

## Volatile Element Chemistry in the Solar Nebula: Na, K, F, Cl, Br, and P

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The results of the most extensive set to date of thermodynamic calculations on the equilibrium chemistry of several hundred compounds of the elements Na, K, F, Cl, Br, and P in a solar composition system are reported. The calculations are carried out over a wide range of temperatures and pressures and along an adiabat in the primitive solar nebula. Two extreme models of accretion are investigated. In one extreme complete chemical equilibrium between condensates and gases is maintained because the time scale for accretion is long compared to the time scale for cooling or dissipation of the nebula. Condensates formed in this homogeneous accretion model include several phases such as whitlockite, alkali feldspars, and apatite minerals which are found in chondrites. In the other extreme complete isolation of newly formed condensates from prior condensates and gases occurs due to a time scale for accretion that is short relative to the time required for nebular cooling or dissipation. The condensates produced in this heterogeneous accretion model include alkali sulfides, ammonium halides, and ammonium phosphates. None of these phases are found in chondrites. Available observations of the Na, K, F, Cl, Br, and P elemental abundances in the terrestrial planets are found to be compatible with the predictions of the homogeneous accretion model.

### INTRODUCTION

One of the most intriguing and perplexing problems in planetary science is the method of retention of volatile elements by the terrestrial planets. The retention of volatiles bears upon the origin of the atmospheres of the terrestrial planets, the origin of the Earth's oceans, and the volatile content of the mantles of the terrestrial planets, a factor which influences local melting and volcanism.

Previous work on the thermodynamics of volatile element retention by the terrestrial planets includes that of Lewis (1972) who briefly addressed water retention and that of Lewis *et al.* (1979) who calculated carbon inventories for the terrestrial planets. In the present study we present the results of an extensive set of equilibrium calculations for the elements Na, K, F, Cl, Br, and P over a wide range of temperatures and pressures.

The objectives of this paper are three-

fold. First, we want to describe the equilibrium chemistry of the elements Na, K, F, Cl, Br, and P in a solar composition system over a wide range of temperatures and pressures. The results of the calculations are presented in some detail because the equilibrium chemistry of the elements studied has been either totally neglected or only cursorily examined by previous workers. No results are presented for Li, Rb, Cs, and I because there are insufficient thermodynamic data for many potentially important gases and condensates of these elements. Some limited information on the equilibrium chemistry of lithium in a solar composition system may however be found in Wai and Wasson (1977).

Second, we want to use the results of the equilibrium calculations to discuss volatile element retention by the terrestrial planets. To this end we compare the results of two extreme models of accretion—the strict homogeneous and strict heterogeneous accretion models—with observational data on

abundances of the elements studied. Our discussion of the two endmember accretion models is based on the concept of a turbulent, chemically homogeneous solar nebula. However, recent work by Cameron (1978) suggests that the nebula may have broken up into a collection of giant gaseous protoplanets, especially at great distances from the Sun. Although the chemical consequences of terrestrial planet formation inside giant gaseous protoplanets may be very different from the consequences of either endmember accretion model we are considering, the complex evolutionary histories proposed for the giant gaseous protoplanets make the chemical consequences of protoplanet formation highly model dependent, and thus difficult to quantify. We will therefore restrict our discussion to a comparison of the two extreme accretion models for terrestrial planet formation in the solar nebula.

Third, we want to provide a firm basis for further discussion of the chemistry of the volatile elements studied. The present results can be used to discuss chondrite mineralogy (Fegley, 1979), and can be integrated into a more quantitative condensation-accretion model in preparation (Barshay and Lewis, 1979).

#### METHOD OF CALCULATION

An adiabatic temperature-pressure profile for the primitive solar nebula was constructed stepwise using the relationship

$$(P/P_0) = (T/T_0)^{C_p/R}, \quad (1)$$

where  $P$  is the total pressure,  $T$  the temperature,  $C_p$  the bulk heat capacity at temperature  $T$ , and  $R$  the ideal gas constant. The starting point for the adiabat ( $P_0$ ,  $T_0$ ) was chosen as  $10^{-4}$  bar,  $600^\circ\text{K}$ , consistent with available compositional data on planets and satellites and Cameron's nebular models (Lewis, 1974, and references therein).

The heat capacity data for hydrogen and helium at various temperatures were obtained from the *Handbook of Chemistry and Physics* (1961), and a solar abundance

ratio (Cameron, 1973) of  $\text{H}_2$  to He ( $0.122 \text{ He} + 0.878 \text{ H}_2$ ) was assumed. The heat capacities of the other gases, which account for less than 1 mole%, were ignored.

