

THE APPLICATIONS OF CHEMICAL THERMODYNAMICS AND
CHEMICAL KINETICS TO PLANETARY ATMOSPHERES RESEARCH

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ABSTRACT

A review of the applications of chemical thermodynamics and chemical kinetics to planetary atmospheres research during the past four decades is presented with an emphasis on chemical equilibrium models and thermochemical kinetics. Several current problems in planetary atmospheres research such as the origin of the atmospheres of the terrestrial planets, atmosphere-surface interactions on Venus and Mars, deep mixing in the atmospheres of the gas giant planets, and the origin of the atmospheres of outer planet satellites all require laboratory data on the kinetics of thermochemical reactions for their solution.

INTRODUCTION

The disciplines of chemical thermodynamics and chemical kinetics have been applied to planetary atmospheres research for over four decades. A large number of investigators (including observers and theoreticians) have used thermodynamics and kinetics to model the chemistry of planetary atmospheres and of atmosphere-surface interactions in order to interpret existing Earth-based, Earth-orbital, and spacecraft spectroscopic data, to guide future observations, and to plan experiments on future spacecraft missions.

In this paper I give a selective review of the history of these applications that leads up to the present day and illustrates the background of several current problems in planetary atmospheres research that require new thermodynamic and kinetic data for their solution. I start with a brief discussion of the retention of chemically reactive volatiles in solid grains in the solar nebula and then proceed to discuss one or more topics of interest for the atmospheres of Venus, Mars, the giant planets, and the outer planet satellites Titan and Triton. My emphasis is on atmosphere-surface interactions for the terrestrial planets, deep atmospheric chemistry for the outer planets, and the origin of the atmospheres of the outer planet

satellites. The companion paper by Yung in this volume focuses on upper atmospheric chemistry and photochemistry for Venus, Mars, Earth, the giant planets, and Titan while the companion paper by Thompson focuses on phase equilibria of cryogenic systems believed to be important for atmosphere-surface interactions on outer planet satellites such as Titan and Triton. The reader is therefore referred to these papers for discussion of these topics.

SOLAR NEBULA CHEMISTRY AND THE ORIGIN OF THE ATMOSPHERES OF THE TERRESTRIAL PLANETS

During the period 1920 - 1950, several authors pointed out that the rare gases (Ne, Ar, Kr, Xe) are much less abundant than chemically reactive volatiles (H, O, C, N, etc.) on the surface of the Earth¹⁻³. These large depletions, which are displayed in Table 1, are generally interpreted as showing that the terrestrial atmosphere is almost entirely secondary and originated as a result of chemical processes connected with the formation of the Earth. These processes would retain the chemically reactive volatiles as chemical compounds in solid grains while the rare gases could only be retained by physical processes such as adsorption and absorption. Similar depletions of non-radiogenic rare gases relative to chemically reactive volatiles, which are observed on Venus and Mars, also imply a secondary origin for these atmospheres as well⁴. Thus, in order to understand the origin of the atmospheres of Venus, Earth, and Mars we must first understand the chemical processes responsible for retention of chemically reactive volatiles (e.g., H₂O, C, N, F, Cl, S, etc.) by the solid grains that accreted to form the planets.

During the early 1950's both Latimer⁹ and Urey¹⁰ became interested in this problem and in two seminal contributions set the stage for much of the subsequent work during the next 3 decades on chemical models of volatile element chemistry in the solar nebula. For example Latimer and Urey both suggested that hydrated silicate formation in the solar nebula was responsible for the retention of the water that eventually formed the Earth's oceans, that carbon and nitrogen could have been retained in solid grains as carbides and nitrides, that sulfur could have been retained as sulfides (primarily as troilite FeS), and that the halogens could have been retained as halide salts such as NH₄Cl, NaCl, CaF₂, etc. Urey also pioneered the application of chemical thermodynamics to models of solar nebula chemistry and showed how for a given set of assumptions about elemental abundances, pressure,

and temperature, the stability fields of volatile-bearing compounds could be calculated. By comparing the calculated stability fields to the pressure, temperature conditions believed to be appropriate for the formation of the different planets Urey could then make predictions about the reactions responsible for volatile retention by the terrestrial planets.

Table 1. Depletions of important volatiles in the Earth relative to solar abundances $[(g/gSi)/(g/gSi)]^a$

| <u>Volatile</u> | <u>Earth^b</u> |
|---------------------|--------------------------|
| CO ₂ | 3×10 ⁻⁵ |
| H ₂ O | 2×10 ⁻⁴ |
| F | 2×10 ⁻² |
| ^{20,22} Ne | 4×10 ⁻¹¹ |
| N ₂ | 4×10 ⁻⁵ |
| S | 7×10 ⁻⁵ |
| Cl | 7×10 ⁻³ |
| ^{36,38} Ar | 2×10 ⁻⁹ |
| ⁸⁴ Kr | 1×10 ⁻⁷ |
| ¹³² Xe | 9×10 ⁻⁸ |

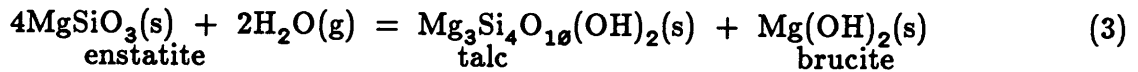
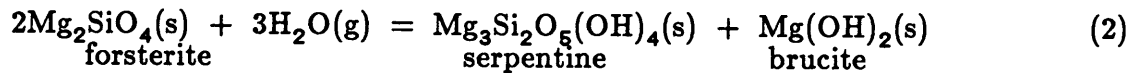
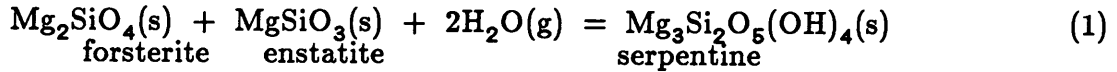
^aSolar abundances from Cameron ⁵. The atmospheric plus oceanic plus crustal inventories for the Earth were obtained from Ronov and Yaroshevsky⁶, Turekian⁷ and Ozima and Podosek⁸.

^bBulk composition model E5 from the Basaltic Volcanism Study Project was used to determine the terrestrial silicon inventory.

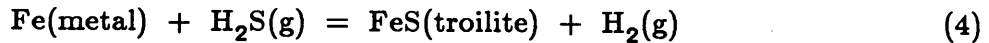
During the next 3 decades, the availability of a large body of thermodynamic data coupled with advances in our knowledge of the solar abundances of the elements led to increasingly sophisticated chemical equilibrium calculations of volatile element chemistry in the solar nebula¹¹⁻²².

The principal results of these calculations can be summarized as follows. The important hydrated silicates serpentine [Mg₃Si₂O₅(OH)₄] and talc [Mg₃Si₄O₁₀(OH)₂], which exemplify the hydrated silicates observed in carbonaceous chondrites²³, do not become thermodynamically stable until low temperatures below 400 K are reached in

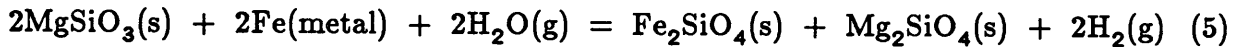
the solar nebula²⁴. (This conclusion is true over a wide range of pressures extending up to 10 bars--a pressure much higher than suggested in any currently accepted models of the solar nebula.) Formation of these silicates is calculated to occur by the hydration of either single or composite mineral grains via reactions exemplified by



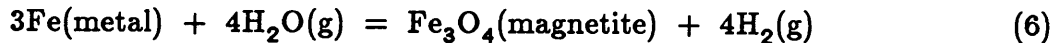
Secondly, retention of sulfur is calculated to occur via sulfurization of Fe metal grains to form troilite via the reaction



which becomes thermodynamically favorable at the pressure independent temperature of 687 K. Fe metal is also calculated to react with enstatite and nebular water vapor via the net thermochemical reaction



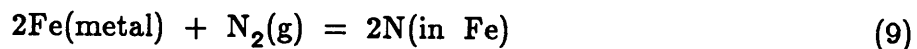
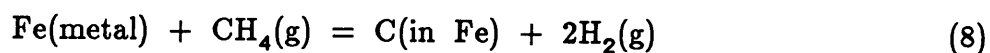
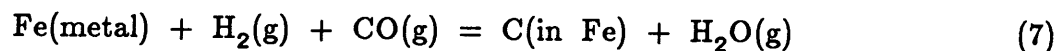
which is predicted to control the oxidation state of the solid grains incorporated into the terrestrial planets^{11,13}. Any unreacted Fe metal grains that remain in contact with the nebular gas may then be "rusted" by reaction with water vapor to form magnetite via the net thermochemical reaction



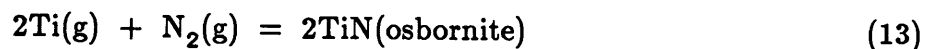
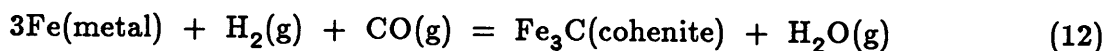
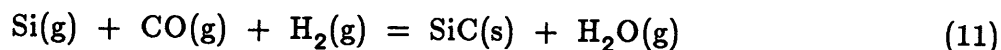
which first becomes thermodynamically favorable at the pressure independent temperature of 400 K.

