are shaded to illustrate the effects of oxygen partitioning between CO and H_2O on formation temperatures of these phases. A plausible pressure, temperature profile for the solar nebula, based on the work of Lewis (1974), is also shown.

net thermochemical reaction

$$2 \, Fe \ (alloy) + 2 \, MgSiO_3 \ (enstatite) + 2 \, H_2O \ (gas) =$$
$$Mg_2SiO_4 \ (forsterite) + Fe_2SiO_4 \ (fayalite) + 2 \, H_2 \ (gas) \qquad (3)$$

in which iron metal is oxidized by water vapor and reacts with enstatite, another high temperature phase. Reaction (3) is represented by the line labeled "Fe^{2+} in silicates" on Fig. 2. The minerals forsterite and fayalite do not form separately, but are in solid solution together in olivine. As discussed by Barshay and Lewis (1976), reaction (3) is complete by about 480 K when the remaining 50% of iron (*i. e.*, the Fe not already in FeS and Fe_3P) has been oxidized to Fe-bearing silicates. Finally, any Fe that escapes reaction (3) for one reason or another can be consumed by nebular water vapor at about 370 K via the net thermochemical reaction

$$3 \, Fe \ (alloy) + 4 \, H_2O \ (gas) = Fe_3O_4 \ (magnetite) + 4 \, H_2 \ (gas). \qquad (4)$$

Reaction (4), like reaction (2), is pressure independent because there is no change in the number of gas molecules during magnetite formation.

It is instructive to also review the cosmochemistry of Mg and Si, the other two major rock-forming elements. The condensation at high temperatures of refractory

silicates such as melilite, a solid solution of gehlenite ($Ca_2Al_2SiO_7$) and åkermanite ($Ca_2MgSi_2O_7$), removes several percent of Mg and Si from the gas. The amount of melilite formed is limited by the Ca and Al abundances, which are about ten times lower than those of Mg and Si (in solar material the atomic Mg/Si ratio is about unity while the atomic Mg/Ca and Mg/Al ratios are about 16 and 12, respectively). Most Mg and Si remain in the gas until forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) condense at about the same temperature as Fe alloy. Forsterite condensation proceeds via the net thermochemical reaction

$$2\,Mg\ (gas) + SiO\ (gas) + 3\,H_2O\ (gas)\ =$$
$$Mg_2SiO_4\ (forsterite) + 3\,H_2\ (gas) \tag{5}$$
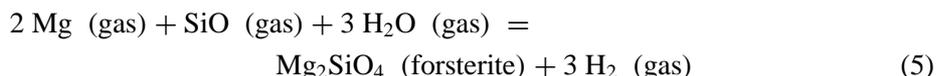
and is shown in Fig. 2. The forsterite and Fe metal curves intersect; forsterite condenses first at lower pressures. Enstatite forms a few tens of degrees below the forsterite condensation curve and a slightly different net thermochemical reaction is involved

$$Mg_2SiO_4\ (forsterite) + SiO\ (gas) + H_2O\ (gas)\ =$$
$$2\,MgSiO_3\ (enstatite) + H_2\ (gas). \tag{6}$$
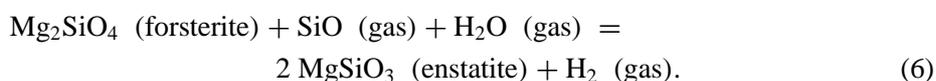
The enstatite condensation line lies close to the forsterite line and is not shown in Fig. 2. As discussed above, thermodynamic calculations predict that oxidation of Fe alloy becomes significant at temperatures of a few hundred degrees Kelvin and forms Fe-bearing silicates. Some enstatite is consumed as a result of reaction (3), but otherwise, forsterite and enstatite are essentially unaltered until very low temperatures where hydrous minerals are predicted to become stable. For example, serpentine formation is predicted via the net thermochemical reaction

$$Mg_2SiO_4\ (forsterite) + MgSiO_3\ (enstatite) + 2\,H_2O\ (gas)\ =$$
$$Mg_3Si_2O_5(OH)_4\ (chrysotile\ serpentine) \tag{7}$$
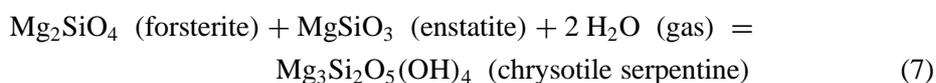
at temperatures from 200 to 400 K depending on the total pressure in the solar nebula. However, as argued by Prinn and Fegley (1987), serpentine formation via reaction (7) is very unlikely because the required solid state diffusion is very slow at the temperatures where serpentine becomes thermodynamically stable. As discussed later, the hydration of isolated forsterite grains is also probably kinetically inhibited. Finally, thermochemical equilibrium modeling predicts that enstatite is finally consumed by formation of talc ($Mg_3Si_4O_{10}(OH)_2$) and brucite ($Mg(OH)_2$) via the net thermochemical reaction

$$4\,MgSiO_3\ (enstatite) + 2\,H_2O\ (gas)\ =$$
$$Mg_3Si_4O_{10}(OH)_2\ (talc) + Mg(OH)_2\ (brucite) \tag{8}$$
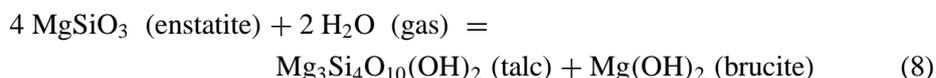
at similar temperatures. Again, as discussed later, kinetic limitations almost certainly prevent reaction (8) from taking place in the solar nebula.

4. Kinetic Considerations

Although thermodynamic predictions like those reviewed above for the major rock-forming elements are a useful starting point, they do not tell us how or how fast chemical reactions actually proceed. I have tried to emphasize this point by repeatedly referring to the net thermochemical reactions involved in Fe alloy condensation, troilite formation, magnetite formation, and so on. Although we can write down chemical equations that are balanced and involve the thermodynamically stable gases and solids, the actual reaction mechanisms are different and considerably more complex. The reaction rates depend upon the reaction mechanisms and are essential for determining whether or not the predicted equilibrium chemistry can take place in the available time. This is true for gas phase chemistry, condensation of solids from gas, gas-grain reactions, gas-melt reactions (if any), and solid state reactions that are predicted in the solar nebula.

For example, the homogeneous condensation of Fe metal and other solids from a gas involves the formation of a critical sized condensation nucleus by statistical fluctuations of atomic or molecular clusters in the gas. Typically, the gas has to be supersaturated before condensation nuclei form and condensation occurs. Cameron and Fegley (1982) discussed this process using Salpeter's (1974) modifications to classical nucleation theory and concluded that substantial super saturation and hence super cooling is required for homogeneous condensation. It is difficult to calculate the exact super saturation that is required because of uncertainties in theory and in the surface energies of condensates, so it is hard to predict the "real" condensation temperatures. Theoreticians modeling the nucleation of dust grains around cool stars reach similar conclusions, namely that significant super cooling is required for homogeneous condensation of solid grains (*e. g.*, Sedlmayr and Krüger, 1997). On the other hand, thermochemical equilibrium calculations for carbon stars predict formation of graphite and SiC grains at temperatures and radial distances that match the observed radial distances for inner edges of the dust shells. This correspondence between thermochemical equilibrium calculations and astronomical observation suggests that for one reason or another very little super cooling occurs during dust formation around carbon stars (Lodders and Fegley, 1997).