The calculated nebular adiabat is shown in Fig. 1. The horizontal scales in Figs. 3 and 4 display numerically the relationships between temperature and pressure and temperature and heliocentric distance along the adiabat. The distance scale was calculated using the relationship

$$(T/T_0) = (R/R_0)^{-1.1}, \quad (2)$$

where  $T$  is the temperature and  $R$  is the heliocentric distance in astronomical units (AU). The starting point for the distance scale ( $T_0$ ,  $R_0$ ) was chosen as  $600^\circ\text{K}$ , 1 AU. Both the chosen functional relationship between temperature and distance in the nebula, and the ( $T_0$ ,  $R_0$ ) point are consistent with the arguments of Lewis (1974).

The assumed solar elemental abundances used in the calculations, which are listed in Table I, were taken from Cameron (1973). The equilibrium stability fields and abundances of some silicate minerals and iron metal along the nebular adiabat were taken

TABLE I  
ABUNDANCES OF THE ELEMENTS<sup>a</sup>

Element	Normalized abundance (Si = $10^6$ )
H	$31.8 \times 10^9$
He	$2.21 \times 10^9$
O	$21.5 \times 10^6$
C	$11.8 \times 10^6$
N	$3.74 \times 10^6$
Mg	$1.06 \times 10^6$
Si	$1.00 \times 10^6$
Fe	$0.83 \times 10^6$
S	$0.50 \times 10^6$
Al	$85 \times 10^3$
Ca	$72 \times 10^3$
Na	$60 \times 10^3$
P	9600
Cl	5700
K	4200
F	2450
Br	13.5

<sup>a</sup> From Cameron (1973).

from Barshay and Lewis (1979), with some recalculations to adjust for changes in the thermodynamic data for iron oxides, iron-bearing silicates, and alkali aluminosilicates. Thermodynamic data were taken from the JANAF Tables and subsequent supplements (Stull and Prophet, 1971; Chase *et al.* 1974, 1975, 1978), the Geological Survey thermodynamic tables (Robie *et al.* 1978; Robie and Waldbaum, 1968), the National Bureau of Standards compilations (Parker *et al.*, 1971; Wagman *et al.*, 1968, 1969, 1976), and a variety of other sources (Duff, 1972a,b; Gottschal, 1958; Jacques, 1963; Komarek, 1963; Letoffe *et al.*, 1974, 1976; Mills, 1974; Oetting and McDonald, 1963; Orville, 1972; Richardson and Jeffes, 1949; Saxena, 1973; Seck, 1971; Weibke and Schrag, 1941; Wellman, 1969). In several cases the tabulated equilibrium constants were incorrect and had to be recalculated. For example, the tabulated  $\log K_f$  data for many phosphorus compounds in Robie and Waldbaum (1968) and Robie *et al.* (1978) are in error because the  $\Delta H_{f,298}^\circ$  values are based upon a white phosphorus reference state while the  $\log K_f$  values are calculated using thermodynamic functions for red phosphorus. When the  $\log K_f$  values are recalculated using a consistent red phosphorus reference state the differences in  $\log K_f$  are found to be on the order of 3 to 4 (differences in  $K_f$  of a factor of  $10^3$  to  $10^4$ ).

It was also necessary in several cases to calculate from the literature data the equilibrium constant for formation of an element or compound from the constituent elements in their designated reference states. If at all possible this calculation was done by a third-law method and double checked using data from a separate source. In some cases a second-law method, which is less accurate, was used. Details of the second- and third-law treatment of equilibrium data are available in the JANAF tables or any standard thermodynamic text.

A special discussion of the thermodynamic data used to calculate  $\log K_f$  values for chlorapatite and bromapatite is also

necessary. Both  $\Delta H_{f,298}^\circ$  (Gottschal, 1958) and  $\Delta G_{f,298}^\circ$  (Duff, 1972b) values for chlorapatite are available. However, the combination of the data yields a  $S_{298}^\circ$  value for chlorapatite which is too low relative to the  $S_{298}^\circ$  values for fluor- and hydroxyapatite. Since the  $\Delta H_{f,298}^\circ$  values measured by Gottschal (1958) for fluorapatite and hydroxyapatite agree within 1% with other experimental and tabulated values (Jacques, 1963; Parker *et al.*, 1971), we have combined his  $\Delta H_{f,298}^\circ$  value for chlorapatite with an estimated  $S_{298}^\circ$  value to calculate  $\log K_f$  values by the second-law method. Only a  $\Delta G_{f,298}^\circ$  value (Duff, 1972a) for bromapatite is available and it was again necessary to estimate a  $S_{298}^\circ$  value in order to calculate  $\log K_f$  values. In both cases the entropy estimates were made by three separate methods which yielded results that agree within 1%. The subsequent uncertainty in the  $\log K_f$  values is probably less than that due to the experimental error in the  $\Delta H_{f,298}^\circ$  and  $\Delta G_{f,298}^\circ$  determinations. Discussion of entropy estimation methods can be found in Stull and Prophet (1967) and Kubaschewski *et al.* (1967).