Finally, depending on the oxidation state of the nebular gas, carbon and nitrogen are predicted to be retained in solid grains either in solution in Fe metal (for nebular gas having the solar C/O atomic ratio of about 0.4) or as carbides

and nitrides (for nebular gas having a C/O atomic ratio greater than or equal to about 0.8). The former retention mechanism is exemplified by the reactions



while the latter process is exemplified by the reactions



These results coupled with models for the variation of temperature and pressure with radial distance in the solar nebula then lead to specific predictions about the volatile endowments of the terrestrial planets. For example, Lewis¹³ has explained the fact that Venus has about 100,000 times less observable water than the Earth by the failure of Venus to have accreted hydrated silicates which did not become thermodynamically stable until further out in the cooler regions of the solar nebula.

However chemical equilibrium models of solar nebula chemistry neglect the fact that chemical interactions between gases and grains in the solar nebula took place in a dynamic environment. Therefore the rate of chemical reactions is as important (if not even more important) than the final equilibrium configuration. It is interesting to note that the importance of chemical kinetics for solar nebula chemistry was probably first recognized by Urey²⁵. While discussing the applications of chemical thermodynamics to solar nebula chemistry he stated that "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 the reactions, at least in homogeneous systems, provided 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 reactions or of photochemical reactions become important."

In recent years it has become recognized that kinetic data for volatile retention reactions such as silicate hydration, iron sulfurization, FeO-bearing silicate formation, and iron oxidation are necessary to compare the rates of these reactions to the rates of nebular mixing and/or nebular cooling to determine quantitatively the extent to which each reaction proceeded in the solar nebula. Unfortunately, this cannot be done at present because the relevant kinetic data are unavailable.

Despite the unavailability of experimental data, reaction rate estimates, which are based on the kinetic theory of gases and on the few available measurements of activation energies, show that some reactions are impossible slow, while others are fairly rapid, and still others are on the borderline. Figure 1 illustrates this point. This estimated chemical time constants t_{chem} for three exemplary volatile retention reactions--troilite formation via reaction (4), magnetite formation via reaction (6), and hydrated silicate formation via reaction (2)--are calculated by considering the initial rate of the gas-grain reaction. This depends on the collision rate of the reactant gas with the grain surfaces, which is given by

$$\sigma_i = 2.635 \times 10^{25} [P_i / (M_i T)^{1/2}] \quad (14)$$

where σ_i has units of $\text{cm}^{-2}\text{sec}^{-1}$, P_i is the partial pressure of reactant gas i , M_i is the molecular weight of gas i , and T is the absolute temperature in Kelvins. The total number of collisions with all grains in each cubic centimeter of the nebula is given by

$$\nu_i = \sigma_i A \quad (15)$$

where ν_i has units of $\text{cm}^{-3} \text{sec}^{-1}$ and A is the total surface area of all reactant grains per each cm^3 of the nebula. The grains are assumed to be monodisperse, spherical particles that are crystalline (i.e., fully dense) and are uniformly distributed at solar abundance in the gas. The results shown in Figure 1 also assume a grain radius of 0.1 micrometers. This grain size is comparable to the very fine-grained matrix found in chondritic meteorites and to the silicate grains observed in

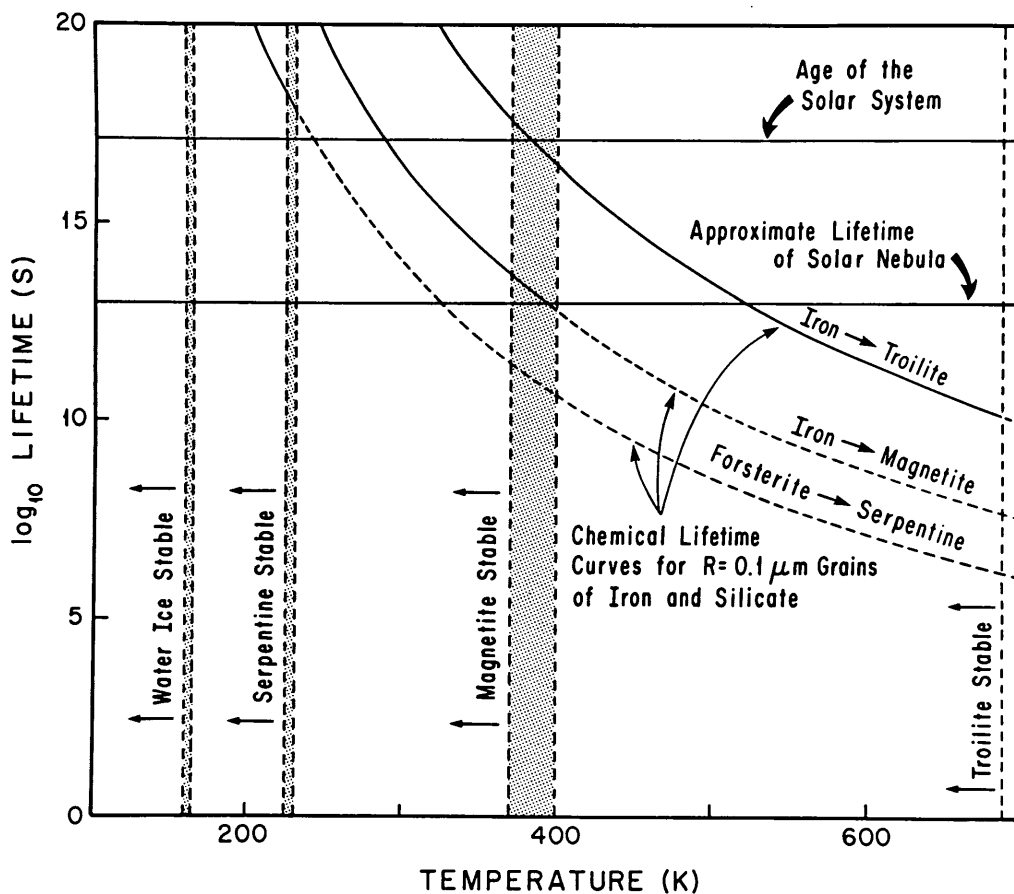


Figure 1. Estimated chemical time constants for three exemplary volatile retention reactions. The thermodynamic stability fields for troilite FeS , magnetite Fe_3O_4 , serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, and water ice are displayed along the horizontal axis. The shaded regions indicate the ranges of formation temperatures appropriate for all carbon being present as CO or CH_4 . The chemical lifetime curves for these three reactions are compared to the solar nebula lifetime (approximately 10^{13} seconds) and the age of the solar system (approximately 10^{17} seconds). All chemical lifetime curves are extended to temperatures above the formation temperatures of the different reaction products to illustrate their trends with temperature. This figure is from Fegley²⁹.

interplanetary dust particles²⁶⁻²⁸, but is significantly smaller than the majority of silicate grains observed in chondrites.

The collision time constant t_{coll} for all reactant gas molecules to collide with all grains in each cm^3 of the nebula is then

$$t_{\text{coll}} = (\nu_i [i])^{-1} \quad (16)$$

where $[i]$ is the molecular number density of gas i . If every collision led to chemical reaction, equation (16) would also be the expression for the chemical time constant t_{chem} . However, only a small fraction of collisions that possess the necessary activation energy lead to chemical reaction. This fraction is given by

$$f_i = \nu_i \exp(-E_a/RT) \quad (17)$$

where E_a is the activation energy and R is the ideal gas constant. The chemical time constant t_{chem} is then given by the expression

$$t_{\text{chem}} = (f_i/[i])^{-1} = t_{\text{coll}}/\exp(-E_a/RT) \quad (18)$$

where the activation energies used in the calculations are taken from the literature reviewed by Fegley²⁹.

Figure 1 compares the calculated chemical time constants with the lifetime of the solar nebula, which is approximately 10^{13} seconds in currently accepted solar nebula models³⁰⁻³², and with the age of the solar system. It is clear that hydrated silicate formation is one of the impossibly slow reactions which probably requires a time greater than the age of the solar system to go to completion. On the other hand, FeS formation is one of the relatively rapid reactions and takes place in a fraction of the solar nebula lifetime. Apparently, magnetite formation is on the borderline and may or may not be possible over the lifetime of the solar nebula.

However, the estimated chemical lifetimes shown in Figure 1 are based on activation energies which are taken from experiments done by materials scientists under conditions of pressure, temperature, and composition which are generally far removed from the conditions hypothesized as appropriate for the solar nebula. Clearly what is needed to confirm or refute the theoretical estimates and to establish the actual rate laws and mechanisms for the volatile retention reactions of

interest are properly designed experimental measurements under the appropriate conditions. For example, a systematic study of how the rate of magnetite formation varies as a function of temperature, H_2 pressure and H_2/H_2O ratio is necessary to determine if this reaction either was or was not important in the solar nebula.

To summarize this section, the principles of chemical thermodynamics have been applied to studies of solar nebula chemistry over the past four decades in an attempt to determine how the volatiles seen in the present day atmospheres of Venus, Earth, and Mars and in the oceans of the Earth were originally retained by these planets. While sophisticated and apparently comprehensive models have been generated as a result of this effort, the neglect of chemical kinetics has left us without a clear understanding of the relative importance of the various reactions hypothesized to have been important for volatile retention in the solar nebula. The kinetic data required to remedy this distressing situation can be obtained only by properly designed experimental measurements under the appropriate conditions.

ATMOSPHERE-SURFACE INTERACTIONS ON VENUS AND MARS

Venus and Mars provide two different natural laboratories for studying the relative contributions of thermochemical and photochemical processes to chemical weathering at the atmosphere-surface interface. The global mean Venus surface temperature is about 740 K and the global mean surface pressure is about 92 bars. Only a few percent of the solar flux incident on Venus manages to penetrate to the lower atmosphere below the clouds and the short wavelength solar UV radiation capable of photolyzing CO_2 does not manage to reach the surface. In contrast, the Martian global mean surface temperature is 214 K and the global mean surface pressure is about 6 millibars⁸³. In other words the Martian surface is about 530 degrees colder than the surface of Venus and the surface pressure is about 15,000 times lower than at the surface of Venus. Furthermore photodissociation of CO_2 , the major atmospheric gas, occurs all the way down to the surface of Mars. Venus would therefore appear to be a good natural laboratory for studying thermochemically dominated chemical weathering processes while Mars would appear to be a good natural laboratory for studying photochemically dominated chemical weathering processes.