It is not yet possible to observe protoplanetary disks at high enough resolution to observe the condensation of refractory dust (and the dust composition) as a function of radial distance and temperature in the disk. However, the existence of Ca,Al-rich inclusions in some meteorites shows that refractory phases similar to those predicted by condensation calculations formed in the solar nebula. Apparently, barriers to homogeneous nucleation were overcome, or preexisting condensation nuclei were available, or some other factors led to condensation of refractory minerals similar to those predicted by thermochemical equilibrium modeling. But the presence of CAIs in meteorites shows that these objects stopped reacting with the nebular gas for some reason. Otherwise, the high temperature minerals in them would have been converted to other, more stable phases at lower temperatures

and the CAIs would not be present in the meteorites. The preservation of CAIs is plausibly related to their rapid cooling after their formation in the solar nebula. Clearly, our understanding of grain nucleation and condensation is incomplete and more experimental and theoretical work is needed to help us to understand grain formation in the solar nebula, other protoplanetary disks, and around cool stars. This area is very important and should not be neglected, as often done by many cosmochemists. However, nucleation theory is not the main subject of this review but is only mentioned to show that kinetic factors are important for nebular chemistry at high, as well as low, temperatures.

Now let's consider gas phase chemistry. As noted earlier, the chapter by Prinn and Fegley (1989) reviews gas phase chemical kinetics in the solar nebula, so this topic is not covered in detail here. However, it is worth briefly discussing the gas phase conversion of CO to CH_4 to stress the point that net thermochemical reactions are different than the actual reaction mechanisms.

In solar composition material, CO is the dominant carbon gas at high temperatures and low pressures, while CH_4 is the dominant carbon gas at low temperatures and high pressures. The conversion between CO and CH_4 occurs via the net thermochemical reaction

$$CO + 3H_2 = CH_4 + H_2O. \tag{9}$$

However, three hydrogen molecules do not simultaneously collide with a CO molecule to yield one methane molecule and one water molecule. Instead, reaction (9) plausibly proceeds via a series of elementary reactions (*i.e.*, the actual chemical steps that take place) such as

$$H_2 = H + H \tag{10}$$
$$CO + H_2 = H_2CO \ \ (formaldehyde) \tag{11}$$
$$H_2CO + H_2 \rightarrow CH_3 + OH \tag{12}$$
$$CH_3 + H + M = CH_4 + M \tag{13}$$
$$H + OH + M = H_2O + M \tag{14}$$
$$Net \ Reaction : CO + 3H_2 = CH_4 + H_2O. \tag{9}$$

The M in Eqs. (13) and (14) is any third body, statistically H_2 or He in the solar nebula, and is necessary to absorb the energy released by forming the H_3C-H bond in methane and the H-OH bond in water. The net effect of this series of elementary reactions is reaction (9), but the actual mechanism is more involved than the net reaction. Kinetic modeling of the CO⟶CH_4 conversion (and of other gas phase reactions) thus needs to take into account the rates of the elementary reactions that make up the reaction mechanism (*cf*. Prinn and Fegley, 1989).

Likewise, gas-grain reactions such as the formation of troilite, magnetite, and hydrous silicates take place via a series of elementary reactions that are different than and not as simple as the net thermochemical reactions. For example, gas

molecules must collide with solid grains to react with them. Initially, reaction rates depend on factors such as the temperature, gas partial pressure, and grain size (surface to volume ratio). Higher temperatures, higher pressures, and smaller grains increase the reaction rate. 'Fluffy' and porous grains react faster because the surface to volume ratio is increased. Amorphous grains react faster than crystalline grains of the same material because they are thermodynamically less stable. Conversely, lower temperatures, lower pressures, and larger grains decrease reaction rates. Once a sufficiently thick adherent, non porous product layer coats the unreacted solid, reaction rates shift from linear kinetics (chemical control) to parabolic kinetics (diffusion control) and slow down. The critical thickness for the transition from linear to parabolic kinetics varies for each reaction and depends on the temperature. An example for troilite (FeS) formation on iron metal is given later. An easily understood derivation of the parabolic rate law is given by Benson (1982). A more detailed discussion of parabolic kinetics and its applicability to gas-solid reactions is presented by Schmalzried (1995).

The extent to which gas-grain chemistry can proceed with decreasing temperature is dependent on the chemical reaction rates relative to the rates of nebular mixing and overall cooling. If the gas-grain reaction is much faster than the rate at which the gas parcel is mixed to cooler nebular regions (or than the rate at which overall cooling or dissipation of the nebula proceeds), then chemical equilibrium will be closely approached as cooling proceeds. However, if the chemical conversion is much slower than the rate at which mixing to cooler regions (or overall cooling) occurs, then the higher temperature chemical equilibrium will be frozen in, or quenched at some point, and the grain chemistry in cooler regions will be the same as that established at the quench point. If we denote the characteristic chemical lifetime for a gas-grain chemical reaction by t_{chem} and the characteristic nebular mixing (or overall cooling) time by t_{neb}, the former case is represented by the inequality $t_{chem} < t_{neb}$ and the latter case is represented by the inequality $t_{chem} > t_{neb}$. The intermediate case which occurs at the quench temperature (T_Q) is represented by the equality $t_{chem} = t_{neb}$. Once expressions for t_{chem} and t_{neb} are available, it is possible to calculate the position of the quench temperature T_Q in a solar nebula model.

The value of t_{neb} depends on the rate of radial mixing in the solar nebula. Some authors have estimated a lower limit for $t_{neb} \sim 3H/V_s \sim 10^8$ seconds (about 3 years), where H is the radial density scale length and V_s is the sound speed in the solar nebula (e. g., Lewis and Prinn, 1980). Others have defined t_{neb} as the time for temperature changes of a dust grain moving with a characteristic inward drift velocity in an accretion disk and used a value of 10^{12} seconds, about 32,000 years (e. g., Eq. 66 of Gail, 1998). The upper limit for t_{neb} is the lifetime of the gaseous solar nebula. This is uncertain, but as discussed by Podosek and Cassen (1994), current estimates for the lifetime of the solar nebula are about 3×10^{12} to 3×10^{14} seconds (about 100,000 years to 10 million years). Taking the upper limit for t_{neb} as the nebular lifetime is equivalent to assuming that the nebula undergoes mixing

once over its lifetime or that the overall cooling time is the same as the lifetime of the gaseous nebula. In reality, the time available for gas-grain chemistry to occur is probably in between the lower and upper limits for t_{neb}, but the longest possible time for chemical equilibrium to be reached is given by the nebular lifetime.