The basic computational method used has been described in detail by Barshay and Lewis (1978) and Grossman (1972), and will only be briefly summarized here. The thermodynamic calculations along the nebular adiabat involve the simultaneous determination of the equilibrium abundances of all compounds (gases and condensed phases) included in the data set. Pure condensed phases, e.g.,  $\text{Fe}_3\text{P}$ , are stable when their thermodynamic activities equal 1 and are unstable at activities less than 1. Condensed phases which form solid solutions such as the alkali feldspars are stable at activities less than 1.

More than 200 gases and condensates were included in the calculations for this paper. Gases were included in Figs. 2–5 if their equilibrium mole fraction along the nebular adiabat was greater than  $10^{-15}$  at any temperature within the range covered by the figure. The abundances and stability

fields of condensates stable at equilibrium are also indicated in the figures. Condensates which were found to be either unstable or unimportant within the temperature range of a figure and gases which did not satisfy the above stated criterion are listed in the Appendix.

#### THE HOMOGENEOUS ACCRETION MODEL

The homogeneous accretion model assumes intimate contact between the condensed and gaseous phases, thereby allowing complete chemical equilibrium between all gases and condensates. The chemical composition of the system is a thermodynamic state function and is path independent. Assuming that chemical equilibrium is attained and that the system has solar composition, the results presented in Figs. 1–5 and Table II therefore apply to condensation from a hot totally vaporized mixture, volatilization of a homogeneous cold gas and dust mixture, or any intermediate case.

Figure 1 shows the condensation and formation curves for condensates of the elements Na, K, F, Cl, Br, and P, the condensation and reaction curves from Barshay and Lewis (1976) for some compounds of the major elements, the adiabatic pressure–temperature profile for the primitive solar nebula, and a qualitative repre-

sentation of the formation zones for the terrestrial planets.

Several important points are demonstrated by Fig. 1. First, the sequence of reactions and the composition of condensed phases present at equilibrium are generally pressure independent. Second, the volatile contents (Na, K, F, Cl, Br, and P) of the terrestrial planets and asteroids are in principle predictable by use of this simplified chemical equilibrium model. Third, the correspondence between the phases present at equilibrium and the observed mineralogy of ordinary chondrites reinforces the plausibility of a close approach to chemical equilibrium in the primitive solar nebula.

Table II and Figs. 2–5 provide information on the equilibrium chemistry of Na, K, F, Cl, Br, and P along the nebular adiabat. The results of the calculations are discussed element by element in order of decreasing abundance. Compounds which do not appear in the figures due to extremely low abundances or activities less than 1 are listed in the Appendix.

#### Sodium

Figure 2 illustrates the equilibrium abundances and stability fields of sodium-bearing compounds along the nebular adiabat. The abundances at equilibrium of both gaseous and condensed sodium-bearing compounds are shown in the figure. Half of all sodium is condensed in plagioclase feldspar ( $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) by 948°K, and condensation is quantitative at about 858°K. Thermodynamic data for analbite (Robie *et al.*, 1978) and activity coefficient data for plagioclase feldspar (Orville, 1972; Saxena, 1973) were used in the calculations. The 50% condensation curve for  $\text{NaAlSi}_3\text{O}_8$  in plagioclase feldspar is shown in Fig. 1. Sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) dissolved in enstatite ( $\text{MgSiO}_3$ ) as an ideal solution never exceeds 1% of total sodium. The albite abundance is reduced by the formation of sodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ ) at