(a) Venus

The concept of chemical equilibrium between the surface of Venus and the reactive gases in its atmosphere was first suggested by Urey^{10,33} and was later developed by Mueller³⁴⁻³⁹ who presented a chemical interaction model to reconcile the known chemical composition of the Venus atmosphere with the high surface temperature of Venus. Lewis and coworkers developed the concept of chemical equilibrium between the atmosphere and surface of Venus in some detail⁴⁰⁻⁴⁶, and used the concept of complete chemical equilibrium plus observational data on the composition of the atmosphere of Venus to place limits on the surface composition, abundance of trace gases in the atmosphere, the oxidation state of the crust, and on chemical weathering of the surface. Several related studies by Soviet investigators⁴⁷⁻⁶² used the assumption of chemical equilibrium, in some cases coupled with Venera and Vega atmospheric and surface chemical analyses, to investigate a variety of topics such as trace gas abundances in the Venus atmosphere, cloud particle compositions, mineral stabilities on the Venus surface, and predicted rock types on the Venus surface.

These chemical equilibrium studies were important pioneering efforts. However, aside from some cursory acknowledgements that the achievement of chemical equilibrium was conditional upon thermochemical reactions proceeding sufficiently rapidly with respect to photolysis of reactants/products or with respect to atmospheric mixing times, none of these studies established the reality of chemical equilibrium at the Venus surface.

In fact a number of recent observations strongly suggest that chemical equilibrium is not achieved at the atmosphere-surface interface on Venus. Lewis and Kreimendahl⁴⁴ showed that at chemical equilibrium the reduced sulfur gases H₂S and COS will be present in much larger concentrations than the most stable oxidized sulfur gas SO₂, and in fact will be the dominant sulfur-bearing gas at and near the surface of Venus. This prediction disagrees with the SO₂ and H₂S absolute abundance data reviewed by von Zahn et al⁶³ which showed that SO₂ dominated H₂S and COS above 22 km altitude and had a mixing ratio of about 150 ppm between 22 km and 50 km (the cloud base). Also, preliminary Pioneer Venus (PV) mass spectrometer data suggested that the H₂S mixing ratio was 3 ± 2 ppm below 20 km while the PV gas chromatograph data showed an upper limit of 2 ppm at 22 km⁶³.

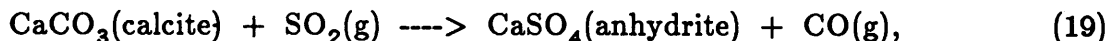
Further evidence against equilibrium is provided by other observations which suggest temporal variations in the abundances of oxidized sulfur gases in the Venus

atmosphere. Esposito⁶⁴ and Esposito et al⁶⁵ analyzed PV Orbiter UV spectrometer data over the 1978-86 time period and concluded that the SO₂ mixing ratio in the clouds decreased by an order of magnitude over this period. In this connection it is interesting to note that in 1978 three groups⁶⁶⁻⁶⁸ discovered SO₂ on Venus at mixing ratios in the range 0.02 to 0.8 ppm, levels which are 2 to 80 times higher than the SO₂ upper limit of 0.01 ppm given by Owen and Sagan⁶⁹ seven years earlier. Also spectroscopic measurements (at 200 to 400 nm) by the Vega spacecraft indicated a SO₂ mixing ratio of 50 ppm between 26 and 53 km⁷⁰. This is a factor of 3 less than the value obtained by the PV and Venera 12 gas chromatographs 6.5 years before. Moroz⁷¹ also reported that the Venera 13 and 14 gas chromatographs showed H₂S and COS levels more than ten times higher than the upper limits for these gases obtained by PV and Venera 11 and 12 four years before.

At the same time, observations of the surface of Venus also suggest chemical disequilibrium. Pettengill et al^{72,73} suggested that high altitude regions of high radar reflectivity may contain substantial abundances of sulfide minerals (e.g., pyrite FeS₂ or troilite FeS). Subsequently Jurgens et al^{74,75} also reported evidence for high radar reflectivity materials on the surface of Venus. However, with the observed H₂S and COS concentrations⁶³, Fe-bearing sulfides are thermodynamically unstable on the surface of Venus and must be spontaneously weathered to form sulfur-bearing gases. Also, Surkov et al^{76,77} reported that the X-ray fluorescence experiments on the Venera 13,14, and Vega 2 landers showed larger amounts of CaO than SO₃ thus implying an excess of Ca-bearing minerals for spontaneous incorporation of SO₂ from atmosphere into sulfate-bearing minerals in the crust.

Taken together, these observations of Venus atmospheric chemistry and surface composition suggest that chemical disequilibrium prevails (at least with respect to sulfur chemistry) at the atmosphere-surface interface on Venus. However, the thermodynamic models of Venus atmosphere-surface chemical interactions do not tell us anything about the rates of gas-solid reactions responsible for incorporating SO₂ into sulfate minerals on Venus. Therefore, these models alone are insufficient to correctly describe the disequilibrium chemistry which is observed on Venus. It is also necessary to have information on the actual reaction rates. Fortunately, in this case a recent study⁷⁸ provides the required reaction rate data.

In this study, the rate of the net reaction



was studied by heating calcite crystals in SO_2 -bearing gas mixtures for varying time periods. The reaction of calcite with SO_2 is predicted to be a net sink for SO_2 on Venus because as Figure 2 illustrates, the observed SO_2 abundance is about 100 times larger than the amount in equilibrium with calcite at Venus surface conditions⁷⁹. Furthermore, calcite is one of the essential phases involved in the Urey equilibrium



which is believed to buffer the CO_2 pressure in the Venus atmosphere^{33,36,42,55,80} because the equilibrium CO_2 pressure of 102 bars at the mean Venus surface temperature of 740 K is identical within the thermodynamic uncertainties to the observed CO_2 partial pressure of 92 bars at the Venus surface.

The experimentally determined reaction rate data are plotted in Figure 3 and a micrograph of a representative reaction product is shown in Figure 4. The rate data shown in Figure 3 can be applied to the problem of atmosphere-surface disequilibrium on Venus by extrapolating the experimental results downward to Venus surface temperatures (which range from 660 to 750 K) using the rate equation⁷⁸ [$R = 10^{(19.64 \pm 0.28)} \exp(-15,248(\pm 2,970)/T)$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$], the PV radar altimetry data⁸¹, and the atmospheric P, T-profile⁸² to take into account the altitude dependence of the rate. The resulting extrapolation is illustrated in Figure 5 and the derived global-mean SO_2 reaction rate is 4.6×10^{10} molecules $\text{cm}^{-2} \text{ sec}^{-1}$. This is equivalent to about 1 micrometer of anhydrite being deposited each year. Aeolian weathering will presumably remove the anhydrite layers on a timescale shorter than the 15-25 years required for a layer to build up to the maximum thickness produced in the laboratory experiments, so the laboratory rate data are applicable to Venus.

Assuming that the derived global-mean rate is representative of the rate at which SO_2 is depleted by reaction with Ca-bearing minerals on the Venus surface, the observed SO_2 column density of 2.2×10^{23} molecules cm^{-2} would be removed from the Venus atmosphere in about 1.9×10^6 years in the absence of a comparable sulfur source.

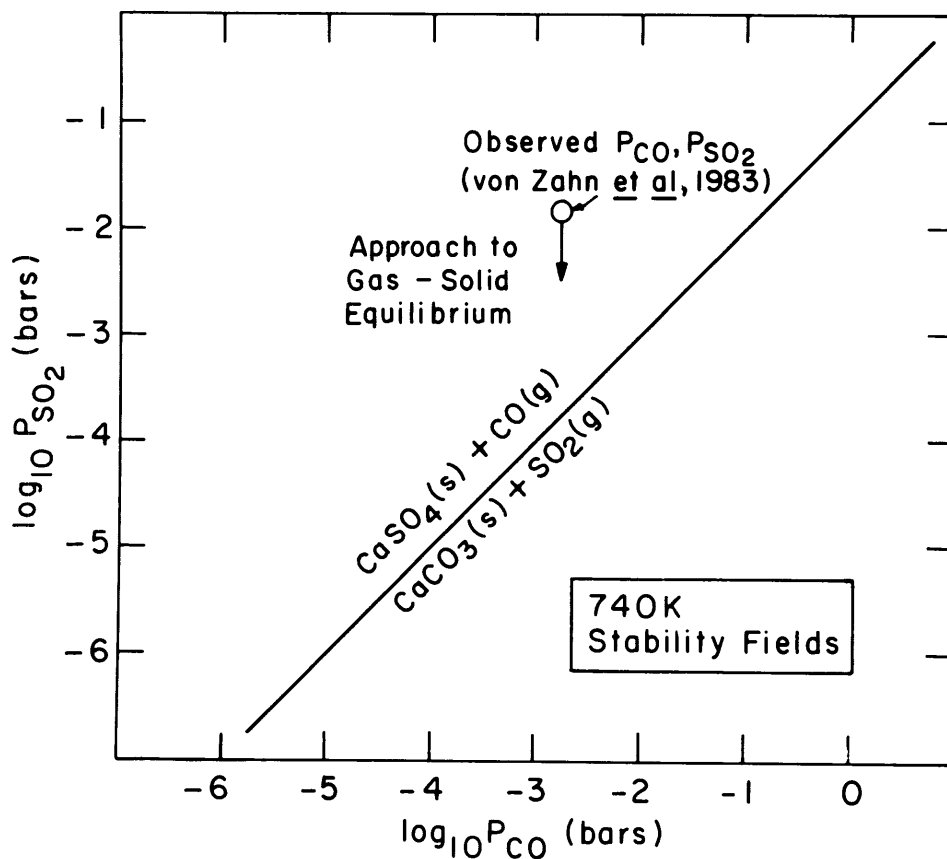


Figure 2. A comparison of the observed sulfur dioxide abundance on Venus with the predicted chemical equilibrium value. The observed value, which is taken from the critical review by von Zahn *et al.*⁶³ of Pioneer Venus and Venera 11 and 12 measurements, is about 100 times higher than the SO_2 abundance in equilibrium at the mean Venus surface temperature of 740 K with the known CO abundance and the calcite-anhydrite mineral assemblage. This figure is from Fegley⁷⁹.