Gas-grain reactions with t_{chem} values $>10^8$ seconds but less than the nebular lifetime may be quenched before proceeding significantly in turbulent, rapidly mixed regions of the solar nebula but might occur in quiescent, poorly mixed regions of the solar nebula. On the other hand, gas-grain reactions with t_{chem} values $>t_{neb}$ will be quenched irrespective of the strength of nebular mixing. But, how do we determine the t_{chem} value for a gas-grain reaction? The t_{chem} value for a gas phase reaction such as conversion of CO to CH_4 is calculated from the rate constant for the rate determining step (*i. e.*, the slowest elementary reaction (Prinn and Fegley, 1989). The mechanistic and kinetic data are known because of experimental studies done in other areas of science and technology. However, very few gas-grain reactions have been studied under solar nebula conditions, so the mechanisms and their rate determining steps are generally unknown. So, a simpler approach was needed initially to model kinetics of gas-grain reactions in the solar nebula.

5. Simple Collision Theory Modeling

Simple collision theory (SCT) was developed to calculate the chemical lifetimes for troilite, magnetite, hydrous silicate, and clathrate hydrate formation in the solar nebula and in the subnebulae believed to exist around Jupiter and the other gas giant planets during their formation (Fegley, 1988; 1993; Fegley and Prinn, 1989). The SCT models assume fully dense, monodispersed spherical grains. A variety of grain sizes, ranging from very fine grains comparable in size to fine grained meteorite matrix to much larger grains comparable in size to chondrules are used for modeling. Real grains may not be spherical, but may have other geometries, for example like the fractal aggregates produced by Blum and colleagues (*e. g.*, Wurm and Blum, 1998). The important effect of grain shape is to alter the surface to volume ratio of the grains, which is why a wide range of grain sizes was modeled. Also one might expect that the size and size distribution of solid grains in the solar nebula was not static, but varied with time as grain growth occurred. Grain growth is important for chemistry because it may decrease the surface/volume ratio of solid grains and decrease the rate of gas-grain reactions. However, the experiments by Wurm and Blum (1998) indicate that large aggregates formed from individual grains can have the same surface to volume ratio as the smaller individual grains.

Now let's discuss the basis of SCT models. The collision rate, σ_i (molecules per cm^2 per second), of a particular gas i with grains is given by the equation

$$\sigma_i = 10^{25.4} \frac{P_i}{(M_i T)^{\frac{1}{2}}}, \tag{15}$$

where P_i is the partial pressure of gas i in bars, M_i is the molecular weight of the gas in g mol^{-1}, and T is the temperature in Kelvin. Equation (15) comes from the kinetic theory of gases. The total number of collisions (per second) of molecules of gas i with all solid grains of a particular type in each cm^3 of the solar nebula is given by

$$\nu_i = \sigma_i \times A, \tag{16}$$

where A is the total surface area of all solid grains of a particular type per each cm^3 of the nebula. For example, if troilite formation (reaction (2)) is being considered, then the total number of collisions of H_2S gas molecules with monodisperse, spherical metal grains that are fully dense and uniformly distributed at solar abundance in the nebular gas is calculated. Typically grain radii from $0.1\,\mu$m to $100\,\mu$m are used in the model calculations.

A collision time constant t_{coll}, which is the time required for all molecules of gas i to collide with all solid grains of a particular type in each cm^3 of the solar nebula, can be calculated from the equation

$$t_{coll} = \frac{[i]}{\nu_i}, \tag{17}$$

where $[i]$ is the molecular number density of gas i. Now, if every collision of a gas molecule with a grain led to chemical reaction, then t_{coll} would also be the chemical time constant t_{chem} for the gas-grain reaction. However, only a small fraction of collisions that have the necessary activation energy E_a lead to a chemical reaction. This fraction of reactive collisions is given by

$$f_i = \nu_i \exp\left(-\frac{E_a}{RT}\right), \tag{18}$$

where R is the ideal gas constant. Then the chemical time constant for the gas-grain reaction is

$$t_{chem} = \frac{[i]}{f_i} = t_{coll} \exp\left(\frac{E_a}{RT}\right). \tag{19}$$

The activation energy used in Eqs. (18) and (19) is different for each reaction and has to be taken from the literature. In some cases, not all the gas can be consumed by the gas-grain reaction and in these cases $[i]$ is multiplied by a stoichiometric factor. For example, in the case of hydrous silicate formation by reaction (7) or an analogous reaction, only a fraction of all water can eventually be reacted because the abundance of silicates such as olivine and enstatite is limited by the Mg and Si abundances, which are smaller than the water vapor abundance. The water vapor number density in Eq. (19) is then multiplied by a stoichiometric factor equal to the olivine/H_2O molar ratio.

The predictions of the SCT models for three exemplary reactions, formation of troilite (FeS), magnetite (Fe_3O_4), and the hydrous silicate chrysotile serpentine

Figure 3. Chemical lifetimes from SCT modeling for the formation of troilite (FeS), magnetite (Fe_3O_4), and chrysotile serpentine ($Mg_3Si_2O_5(OH)_4$) in the solar nebula. The vertical dashed lines show the temperatures where these three phases become stable. A range of temperatures, indicated by the shading, is shown for magnetite, serpentine, and water ice because the distribution of oxygen between CO and H_2O affects these condensation temperatures. The chemical lifetime (t_{chem}) curves are extended as dashed lines to temperatures above the formation temperatures of these phases to illustrate temperature-dependent trends. The thick shaded horizontal bar shows the current estimates of 0.1–10 million years for the solar nebula lifetime. Troilite formation can easily occur within the nebular lifetime, but serpentine formation cannot because it apparently requires times about equal to the age of the solar system. Modified from Fegley (1988).
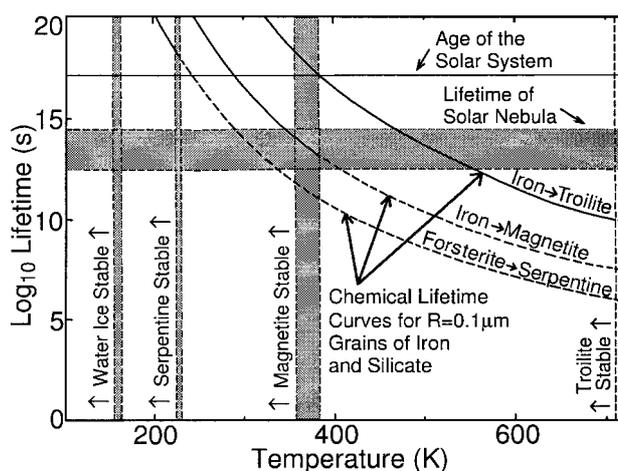
($Mg_3Si_2O_5(OH)_4$) are illustrated in Fig. 3. In all cases grain sizes of 0.1 μm, about the same as the size of interstellar grains and fine-grained meteorite matrix, were assumed. Thus, the predicted reaction rates are faster than would be the case for larger grains. As discussed above, thermochemical calculations predict that these three reactions are important for retention of sulfur, oxidized iron, and water in the solid grains accreted by the terrestrial planets. The SCT models predict that troilite formation is very rapid relative to the lifetime of the gaseous solar nebula. In contrast, the SCT models predict that the time required for magnetite formation is about equal to the nebular lifetime and serpentine formation is impossibly slow. These three reactions thus exemplify gas grain reactions that proceed to completion, that are quenched after incomplete reaction, and that do not proceed at all. They are discussed in some more detail in the next three sections.