TABLE II

HOMOGENEOUS ACCRETION MODEL: CHEMICAL REACTIONS ALONG THE NEBULAR ADIABAT

T(°K)	Reaction
1520	Condensation of Fe–Ni alloy
1455	Condensation of $\text{MgSiO}_3$ (enstatite)
1225	Condensation of $\text{Fe}_3\text{P}$ (schreibersite)
950–1050	50% Condensation of $(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$ in plagioclase feldspar
895	Formation of $\text{Na}_4(\text{AlSiO}_4)_3\text{Cl}$ (sodalite)
766	Formation of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (fluorapatite)
714	Formation of $\text{Ca}_5(\text{PO}_4)_2$ (whitlockite)
687	$\text{Fe–Ni alloy} + \text{H}_2\text{S (g)} = (\text{Fe},\text{Ni})\text{S}$
480	Calcium silicates + $\text{H}_2\text{O(g)} = \text{tremolite}$
~460	Whitlockite reacts to form $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
~350	Formation of $\text{Ca}_5(\text{PO}_4)_3\text{Br}$ (bromapatite)

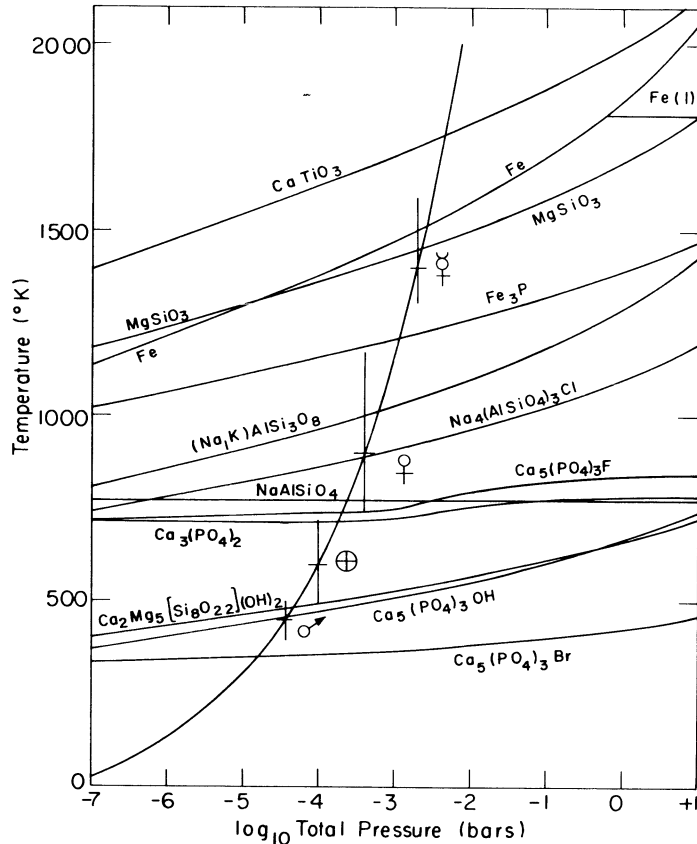


FIG. 1. Stability limits of condensates at chemical equilibrium in the primitive solar nebula from 0 to 2100°K and  $10^{-7}$  to 10 bars total pressure. The  $\text{CaTiO}_3$  condensation curve, which represents the condensation limits of several refractory oxides, the Fe condensation curve, the  $\text{MgSiO}_3$  condensation curve, and the tremolite  $[\text{Ca}_2\text{Mg}_5[\text{Si}_8\text{O}_{22}](\text{OH})_2]$  condensation curve are from Barshay and Lewis (1976). An adiabatic pressure-temperature profile in the solar nebula and qualitative formation zones for the terrestrial planets are also shown.

about 895°K and later by nepheline formation at about 775°K. The albite, sodalite, and nepheline stability fields all extend below 500°K. The high temperature limits of the sodium silicate and albite stability fields correspond to the appearances of enstatite and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), respectively. The low temperature limit to the  $\text{Na}_2\text{SiO}_3$  stability field coincides with the disappearance of enstatite at about 511°K. Our albite condensation results are in good agreement with earlier estimates by Grossman (1972).

### Phosphorus

The abundances and stability fields of phosphorus-bearing compounds under

equilibrium conditions along the nebular adiabat are shown in Fig. 3. The first phosphorus-bearing condensate is schreibersite ( $\text{Fe}_3\text{P}$ ) which appears at about 1225°K. Phosphorus is 50% condensed at about 1169°K and is completely condensed by 1053°K. Fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ] is formed from  $\text{Fe}_3\text{P}$  at 766°K and the remaining schreibersite reacts to form whitlockite [ $\text{Ca}_3(\text{PO}_4)_2$ ] at 714°K. The whitlockite and fluorapatite stability fields extend below 500°K. Hydroxyapatite formation as a pure phase and as an ideal solid solution in fluorapatite has also been considered. In the former case hydroxyapatite formation depletes the remaining whitlock-