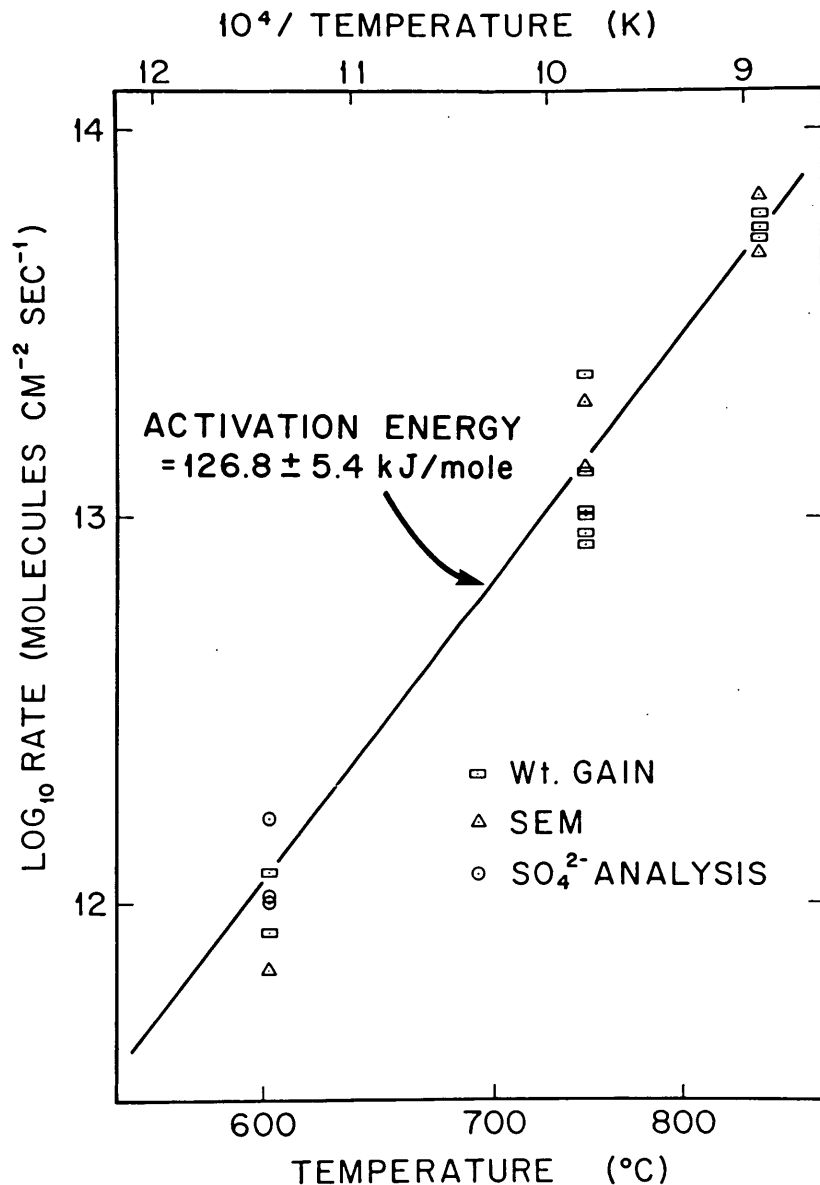


Figure 3. An Arrhenius plot of rate data for the reaction of SO_2 with calcite versus $1/T$. The line is a weighted linear least squares fit. Rates determined from two or more independent methods for the same sample agree within the one sigma experimental uncertainties. The experimentally determined rate law is $R(\text{molecules cm}^{-2} \text{ sec}^{-1}) = 10^{(19.64 \pm 0.28)} \exp(-15,248 (\pm 2,970)/T)$, and the activation energy $E_a = 126.8 \pm 5.4 \text{ KJ/mole}$.

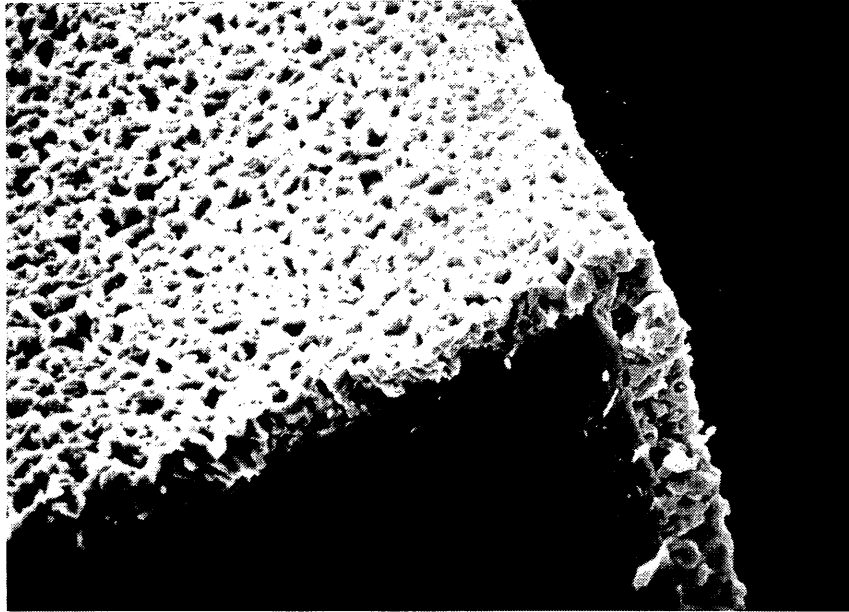


Figure 4. A scanning electron microscope photograph of the fracture surface of a reacted calcite crystal. The scale bar is 100 micrometers long. All external surfaces of the crystal are covered with a layer of anhydrite (CaSO₄) grains. The layer gradually becomes thicker and more dense as the gas-solid reaction continues. This figure is from Fegley¹²⁹.