6. Kinetics and Mechanism of Iron Sulfide Formation

Troilite (ideally FeS) is predicted to form via reaction (2) at a pressure independent temperature of 710 K in the solar nebula (see Fig. 2). This reaction is important for several reasons. It involves two of the four most abundant rock-forming elements in the solar system and it is predicted to be the mechanism by which sulfur is retained in solids accreted by the terrestrial planets during their formation. Sulfur is a biologically important element found in essential amino acids (methionine and cysteine) and in proteins (where the disulfide linkages provide three dimensional structure and mechanical strength). It is also important for planetary differentiation and evolution because the melting of a Fe-FeS eutectic mixture occurs at

about 1260 K, about 550 degrees lower than the melting point of pure iron, thus facilitating segregation of metal-sulfide melt and core formation on the terrestrial planets and for rocky planets in other planetary systems. In addition, sulfur gases and aerosols in the atmospheres of Venus and Earth are major influences on the climates of these two planets. Reaction (2) is also of interest because iron sulfides are ubiquitous in meteorites. So there are a number of very good reasons for being interested in FeS formation.

Simple collision theory modeling predicts that FeS formation was rapid in the solar nebula (Fegley, 1988). For example, calculations for 0.1 μm radius metal grains predicted a t_{chem} for FeS formation of about 320 years at the FeS formation temperature (see Fig. 3). This is very rapid relative to all estimates of the solar nebula's lifetime and relative to estimates of radial mixing in the nebula. The SCT model predictions agree with the intuitive expectation that "tarnishing" of iron metal by H_2S in the solar nebula (like tarnishing of sterling silverware by atmospheric sulfur gases) is facile. However, the SCT modeling used an activation energy measured for FeS formation from Fe metal in H_2 gas mixtures containing 1–70% H_2S. These gas mixtures are much richer in H_2S than solar composition gas where the H_2S/H_2 ratio is about 33 parts per million by volume (ppmv) and where the activation energy may be different. In any case, the prediction that FeS formation is rapid led my group to study FeS formation from high purity Fe metal and from iron meteorite metal first, before studying other gas-grain reactions, which are expected to be much slower (Lauretta et $al.$, 1996a; 1996b; 1996c; Lauretta et $al.$, 1997; 1998).

The experiments were done by heating metal samples at atmospheric pressure in H_2S/H_2 gas mixtures for different times at several different temperatures. Several gas mixtures with H_2S concentrations ranging from ~25 ppmv to ~10,000 ppmv were used, and they span the expected H_2S/H_2 ratio of 33 ppmv in the solar nebula. We were able to measure the effect of H_2 on the FeS formation rate by using the different concentration gas mixtures (Lauretta et $al.$, 1996a). The corrosion of metal samples has been extensively studied, but the prior work on Fe sulfide formation was done in gases relevant to industrial applications (sulfur vapor, OCS/CO/CO_2 mixtures, H_2S-rich gases). Our experiments are the only ones done in H_2S/H_2 mixtures at the low H_2S concentrations relevant to the solar nebula and to other protoplanetary disks around solar (or near solar) composition stars.

The reacted samples were analyzed by different techniques that give information on their chemistry, microstructure, and morphology. For example, Figure 4 displays photomicrographs of iron metal foils that were heated isothermally for different times in gas with an H_2S/H_2 ratio of about 1000 ppmv. These cross section views show that reaction (2) proceeds by the formation of an Fe sulfide layer on the iron metal. The thickness of the sulfide layer varies linearly with time until a critical thickness is reached. Then the diffusion of Fe^{2+} ions to the solid-gas interface where the chemical reaction occurs becomes rate limiting. The sulfide layer then grows at a slower parabolic rate which is proportional to the square root
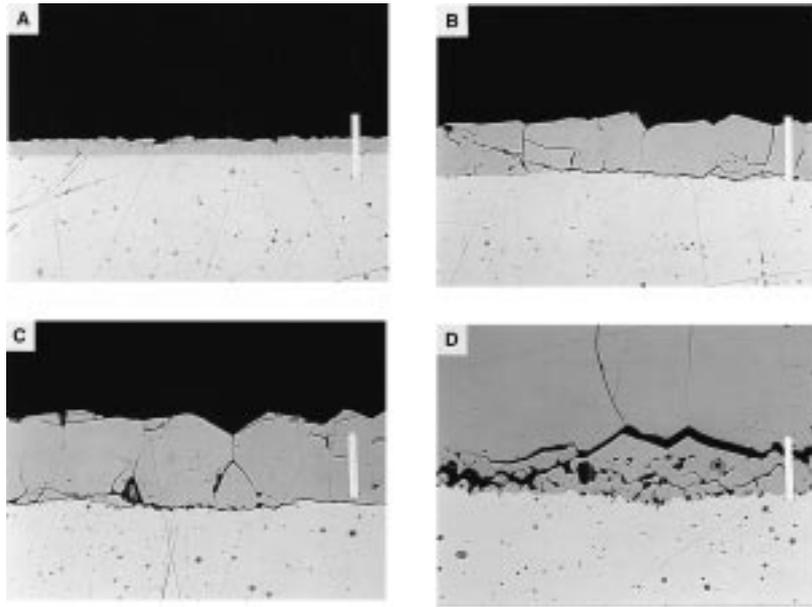
Figure 4. Four optical, reflected light photomicrographs of the cross sections of iron metal samples that have been partially reacted to iron sulfide. All samples were formed in a H_2S/H_2 gas mixture containing about 1,000 ppmv H_2S at 778 K. Reaction times are 5, 24, 48, and 450 hours for Figs. 4A to 4D, respectively. Each scale bar is 32 mm long. From Lauretta *et al.* (1996a).

of time. The outward diffusion of iron causes the formation of a void between the sulfide layer and the metal. The sulfide layer deforms plastically to fill this gap, but eventually a deformation limit is reached and the sulfide layer cracks. The cracks allow the gas to penetrate to the metal surface and formation of a new sulfide layer begins. Sometimes the inner layer also cracks and a third layer develops; sometimes blistering of a layer occurs. Other morphological variations that are correlated with the temperature and H_2S/H_2 ratio are also observed and are illustrated in Fig. 4 of Lauretta *et al.* (1996a). Generally, two sulfide layers develop and the inner layer is composed of smaller, randomly oriented crystals while the outer layer is composed of larger, uniformly oriented crystals.

The weight gain (Δw) of reacted samples shows the same behavior as the thickness of the sulfide layers. Initially, Δw varies linearly with time and the equation

$$\frac{\Delta w}{A} = k_1 t, \tag{20}$$

where A is the surface area of the sample gives the apparent linear rate constant (k_1) with units of g cm^{-2} hr^{-1}. Then a transition occurs and a slower weight gain that varies parabolically and follows the equation

$$\left(\frac{\Delta w}{A}\right)^2 = k_p t \tag{21}$$

is observed. The parabolic rate constant (k_p) has units of g^2 cm^{-4} hr^{-1}. The thickness change of the sulfide layer with time can also be used to express the linear and parabolic rate constants (*e. g.*, cm hr^{-1} and cm^2 hr^{-1}, respectively).

The rate of FeS formation in the linear and parabolic kinetic regimes and the critical thickness at which the transition from linear to parabolic kinetics occurs were measured experimentally. These data allowed Lauretta *et al.* (1996a) to model the rate of FeS formation from Fe grains of different sizes in the solar nebula. This work shows that FeS formation is very rapid and will easily proceed to completion removing all H$_2$S from the gas within a small fraction of the nebular lifetime. Reaction (2) is a gas-grain reaction that reaches equilibrium in a short time in the solar nebula.

Additional work on the corrosion of iron meteorite metal by H$_2$S/H$_2$ gas mixtures also gave kinetic data for Fe sulfide formation, and showed how Ni and other trace elements (Co, P) affect the reaction (Lauretta *et al.*, 1996c; 1997; 1998). This work is very interesting for interpreting the origin of sulfides in chondritic meteorites that have not experienced much heating and metamorphic alteration on their parent bodies. Characteristic chemical signatures are observed in sulfides formed from Fe alloys. For example, the bulk Fe/Ni ratios in sulfide and metal are the same within error, the Ni concentration increases from the metal-sulfide to the sulfide-gas interface, and pentlandite [(Fe,Ni,Co)$_{9-x}$S$_8$] inclusions form in the sulfide layers. These features can be destroyed during thermal metamorphism, and hold the potential for distinguishing nebular from parent body sulfides. These experiments show that it is important to do more analytical studies of Ni-bearing sulfides in chondrites to see which (if any) Ni-bearing sulfides are nebular remnants and which are parent body products.

7. Kinetics and Mechanism of Magnetite Formation

As shown in Fig. 2, magnetite (ideally Fe$_3$O$_4$) is predicted to form via reaction (4) at about 370 K in the solar nebula. The exact temperature depends on the partitioning of oxygen between water vapor and CO (see Fig. 2). Intuitively, we might think that metal grains will react rapidly in a moist environment. However, at the temperature where magnetite becomes thermodynamically stable in the nebula, the partial pressure of water vapor is very low. As shown in Fig. 1, nebular models predict total pressures of 10^{-5} bars (or less) at 370 K, and in a solar composition gas the H$_2$O partial pressure is about 1000 times lower than the total pressure. So, at 370 K the H$_2$O partial pressure will be 10^{-8} bars (or less) and we have to ask how rapidly H$_2$O vapor will react with Fe at these low temperatures and pressures.

As illustrated in Fig. 3, the SCT models predict that magnetite formation from 0.1 μm radius metal grains takes $\sim$320,000 years in the solar nebula (Fegley, 1988). This is about equal to Cameron's (1978) estimate of 10^{13} seconds for the lifetime of the solar nebula, but is within the range of 0.1–10 million years given by Podosek and Cassen (1994). Depending on the assumed lifetime of the gaseous solar nebula,

magnetite formation may or may not be kinetically favorable according to the SCT models. However, as noted by Fegley (1988), the activation energy for wüstite ($Fe_{0.947}O$) formation at high temperatures in water-rich H_2/H_2O gas mixtures had to be used to calculate the t_{chem} for magnetite formation because the activation energy for magnetite formation in H_2/H_2O mixtures was unknown at the time.

Hong and Fegley (1998) studied reaction (4) in H_2/H_2O gas mixtures using pure iron metal and metal from the Gibeon iron meteorite. They found that the rate of magnetite formation from both samples was very much slower than the rate of FeS formation at the same temperature. In fact, their initial experiments showed that magnetite layers grew so slowly that they used powders instead of foils in most of their experiments. The contrast between the formation rates of magnetite and FeS reflects the slower Fe^{2+} diffusion rate in magnetite than in Fe sulfide. Iron diffusion is much slower in magnetite because at low temperatures magnetite is essentially stoichiometric with a very small number of vacancies while Fe sulfide is non-stoichiometric and has a much larger number of vacancies, which provide a pathway for rapid diffusion. Magnetite formed more slowly on the Gibeon iron meteorite metal than on pure Fe metal and also contained fairly large amounts of Ni and Co, presumably as the spinels $NiFe_2O_4$ and $CoFe_2O_4$ dissolved in Fe_3O_4. Hong and Fegley (1998) found that magnetite formation followed parabolic (*i.e.*, diffusion controlled) kinetics. They used their kinetic data for pure Fe and Gibeon iron meteorite metal to calculate the Fe_3O_4 formation rate in the solar nebula. The reaction times for 0.1–1 μm radius metal grains are generally within estimated lifetimes of the solar nebula (0.1–10 million years). However, the calculated reaction times are probably lower limits because they used gas mixtures with H_2/H_2O ratios of 4–41, much smaller than the values of 794 (all C as CH_4) to 1808 (all C as CO) expected in the solar nebula. By analogy with FeS formation, the magnetite formation rate is expected to decrease as the H_2/H_2O ratio increases, and magnetite formation in the solar nebula is probably very slow relative to the nebular lifetime.
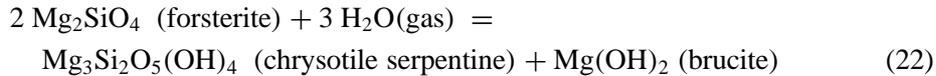
As argued earlier (Fegley, 1993), and now supported by the kinetic data of Hong and Fegley (1998), bulk magnetite formation in the solar nebula (*i.e.*, conversion of all remaining Fe to Fe_3O_4) is unlikely although formation of thin magnetite rims on metal grains could occur. Magnetite-rimmed metal grains have been observed in some unequilibrated ordinary chondrites (*e. g.*, Nagahara, 1984), and could be nebular products. But, in many other cases, the observed morphologies and mineral assemblages suggest that magnetite formed during low temperature alteration on the meteorite parent body, in particular in CI carbonaceous chondrites (*e. g.*, DuFresne and Anders, 1962; Boström and Fredriksson, 1966; Jedwab, 1967; 1971; Kerridge *et al.*, 1979). The different magnetite morphologies and mineral assemblages found in different chondrites and even within one chondrite, *e. g.*, Orgueil (Jedwab, 1971; Hua and Buseck, 1998), probably indicate that not all of the magnetite assemblages in chondrites have the same origin. Finally, it should be mentioned that thermodynamic calculations and the SCT models predict that

magnetite formation is kinetically and thermodynamically favorable in the Jovian protoplanetary subnebulae (Fegley and Prinn, 1989; Fegley, 1993).