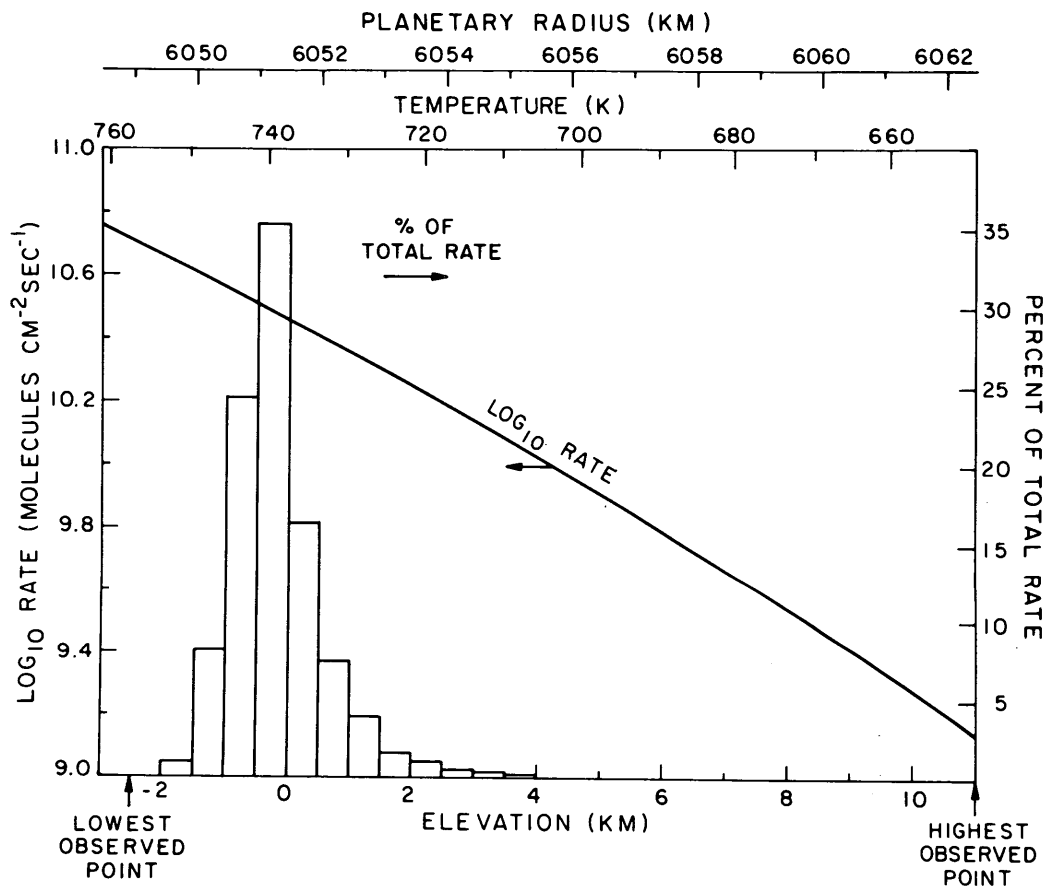


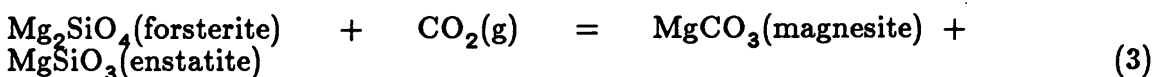
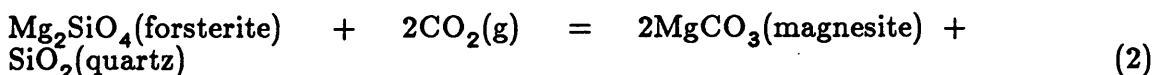
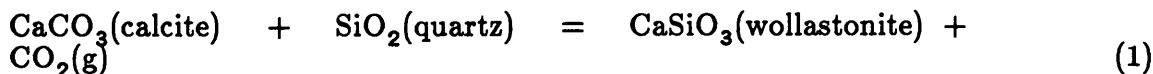
Figure 5. The rate of the $\text{SO}_2 + \text{calcite}$ reaction as a function of temperature and elevation on Venus. The bar graph shows the % of the total rate in each elevation increment. The solid line shows how the rate decreases with decreasing temperature and is an extrapolation of the line in Figure 3. The global mean rate is about 4.6×10^{10} molecules $\text{cm}^{-2} \text{sec}^{-1}$ and corresponds to a 1 micrometer thick layer of anhydrite being deposited each year.

(This calculation also assumes that because of similar rock and oxide densities, the areal percentage of CaO on the Venus surface is equal to 7.90%, the weighted mean of the Venera 13,14 and Vega 2 analyses^{76,77}). This geologically short lifetime for SO₂ in the atmosphere of Venus has been used to argue that maintenance of the global sulfuric acid clouds requires volcanism to replenish the SO₂⁷⁸, which is the precursor of the clouds.

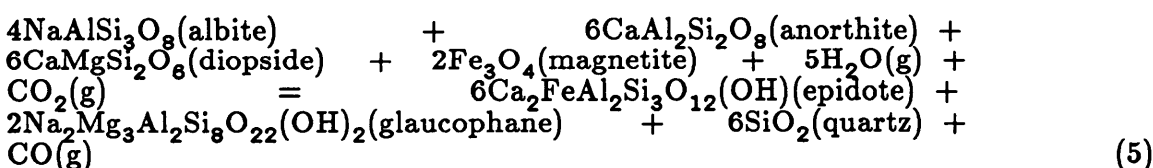
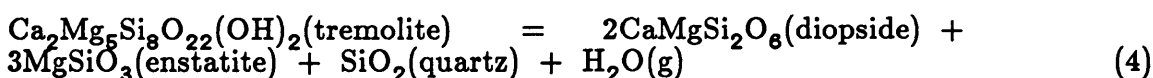
However, there are a large number of other atmosphere-surface reactions, exemplified by those listed in Table 2, which have been proposed to be important on Venus. These reactions include the formation/decomposition of carbonates, the formation/decomposition of hydrated minerals, the formation/decomposition of halogen-bearing phases, and oxidation/reduction reactions. Although some of these proposed reactions, such as those involving the chemically reactive hydrogen halides HCl and HF, may approach equilibrium on a very short timescale, other proposed reactions such as those involving water vapor and oxidation/reduction reactions involving CO/CO₂ equilibria may be very sluggish, even under the high temperatures and pressures at the Venus surface. Unfortunately, no rate data are available for any of these reactions and therefore the critical questions that remain to be answered, such as the history of water and CO₂ on Venus, trace gas atmospheric lifetimes, and chemical weathering rates will remain the subject of speculation until the appropriate laboratory measurements are made. To summarize this section, chemical equilibrium models of atmosphere-surface interactions on Venus have been used to predict the abundances of trace gases in the atmosphere, the oxidation state of the crust, mineral stabilities on the Venus surface, the abundances of possible cloud forming condensates, and so on. However, these models cannot explain the observed disequilibrium chemistry for sulfur, which is indicated by in situ spacecraft analyses of the lower atmosphere and crust, by Earth-based radar observations, and by the PV Ultraviolet Spectrometer orbital analyses of the upper atmosphere of Venus. Instead, reaction rate data for an important SO₂ sink on Venus have been used to estimate the lifetime of SO₂ (and thus the sulfuric acid clouds) in the atmosphere of Venus and to infer the existence of extant volcanism on Venus. Laboratory measurements of the kinetics of other gas-solid reactions postulated to occur on Venus are also needed to determine the importance of these reactions for the chemical cycles of other trace gases (e.g., H₂O, CO₂, HCl, HF, etc.) in the Venus surface-atmosphere system.

Table 2. Exemplary Atmosphere-Surface Reactions on Venus*

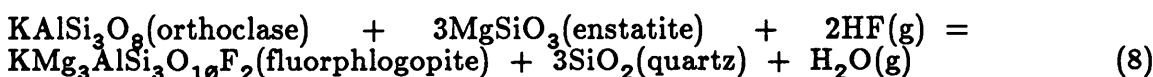
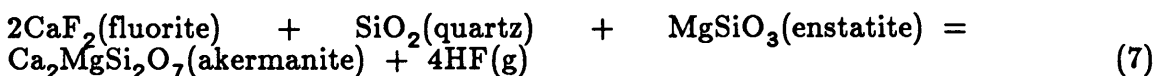
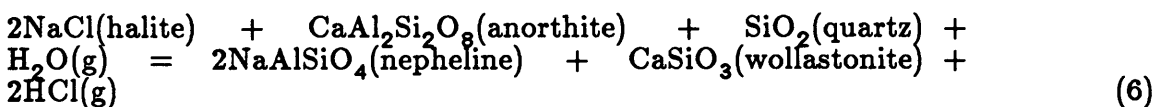
Formation/Decomposition of Carbonates



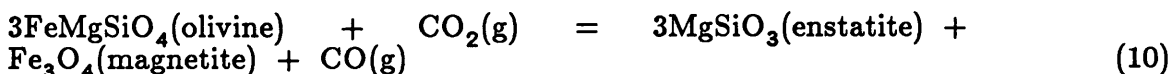
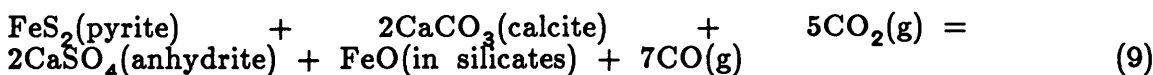
Formation/Decomposition of Hydrated Minerals



Formation/Decomposition of Halogen-Bearing Phases



Oxidation/Reduction Reactions



*Reactions taken from several papers by Lewis^{42,44,46} and Khodakovsky⁵².

(b) Mars

Historically, thermochemically controlled weathering reactions were the first ones to be examined on Mars. Beginning in the early 1960's several authors became interested in the thermodynamic stabilities of Fe-bearing minerals on the Martian surface (e.g. hematite Fe_2O_3 , goethite $\text{FeO}(\text{OH})$, siderite FeCO_3), the possibility that "fossil" weathering products could survive to the present day on the Martian surface, the thermodynamic stabilities of various clay minerals, and the major gas-solid decomposition reaction involving the major mineral constituents of mafic igneous rocks⁸³⁻⁸⁹. Although a substantial body of information now exists about the preferred thermodynamically driven weathering reactions and the stable weathering products on the Martian surface, virtually nothing is known about the kinetics of these reaction. In fact, aside from some general considerations about gas-solid reaction rates given by Gooding^{88,90} the topic of reaction rates has been virtually ignored in the literature, in large part due to lack of relevant experimental data.

More recently, photochemically driven weathering reactions have been studied experimentally. This work began in the early 1970's with experiments by Huguenin on the photostimulated oxidation of magnetite^{91,92} and later was extended to the formation of goethite and hydrated clay minerals on Mars⁹³ and to the unusual chemical activity observed in the Viking biology experiments^{94,95}. Although Huguenin reported the photostimulated oxidation of magnetite, and derived rate laws and proposed a reaction mechanism, attempts to repeat his work by other investigators, for example by Morris and his colleagues^{96,97}, have been unsuccessful. Furthermore a study of carbonate formation under Martian surface conditions by Booth and Kieffer⁹⁸ found that direct UV illumination of the reactants did not significantly alter carbonate formation.

Despite the apparently contradictory experimental results published in the literature, theoretical considerations imply that photochemically driven chemical weathering may be an important process at the Martian surface. The penetration of UV radiation with wavelengths as short as 195 nm to the Martian surface⁹⁹ and the predicted production of significant amount of reactive species such as hydrogen peroxide H_2O_2 at the Martian surface^{99,100} indicate a chemically reactive environment. Further laboratory experiments, perhaps with surface sensitive analytical techniques, appear to be in order to resolve the question of photochemically driven chemical weathering on Mars.

Thus, to summarize this section extensive theoretical studies of thermochemical weathering reactions have led to predictions of the preferred weathering reactions and stable reaction products. However, no data are available on the kinetics of the relevant reactions and their rates under present day Martian surface conditions cannot be evaluated. On the other hand, theoretical considerations and some published laboratory experiments indicate that photochemical weathering reactions may proceed rapidly under present day Martian surface conditions. But other published laboratory experiments find negative results and the contradictory situation has not yet been satisfactorily resolved.