8. The Kinetics and Mechanism of Hydrous Mineral Formation

The three most important hydrous minerals that are predicted to form in the solar nebula are the chrysotile form of serpentine [$Mg_3Si_2O_5(OH)_4$] which contains 13.0% water, talc [$Mg_3Si_4O_10(OH)_2$] which contains 4.8% water, and brucite [$Mg(OH)_2$] which contains 8.3% water. Hydrous phases that are similar to these minerals are found in CI and CM2 carbonaceous chondrites (Lodders and Fegley, 1998, Tab. 16.7). Three other hydrous minerals (hydroxyapatite [$Ca_5(PO_4)_3OH$] containing 1.8% water, sodium phlogopite [$NaMg_3AlSi_3O_{10}(OH)_2$] with a water content of 4.5%, and tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$] containing 2.2% water) are also predicted to form in the solar nebula. However, these phases are less important than chrysotile, talc, and brucite because they contain less water and because they are seldom (if ever in the case of tremolite) observed in meteorites. The question of whether these hydrous minerals formed in the solar nebula or on meteorite parent bodies is a long standing problem in cosmochemistry and planetary science. This question is also important for understanding the source of water for Earth, Venus, and Mars, and the relative amounts of water accreted by the three planets. Here I focus on formation of the major hydrous phases because they contain the most water and potentially are most important for planetary water inventories.

Chrysotile formation via the net thermochemical reaction

$$2\,Mg_2SiO_4\ (forsterite) + 3\,H_2O(gas)\ =$$
$$Mg_3Si_2O_5(OH)_4\ (chrysotile\ serpentine) + Mg(OH)_2\ (brucite) \tag{22}$$

occurs at about 225 K for the solar nebula profile shown in Fig. 2. The H_2O pressure at 225 K where chrysotile becomes stable is about 10^{-9} bars. Reaction (7), which also forms chrysotile, and reaction (8), which forms talc, occur at similar temperatures (*e. g.*, see Tab. III of Prinn and Fegley, 1989). But it is easy to show that reaction (7) cannot occur within the nebular lifetime because the required solid state diffusion is too slow at the low temperature where chrysotile becomes stable (Prinn and Fegley, 1989). Reaction (8) occurs at about 250 K and is subject to the same kinetic limitations as reaction (22).

Chrysotile formation kinetics were modeled because serpentine contains more water than talc and both minerals form at about the same temperature. The SCT models predict that chrysotile formation from 0.1 μm radius forsterite grains takes ~4.5 billion years in the solar nebula (see Fig. (3), and Fegley, 1988). This time is about equal to the age of the solar system and agrees with the intuitive expectation that hydrating rock in a near-vacuum, at or below room temperature, is a very slow process. On the other hand, the SCT models predict that hydrated silicates can form in the subnebulae around Jupiter and Saturn (Fegley and Prinn, 1989). The higher pressures in the subnebulae lead to faster reaction rates. Also, the hydrous silicates

become stable at higher temperatures because of the higher pressures in the Jovian protoplanetary subnebulae. In fact, the hydrous minerals found in accretionary dust mantles in CM chondrites may have formed in these environments (Metzler *et al.*, 1992).

The SCT model calculations used the activation energy for water vapor reacting with periclase (MgO) to form brucite [$Mg(OH)_2$] (Bratton and Brindley, 1965; Layden and Brindley, 1963). This was done because there are no experimental data for the activation energy and kinetics of water vapor reacting with forsterite to form chrysotile serpentine at low pressures like those in the solar nebula. Some petrologists have studied hydrous mineral formation by reaction of high pressure water with anhydrous minerals, but these experimental conditions are much different than those expected in the solar nebula. Typically the water pressure in hydrothermal bomb experiments is several kilobars. This is about 10^{12} times higher than the expected water vapor pressures in the solar nebula. Furthermore, it has been known for a long time that high pressure supercritical water dissolves rock (*e. g.*, Morey, 1957).

This solubility may accelerate reactions by facilitating ionic transport and diffusion. For example, Wegner and Ernst (1983) studied forsterite hydration to serpentine plus brucite and serpentine dehydration in hydrothermal bombs at pressures of 1–3 kilobars and temperatures of 188–388° C (for hydration) and 381–500° C (for dehydration). They found that forsterite hydration proceeded by the growth of the hydrous products (brucite + serpentine) on forsterite crystals at one kilobar water pressure. It seems plausible that serpentine hydration and dehydration in a hydrothermal bomb involve high pressure supercritical water as a solvent or transport medium for Mg and/or Si. For example, as discussed by Layden and Brindley (1963), MgO hydration by liquid water probably occurs by dissolution of MgO to give a solution supersaturated with respect to brucite, followed by precipitation of $Mg(OH)_2$.

However, serpentine formation in the solar nebula is predicted to take place in a very different environment without any liquid water and at water vapor pressures lower than the saturation vapor pressure. In these cases serpentine formation probably occurs by a different mechanism than observed in the hydrothermal bomb experiments and one would not expect that the activation energy determined by Wegner and Ernst (1983) necessarily applies. For example, the forsterite hydration rate in the solar nebula is possibly controlled initially by chemical reaction at the gas-solid interface and later by diffusion of some species through the hydrous product layer. It is also plausible that diffusion through the hydrous product layer on forsterite grains in the solar nebula is less rapid than in the hydrothermal bomb experiments where fluid water is present. Thus the reaction rates and mechanisms in the hydrothermal bomb experiments are probably different than those in the solar nebula.

Experimental studies of water loss and thermal decomposition of micas and amphiboles show that water loss is more rapid than breakdown of hydrous miner-

als to the thermodynamically stable reaction products (Johnson and Fegley, 1998; Zolotov *et al.*, 1997). Cation diffusion is the slow step for forming the predicted anhydrous assemblage. This implies that cation diffusion is also the rate limiting step for hydration of anhydrous minerals. But cation diffusion is very slow at the temperatures where hydrous minerals become thermodynamically stable in the solar nebula. Formation of hydrous silicates in Jovian protoplanetary subnebulae, and on meteorite parent bodies seems more plausible than hydrous silicate formation via nebular gas-grain reactions. In fact, the formation of hydrous minerals on meteorite parent bodies is strongly supported by petrographic studies of CI and CM2 carbonaceous chondrites (*e. g.*, DuFresne and Anders, 1962; Boström and Fredriksson, 1966; Bunch and Chang, 1980),

9. Concluding Remarks

Although thermochemical equilibrium calculations have traditionally been used to model nebular chemistry, it is necessary to consider the rates of chemical reactions to understand chemical processes, especially those at low temperatures, in the solar nebula and in other protoplanetary disks. Investigations of solar nebula kinetics began in the early 1980s with theoretical studies of the CO to CH_4 and N_2 to NH_3 conversions. Later, simple collision theory models and experimental measurements were used to study the rates of exemplary gas-grain reactions such as the formation of troilite, magnetite, and hydrous minerals. This work leads to several conclusions about nebular chemistry, which are summarized below.

1. Gas phase, gas-grain, and solid state chemical reactions proceed at different rates, which generally vary exponentially with temperature, and take different amounts of time to approach chemical equilibrium. Thermochemical reactions taking place at high temperatures are more likely to approach equilibrium within a given amount of time than thermochemical reactions taking place at low temperatures. The maximum amount of time available for gas phase and gas-grain chemistry to occur is the lifetime of the gaseous solar nebula, which is estimated to be 0.1–10 million years. The time available for chemistry may be significantly shorter in turbulent regions of the solar nebula.

2. In general, a comparison of the characteristic time for chemical reaction (t_{chem}) and the characteristic time for nebular cooling or mixing (t_{neb}) shows whether or not reactions take place to any appreciable extent and chemical equilibrium is approached. If $t_{chem} < t_{neb}$, chemical equilibrium can be reached while if $t_{chem} > t_{neb}$ chemical equilibrium cannot be reached. The intermediate case, in between these two extremes, is when $t_{chem} = t_{neb}$ and quenching occurs at a quench temperature (T_Q). The t_{chem} values are calculated from kinetic data and the t_{neb} values are calculated from solar nebula models.

3. Experimental studies and theoretical models have been done for three exemplary gas-grain reactions, formation of troilite, magnetite, and chrysotile ser-

pentine. Troilite formation is rapid enough that H_2S in nebular gas will react completely with Fe grains within the nebular lifetime. Magnetite formation is much slower than troilite formation. Thin magnetite rims might form around Fe grains, but the metal grains probably cannot react completely within the nebular lifetime. Chrysotile serpentine, and other hydrous minerals such as talc and brucite would have formed very slowly in the solar nebula and it is unlikely that they formed at all. Instead the hydrous minerals observed in meteorites and interplanetary dust particles probably formed later on the parent bodies of these objects. It is also plausible that the hydrous minerals in accretionary dust mantles in CM chondrites formed in the protoplanetary subnebulae hypothesized to exist around the Jovian planets during their formation.

Acknowledgements

References

Barshay, S. S., and Lewis, J. S.: 1976, 'Chemistry of Primitive Solar Material', *Ann. Rev. Astron. Astrophys.* **14**, 81–90.

Benson, S. W.: 1982, *The Foundations of Chemical Kinetics*, Krieger Publishing Co., Malabar, Florida.

Boss, A. P.: 1998, 'Temperatures in Protoplanetary Disks', *Annu. Rev. Earth Planet. Sci.* **26**, 53–80.

Boström, K., and Fredriksson, K.: 1966, 'Surface Condition of the Orgueil Meteorite Parent Body as Indicated by Mineral Associations', *Smithsonian Misc. Coll.* **151(3)**, 39 pp.

Bratton, R. J., and Brindley, G. W.: 1965, 'Kinetics of Vapour Phase Hydration of Magnesium Oxide Part 2: Dependence on Temperature and Water Vapour Pressure', *Trans. Faraday. Soc.* **61**, 1017–1025.

Bunch, T. E., and Chang, S.: 1980, 'Carbonaceous Chondrites–II. Carbonaceous Chondrite Phyllosilicates and Light Element Geochemistry as Indicators of Parent Body Processes and Surface Conditions', *Geochim. Cosmochim. Acta* **44**, 1543–1577.

Cameron, A. G. W.: 1978, 'Physics of the Primitive Solar Accretion Disk', *Moon and Planets* **18**, 5–40.

Cameron, A. G. W., and Fegley, M. B.: 1982, 'Nucleation and Condensation in the Primitive Solar Nebula', *Icarus* **52**, 1–13.

Cameron, A. G. W.: 1995, 'The First Ten Million Years in the Solar Nebula', *Meteoritics* **30**, 133–161.

DuFresne, E. R., and Anders, E.: 1962, 'On the Chemical Evolution of the Carbonaceous Chondrites', *Geochim. Cosmochim. Acta* **26**, 1085–1114.

Fegley, B., Jr.: 1988, 'Cosmochemical Trends of Volatile Elements in the Solar System', J. A. Nuth and P. Sylvester (eds.), *Workshop on The Origins of Solar Systems*, LPI Technical Report No.88-04, Houston, Texas, pp. 51–60.

Fegley, B., Jr.: 1993, 'Chemistry of the Solar Nebula', *in* M. Greenberg, C. X. Mendoza-Gomez, and V. Pirronello (eds.), *The Chemistry of Life's Origins*, NATO Advanced Science Institute, Series C vol. 416, Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 75–147.

Fegley, B., Jr.: 1997, 'Cosmochemistry', *in* J. H. Shirley and R. W. Fairbridge (eds.), *Encyclopedia of Planetary Sciences*, Chapman and Hall, London, UK, pp. 169–177.

Fegley, B., Jr.: 1998, 'Iron Grain Catalyzed Methane Formation in the Jovian Protoplanetary Subnebulae and the Origin of Methane on Titan', *Bull. Amer. Astron. Soc.* **30**, 1092.

Fegley, B., Jr.: 1999, 'Chemical and Physical Processing of Presolar Materials in the Solar Nebula and the Implications for Preservation of Presolar Materials in Comets', *in* K. Altwegg, J. Geiss, W. Hübner (eds.), *The Origin and Composition of Cometary Material*, Kluwer Academic Publishers, Dordrecht, Netherlands.

Fegley, B., Jr., and Lewis, J. S.: 1980, 'Volatile Element Chemistry in the Solar Nebula: Na, K, F, Cl, Br, and P', *Icarus* **41**, 439–455.

Fegley, B., Jr., and Prinn, R. G.: 1989, 'Solar Nebula Chemistry: Implications for Volatiles in the Solar System', *in* H. Weaver and L. Danly (eds.), *The Formation and Evolution of Planetary Systems*, Cambridge Univ. Press, Cambridge, UK, pp. 171–211.

Fegley, B., Jr., and Hong, Y.: 1998, 'Experimental Studies of Grain Catalyzed Reduction of CO to Methane in the Solar Nebula', *EOS Trans. AGU* **79**, S361–S362.

Gail, H. P.: 1998, 'Chemical Reactions in Protoplanetary Accretion Disks IV. Multicomponent Dust Mixture', *Astron. Astrophys.* **332**, 1099–1122.

Grossman, L.: 1972, 'Condensation in the Primitive Solar Nebula', *Geochim. Cosmochim. Acta* **36**, 597–619.

Hong, Y. and Fegley, B., Jr.: 1998, 'Experimental Studies of Magnetite Formation in the Solar Nebula', *Meteoritics and Planetary Science* **33**, 1101–1112.

Hua, X., and Buseck, P. R.: 1998, 'Unusual Forms of Magnetite in the Orgueil Carbonaceous Chondrite', *Meteoritics and Planetary Science* **33**, A215–A220.

Jedwab, J.: 1967, 'La Magnetite en Plaquettes des Meteorites Carbonées d'alais, Ivuna et Orgueil', *Earth Planet. Sci. Lett.* **2**, 440–444.

Jedwab, J.: 1971, 'La Magnétite de la Météorite d'Orgueil Vue au Microscope Electronique a Balayage', *Icarus* **15**, 319–340.