DEEP MIXING IN THE ATMOSPHERES OF JUPITER, SATURN, URANUS, AND NEPTUNE

The atmospheres of the four gas giant planets (Jupiter, Saturn, Uranus, and Neptune) are qualitatively different from those of the terrestrial planets. Whereas the atmospheres of the terrestrial planets make up about 100 ppm of the total planetary mass, are relatively oxidizing, and are terminated by sharp atmosphere-surface boundaries; the atmospheres of the gas giant planets are the dominant fraction of the masses of Jupiter and Saturn and a significant fraction of the masses of Uranus and Neptune, are dominated by H_2 , and do not have distinct lower boundaries. Furthermore, three of the gas giant planets (Jupiter, Saturn, and Neptune) emit more heat than they absorb from the Sun and thus have internal heat sources. Convection is required to transport the observed heat out of these planets and also provides a mass transport mechanism between the cooler, observable regions of their atmospheres, and the hotter unobservable regions thousands of kilometers below the visible cloud decks. Although an internal heat source has not been observed on Uranus, interior structure models and the need to replenish the CH_4 lost by photodecomposition in the upper atmosphere also imply the existence of vertical transport on this planet.

Historically, it was thought that the deep, hot atmospheres of the gas giant planets, which are believed to reach temperatures of 1000 - 2000 K and pressures of hundreds to thousands of bars, are the perfect environments for chemical reactions to come to equilibrium. Indeed, the first comprehensive chemical model of Jupiter which attempted to predict the abundances of a large number of spectroscopically active species explicitly assumed complete chemical equilibrium¹⁰¹. However, the observation of PH_3 in the atmosphere of Jupiter¹⁰² at an abundance about 30

orders of magnitude greater than its predicted equilibrium value¹⁰¹ demonstrated the existence of a powerful disequilibrating mechanism in the Jovian atmosphere. The subsequent observations¹⁰³⁻¹⁰⁷ of other gases (CO, GeH₄, HCN) on Jupiter at abundances which are also many orders of magnitude greater than their predicted chemical equilibrium values¹⁰¹ and of PH₃, CO, GeH₄, and AsH₃ on Saturn¹⁰⁸⁻¹¹¹ reinforced the existence of a potent disequilibrating mechanism in the atmospheres of these two gas giant planets. Table 3 summarizes the observed abundances of these species on Jupiter and Saturn.

Table 3. Observed Abundances of Disequilibrium Trace Gases on Jupiter and Saturn.

| <u>Gas</u> | <u>Jupiter</u> | <u>Saturn</u> |
|------------------|----------------------|----------------------|
| PH ₃ | 7×10 ⁻⁷ | 4×10 ⁻⁶ |
| AsH ₃ | <3×10 ⁻¹⁰ | 2×10 ⁻⁹ |
| GeH ₄ | 7×10 ⁻¹⁰ | 5×10 ⁻¹⁰ |
| CO | 1×10 ⁻⁹ | 1.6×10 ⁻⁹ |
| HCN | 2×10 ⁻⁹ | <7×10 ⁻⁹ |

Very shortly after the discovery of PH₃ on Jupiter, it was recognized that the disequilibrating mechanism responsible for the observed PH₃ is rapid vertical mixing from the deep atmosphere of Jupiter¹¹². As Figure 6 illustrates, PH₃ is the dominant phosphorus-bearing gas in the deep atmosphere of Jupiter. As the temperature decreases with increasing altitude however, PH₃ becomes thermodynamically unstable with respect to oxidation by water vapor and if chemical equilibrium is attained PH₃ will eventually be totally converted to P₄O₆ gas. At even cooler temperatures (and even higher levels in the atmosphere) the P₄O₆ gas will itself become thermodynamically unstable and will react with the atmospheric NH₃ to form a condensate cloud of NH₄H₂PO₄ solid.

A comparison of Table 3 and Figure 6 shows that the observed PH₃ mixing ratio of about 0.7 ppm is the same as the PH₃ mixing ratio in the deep atmosphere of Jupiter at temperatures greater than about 1100 K.

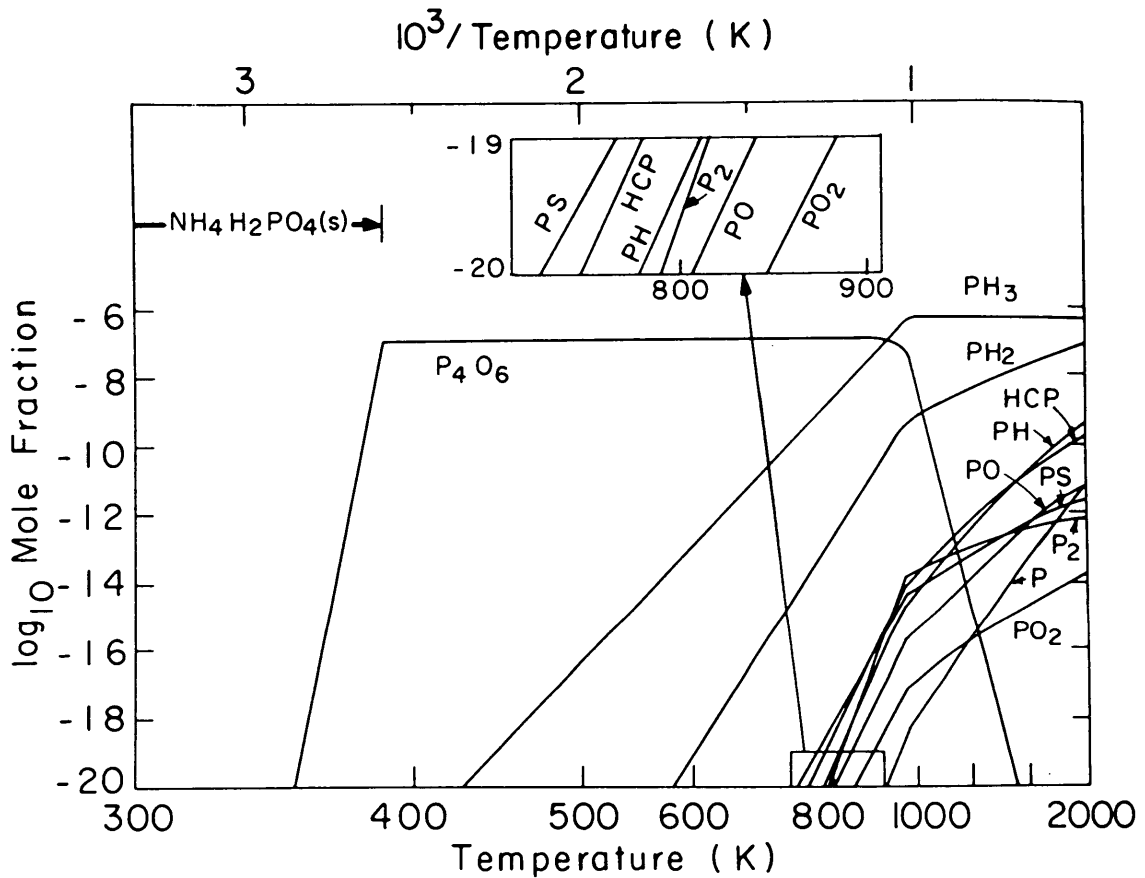


Figure 6. The predicted equilibrium chemistry of phosphorus in the deep atmosphere of Jupiter. At high temperatures PH_3 is 100% of the total phosphorus abundance, but as temperature decreases it becomes thermodynamically unstable and is converted to P_4O_6 gas via oxidation by water vapor. The P_4O_6 in turn becomes thermodynamically unstable at lower temperatures and reacts with atmospheric NH_3 to condense out as $\text{NH}_4\text{H}_2\text{PO}_4$ solid. The observed PH_3 abundance near the Jovian cloud tops is the same as the PH_3 abundance at and below the 1100 K level in Jupiter's deep atmosphere. Rapid vertical mixing at a rate consistent with that required to transport the observed internal heat flux on Jupiter is able to supply the observed PH_3 . This figure is from Barshay and Lewis¹³⁰.

Rapid vertical mixing from these deep atmospheric regions could thus provide the observed PH_3 abundance in the much cooler observable regions of Jupiter's upper atmosphere if the mixing were sufficiently rapid to transport the PH_3 upward at a rate faster than the rate at which it is destroyed by oxidation to P_4O_8 gas. (Once the PH_3 reaches the observable regions the temperature is sufficiently low (e.g., 200 K) to prevent any thermochemical destruction from occurring even on a geologically long time period.) Similarly, the observed abundances of CO , HCN , and GeH_4 on Jupiter are the same as the abundances of these gases at temperatures of about 900 to 1500 K in the deep atmosphere of Jupiter and the observed abundances of AsH_3 , GeH_4 , PH_3 , and CO on Saturn also match the predicted abundances at much deeper atmospheric levels.

Because nonequilibrium gases such as PH_3 , GeH_4 , AsH_3 , CO and HCN are being transported upward from much deeper atmospheric levels on Jupiter and Saturn they have been called chemical probes of the deep atmospheres of these two planets. Given a quantitative framework for relating the vertical transport rates on Jupiter and Saturn to the thermochemical destruction rates for these gases it should then be possible to use the observed chemical probes to deduce the strength of vertical mixing in the 1000 to 2000 K region of the atmospheres of these two planets. Conversely, given an independent constraint on the strength of vertical mixing in the deep atmospheres of Jupiter and Saturn the same quantitative framework should permit deductions about the chemistry in these atmospheric regions. Mathematically, the situation can be described as follows. Vertical mixing is parameterized using the one dimensional vertical eddy diffusion coefficient K_{eddy} . Then, the characteristic convective mixing time t_{conv} over a pressure scale height H , which is just the time required for the convection driven by the internal heat flux to lift a gas parcel over a pressure scale height, is given by

$$t_{\text{conv}} = H^2/K_{\text{eddy}}. \quad (21)$$

In order to determine how rapid vertical mixing must be in order to transport a nonequilibrium gas such as PH_3 upward without any destruction, the convective mixing time t_{conv} must be compared to the characteristic thermochemical destruction time t_{chem} , which depends on the rates of the reactions responsible for destroying the nonequilibrium gas. Now the convective mixing time is fairly insensitive to temperature because the pressure scale height H (equal to $RT/\mu g$ where R is the gas constant, μ is the molecular weight of atmospheric gas, and g is

the gravitational acceleration) is proportional to the temperature. However the thermochemical destruction time is very sensitive to temperature because it depends on reaction rates which themselves are exponential functions of temperature. At some constant vertical mixing rate, there is a level in the atmosphere at which $t_{\text{conv}} = t_{\text{chem}}$; this is defined as the quench level because for reactions with sufficiently large activation energies, vertical mixing over a very small distance compared to the pressure scale height H results in the thermochemical reactions being quenched at the equilibrium concentrations prevailing at the quench level. At lower levels below the quench level, there is a region where t_{chem} is less than t_{conv} , or in other words, chemistry is proceeding more rapidly than dynamics. Conversely at higher levels above the quench level, there is a region where t_{chem} is greater than t_{conv} , or in other words a region where chemistry is proceeding more slowly than dynamics. It is clear from equation (21) that as K_{eddy} increases, t_{conv} decreases and thus the quench level will be at higher temperatures (i.e., lower in the atmosphere) where t_{chem} is also smaller. Conversely, as K_{eddy} decreases, t_{conv} increases and thus the quench level will be at lower temperatures (i.e., higher in the atmosphere) where t_{chem} is also larger. Because the nonequilibrium trace gas abundances are generally also decreasing with decreasing temperature, larger K_{eddy} values (meaning faster vertical mixing) generally results in larger abundances of the nonequilibrium gases (and vice versa).

So given an atmospheric model (e.g., pressure, temperature, and composition) and the relevant mechanisms and kinetic data for the thermochemical destruction of nonequilibrium trace gases such as PH_3 , GeH_4 , AsH_3 , CO and HCN it should then be possible to use the observed abundances of these gases to make deductions about the deep atmospheres of Jupiter and Saturn. In fact, this is what has been done in a recent series of papers¹¹³⁻¹²⁰, which have established the deep mixing origin of the observed nonequilibrium trace gases, predicted many other potential chemical probes of the deep atmospheres of Jupiter and Saturn, and extended the deep mixing theory to Uranus and Neptune.

However, despite this progress, further advances in our knowledge of the chemistry of the deep atmospheres of the gas giant planets require advances in our knowledge of the reaction mechanisms and rate constants for the thermochemical reactions responsible for the destruction of several nonequilibrium trace gases. For example, in some cases absolutely no kinetic data are available and the reaction mechanisms and rate constants have been proposed by analogy with other species and on the basis of qualitative studies. In other cases, rate constants have been

calculated from the equilibrium constants and the rate constants of the reverse reactions. While better knowledge of the reaction mechanisms and rate constants is unlikely to qualitatively change our present understanding (e.g., metal hydrides such as PH_3 , AsH_3 , and GeH_4 must be provided by deep mixing because there is no extraplanetary source that would provide these species and at the same time not provide enormously larger quantities of SiH_4 --which is not observed--on Jupiter and Saturn), this improved knowledge may help to resolve some of the minor discrepancies between theory and observation that currently exist. More importantly, these laboratory data will provide a firm quantitative footing for using species such as PH_3 , GeH_4 , AsH_3 , etc. to probe dynamics at different levels in the atmospheres of Jupiter and Saturn and for using spatially resolved observations (e.g., as may be possible from the CASSINI orbiter) to probe the depth of various storm features in these atmospheres.

To summarize this section, the first chemical models of the atmosphere of Jupiter assumed that chemical equilibrium governed the abundances of gases at all levels in the atmosphere. However, the detections of nonequilibrium trace gases such as PH_3 , GeH_4 , CO , HCN , and AsH_3 at abundances orders of magnitude greater than their chemical equilibrium values in the cool, observable regions of the Jovian and Saturnian atmospheres demonstrated the existence of a powerful disequilibrating mechanism in the atmospheres of these two planets. The similarity of the observed abundances with the predicted abundances of these nonequilibrium gases in the much hotter, deep unobservable regions of the atmospheres of Jupiter and Saturn suggests that rapid vertical mixing driven by the internal heat sources on these planets is the source of these species. Quantitative calculations of the amounts of nonequilibrium gases transported upward as a function of the assumed vertical mixing rate and atmospheric bulk composition have established the validity of the deep mixing model. However advances in our knowledge of reaction mechanisms and rate constants for several nonequilibrium gases will allow us to use spatially and temporally resolved observations of gaseous abundances to probe atmospheric dynamics at different levels and at different times in the atmospheres of the gas giant planets.

ORIGIN OF THE ATMOSPHERES OF OUTER PLANET SATELLITES

The two large icy satellites Titan, which is a satellite of Saturn, and Triton, which is a satellite of Neptune, possess atmospheres composed of N_2 and CH_4 . The atmosphere of Titan was discovered in 1944 by Kuiper¹²¹ and the atmosphere of Triton was first positively identified by observations from the Voyager 2 spacecraft^{122,123}. Both atmospheres are most plausibly derived from the outgassing of carbon and nitrogen-bearing volatiles in Titan and Triton, and an understanding of their origin therefore depends on an understanding of the solid materials that were accreted to form these two satellites.

Extensive theoretical studies of low temperature condensation chemistry in the solar nebula^{24,124-127} have provided a framework for discussing the composition of the solid grains that were accreted to form the icy satellites of the gas giant planets. In the outer regions of the solar nebula, the first major volatile-bearing condensate to form is water ice. As the temperature continues to decrease, CO and N_2 , which are the dominant gaseous forms of carbon and nitrogen in the solar nebula are predicted to equilibrate with the water ice and form clathrate compounds having the ideal formula $G \cdot 6H_2O$ ($G = \text{gas}$). The actual clathrate formed will probably be a solid solution containing both CO and N_2 with the equilibrium composition depending on the thermodynamic properties of the two endmember clathrates and the mixing properties of the solid solution (i.e., the extent of nonideality). Further decreases in temperature are predicted to lead to the condensation of pure CO and N_2 ices.

In the higher pressure environments of the subnebulae, which are believed to have existed around Jupiter, Saturn, and possibly also around Uranus and Neptune during their formation, the initial volatile-bearing condensate is still predicted to be water ice but the subsequent condensates are different. As discussed in detail elsewhere²⁴, the dominant gaseous forms of carbon and nitrogen in the hypothesized outer planet subnebulae are predicted to be CH_4 and NH_3 , respectively. As the temperature decreases below the water ice condensation point, NH_3 is predicted to react with the ice to form ammonia hydrate $NH_3 \cdot H_2O$. Subsequent decreases in temperature lead to formation of methane clathrate $CH_4 \cdot 6H_2O$ and eventually to the condensation of pure CH_4 ice.

As Figures 7 and 8 illustrate, the composition of low temperature condensates formed in the solar nebula and in the hypothesized outer planet subnebulae are quite different and are manifested not only in terms of the volatile-bearing phases themselves, but also in the composition of the outgassed volatiles and in the ice to rock ratios in the two cases. These points and their implications for the origin of the atmosphere of Titan have been discussed at length in the literature^{24,128}. However, despite the importance of the low temperature condensation models for questions such as the origin of the atmosphere of Titan, some of the fundamental thermodynamic and kinetic data which are inputs to the models are poorly known. A few examples will serve to illustrate this point.

The models of low temperature chemistry predict that clathrate compounds (e.g., CH₄, CO, and N₂ clathrates) will form at temperatures below 100 K in the outer nebula or in the outer planet subnebulae. (This is true over a wide range of pressures believed to be appropriate in these environments.) However, virtually no laboratory measurements exist for clathrate stabilities under these conditions. In the case of methane clathrate, most of the available laboratory studies are at much higher temperatures, are directed toward understanding the formation of clathrates in natural gas pipelines, and are up to 50 years old. In the case of N₂ and CO clathrates, virtually no laboratory data on clathrate stabilities are available at all. Furthermore, very little experimental data is available on the solid solution properties of CH₄-CO-N₂ clathrates. Again, the laboratory data that are available have mainly been obtained under conditions of significantly higher temperature and pressure than believed to be appropriate for the natural environments of interest to the cosmochemist.

However, to some extent, theoretical models of clathrate thermodynamics and solid solution properties can be used in place of the missing experimental data. What is much more difficult to remedy by theory is the lack of data on the kinetics of clathrate formation under pressure and temperature conditions believed to have existed in the outer solar nebula and in the outer planet subnebulae. Furthermore, theoretical reaction rate estimates based on the kinetic theory of gases, indicate that clathrate formation is probably kinetically inhibited in the solar nebula but not in the outer planet subnebulae^{24,29}. Thus, laboratory measurements of the rate of clathrate formation are highly desirable.