Johnson, N. M., and Fegley, B., Jr.: 1998, 'Tremolite Dehydroxylation and the History of Water on Venus', *Bull. Amer. Astron. Soc.* **30**, 1106.

Jones, T. D., Lebofsky, L. A., Lewis, J. S., and Marley, M. S.: 1990, 'The Composition and Origin of the C, P, and D Asteroids: Water as a Tracer of Thermal Evolution in the Outer Belt', *Icarus* **88**, 172–192.

Kerridge, J. F., MacKay, A. L., and Boynton, W. V.: 1979, 'Magnetite in CI Carbonaceous Meteorites: Origin by Aqueous Activity on a Planetesimal Surface', *Science* **205**, 395–397.

Larimer, J. W.: 1988, 'The Cosmochemical Classification of the Elements', *in* J. F. Kerridge and M. S. Matthews (eds.), *Meteorites and the Early Solar System*, Univ. of Arizona Press, Tucson, Arizona, pp. 375–389.

Lauretta, D. S., Kremser, D. T., and Fegley, B., Jr.: 1996a, 'The Rate of Iron Sulfide Formation in the Solar Nebula', *Icarus* **122**, 288–315.

Lauretta, D. S., Fegley, B., Jr., Lodders, K., and Kremser, D. T.: 1996b, 'The Kinetics and Mechanism of Iron Sulfide Formation in the Solar Nebula', *Proc. NIPR Symp. Antarct. Meteorites* **9**, Tokyo, Japan, pp. 111–126.

Lauretta, D. S., Kremser, D. T., and Fegley, B., Jr.: 1996c, 'A Comparative Study of Experimental and Meteoritic Sulfide Assemblages', *Proc. NIPR Symp. Antarct. Meteorites* **9**, Tokyo, Japan, pp. 97–110.

Lauretta, D. S., Lodders, K., and Fegley, B., Jr.: 1997, 'Experimental Simulations of Sulfide Formation in the Solar Nebula', *Science* **277**, 358–360.

Lauretta, D. S., Lodders, K., and Fegley, B., Jr.: 1998, 'Kamacite Sulfurization in the Solar Nebula', *Meteoritics Planet. Sci.* **33**, 821–834.

Layden, G. K., and Brindley, G. W.: 1963, 'Kinetics of Vapor-Phase Hydration of Magnesium Oxide', *J. Am. Ceram. Soc.* **46**, 518–522.

Lewis, J. S.: 1974, 'The Temperature Gradient in the Solar Nebula', *Science* **186**, 440–443.

Lewis, J. S., and Prinn, R. G.: 1980, 'Kinetic Inhibition of CO and N_2 Reduction in the Solar Nebula', *Astrophys. J.* **238**, 357–364.

Lodders, K., and Fegley, B., Jr.: 1997, 'Condensation Chemistry of Carbon Stars', *in* T. J. Bernatowicz and E. Zinner (eds.), *Astrophysical Implications of the Laboratory Study of Presolar Materials*, American Institute of Physics, Woodbury, New York, pp. 391–423.

Lodders, K., and Fegley, B., Jr.: 1998, *The Planetary Scientist's Companion*, Oxford University Press, New York.

Metzler, K., Bischoff, A., and Stöffler, D.: 1992, 'Accretionary Dust Mantles in CM Chondrites: Evidence for Solar Nebula Processes', *Geochim. Cosmochim. Acta* **56**, 2873–2897.

Morey, G. W.: 1957, 'The Solubility of Solids in Gases', *Econ. Geol.* **52**, 225–251.

Nagahara, H.: 1984, 'Matrices of Type 3 Ordinary Chondrites – Primitive Nebular Records', *Geochim. Cosmochim. Acta* **48**, 2581–2595.

Norris, T. L.: 1980, 'Kinetic Model of Ammonia Synthesis in the Solar Nebula', *Earth Planet. Sci. Lett.* **47**, 43–50.

Palme, H., and Fegley, B., Jr.: 1990, 'High-Temperature Condensation of Iron-Rich Olivine in the Solar Nebula', *Earth Planet. Sci. Lett.* **101**, 180–195.

Podosek, F. A., and Cassen, P.: 1994, 'Theoretical, Observational, and Isotopic Estimates of the Lifetime of the Solar Nebula', *Meteoritics* **29**, 6–25.

Prinn, R. G., and Fegley, B., Jr.: 1981, 'Kinetic Inhibition of CO and N_2 Reduction in Circumplanetary Nebulae: Implications for Satellite Composition', *Astrophys. J.* **249**, 308–317.

Prinn, R. G., and Fegley, B., Jr.: 1987, 'The Atmospheres of Venus, Earth, and Mars: A Critical Comparison', *Ann. Rev. Earth Planet. Sci.* **15**, 171–212.

Prinn, R. G., and Fegley, B., Jr.: 1989, 'Solar Nebula Chemistry: Origin of Planetary, Satellite, and Cometary Volatiles', *in* S. Atreya, J. Pollack, and M. S. Matthews (eds.), *Origin and Evolution of Planetary and Satellite Atmospheres*, Univ. of Arizona Press, Tucson, Arizona, pp. 78–136.

Salpeter, E .E.: 1974, 'Nucleation and Growth of Dust Grains', *Astrophys. J.* **193**, 579–584.

Schmalzried, H.: 1995, *Chemical Kinetics of Solids*, VCH Publishers, New York.

Sedlmayr, E., and Krüger, D.: 1997, 'Formation of Dust Particles in Cool Stellar Outflows', *in* T. J. Bernatowicz and E. Zinner (eds.), *Astrophysical Implications of the Laboratory Study of Presolar Materials*, American Institute of Physics, Woodbury, New York, pp. 425–450.

Stevenson, D. J., and Lunine, J. I.: 1988, 'Rapid Formation of Jupiter by Diffusive Redistribution of Water Vapor in the Solar Nebula', *Icarus* **75**, 146–155.

Urey, H. C.: 1953, 'Chemical Evidence Regarding the Earth's Origin', *in* Thirteenth International Congress: Pure and Applied Chemistry and Plenary Lectures, Almquist and Wiksells, Stockholm, Sweden, pp. 188–217.

Wegner, W. W., and Ernst, W. G.: 1983, 'Experimentally Determined Hydration and Dehydration Reaction Rates in the System MgO-SiO_2-H_2O', *Am. J. Sci.* **283A**, 151–180.

Willacy, K., Klahr, H. H., Millar, T. J., and Henning, Th.: 1998, 'Gas and Grain Chemistry in a Protoplanetary Disk', *Astron. Astrophys.* **338**, 995–1005. Urey, H. C.: 1952, *The Planets*, Yale University Press, New Haven, Cincinnati.

Wurm, G., and Blum, J.: 1998, 'Experiments on Preplanetary Dust Aggregation', *Icarus* **132**, 125–136.

Zolotov, M. Yu., Fegley, B., Jr., and Lodders, K.: 1997, 'Hydrous Silicates and Water on Venus', *Icarus* **130**, 475–494.

Address for Offprints: Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899 USA; `bfegley@levee.wustl.edu`