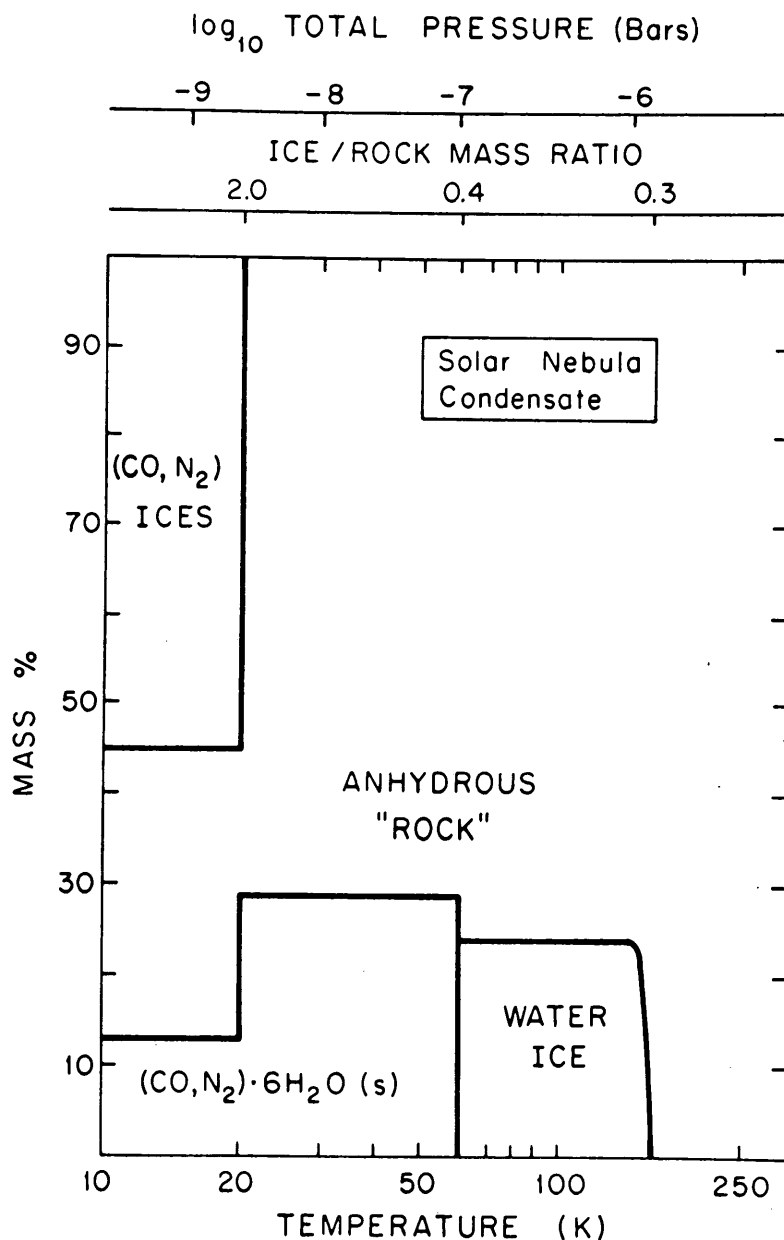


Figure 7. The predicted compositions of low temperature condensates formed in the solar nebula. Theoretical estimates of reaction rates^{24,29} predict that the formation of CH₄, NH₃, and of hydrous "rock" will be kinetically inhibited under the prevailing pressure/temperature conditions in the solar nebula. Furthermore CO and N₂ clathrate formation may also be kinetically inhibited^{24,29} and experimental measurements of clathrate formation rates are needed to assess this prediction. From Fegley and Prinn²⁴.

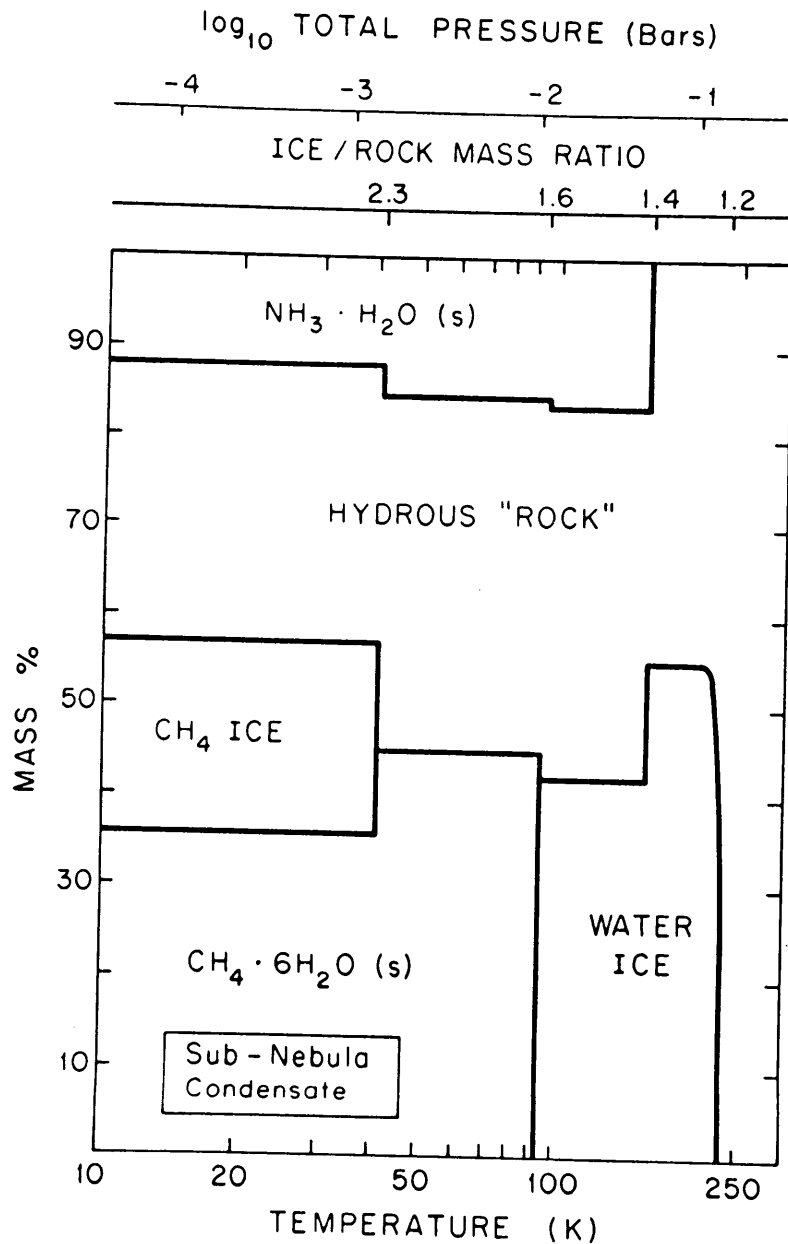


Figure 8. The predicted composition of low temperature condensates formed in an outer planet subnebula. Theoretical estimates of reaction rates^{24,29} predict that the formation of CH₄, NH₃, and of hydrous "rock" will be kinetically favorable under the prevailing pressure/temperature conditions in the subnebulae. Furthermore, CH₄ clathrate formation is also predicted to be kinetically favorable²⁹ and experimental measurements of clathrate formation rates are needed to assess this prediction. From Fegley and Prinn²⁴.

A related topic which also requires laboratory measurements of reaction rates to remedy our lack of knowledge is the action of solar UV light and charged particles on clathrates. Even if it is kinetically feasible to form a clathrate in a particular environment, long term exposure to solar UV photons or to cosmic rays or to charged particles in a magnetosphere may adversely affect the clathrate (e.g., by releasing the trapped CO, CH₄, or N₂; by chemically reprocessing the trapped volatiles into different and perhaps less volatile species; etc.). Our knowledge of these effects is very limited and potentially is a stumbling block to our understanding of the origin and long term evolution of the atmospheres of icy bodies in the outer solar system.

SUMMARY AND RECOMMENDATIONS

The application of chemical thermodynamics and chemical kinetics to planetary atmospheres research during the past four decades has produced an impressive array of accomplishments which have widely expanded our knowledge of the origin, evolution, and chemistry of planetary atmospheres. Nevertheless despite these advances, our knowledge of many fundamental questions is still in its infancy. For example, we still do not know why Venus has 100,000 times less observable water than the Earth, the rates of atmosphere-surface chemical interactions on Venus and Mars, the relative importance of photochemical versus thermochemical weathering at the atmosphere-surface interface on Mars, the nature of the deep atmospheres of the gas giant planets, and so on.

Although it is likely that a combination of experimental, observational, and theoretical studies will be essential to improve our understanding of these (and other) unresolved issues tied to the origin, evolution, and chemistry of planetary atmospheres, I believe that the following experimental studies are worth emphasizing:

1. Quantitative laboratory studies of the kinetics and mechanisms of important volatile retention reactions in the solar nebula. These reactions include the vapor phase hydration of anhydrous silicates, the formation of magnetite Fe₃O₄ and FeO-bearing silicate formation (both reactions are important for controlling the oxidation state of solid grains that formed the terrestrial planets), and clathrate formation (especially for CO, CH₄, and N₂-bearing clathrates).

2. Quantitative laboratory studies of the kinetics and mechanisms of important thermochemical weathering reactions at the atmosphere-surface interface on Venus. These reactions include the formation/decomposition of hydrated silicates, the release/retention of hydrogen halides, the weathering of sulfide minerals, and the incorporation of SO_2 into crustal minerals.
3. Quantitative laboratory studies to determine if photochemically stimulated chemical weathering reactions such as the oxidation of ferrous to ferric iron are taking place under present day conditions at the atmosphere-surface interface on Mars.
4. Quantitative laboratory measurements of the kinetics and mechanisms of thermochemical reactions postulated to destroy chemical probes of atmospheric dynamics on the gas giant planets. The species of interest include CO , PH_3 , GeH_4 , AsH_3 , and HCN . Unlike the other studies listed above, these studies are homogeneous gas phase chemical kinetic studies.
5. Quantitative laboratory measurements of the effects of UV photons and charged particles on the stability of clathrate compounds of CH_4 , CO , and N_2 . It is especially important to examine mixed clathrates containing both carbon and nitrogen species.

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