The Generation of N₂–CO₂–H₂O Fluids For Use In Hydrothermal Experimentation
II. Melting of Albite in a Multispecies Fluid

S. E. Kesson

Departments of Chemistry and Geology

J. R. Holloway

Division of Geochemistry, Department of Chemistry

Arizona State University, Tempe, Arizona 85281

Abstract

Three fluid compositions in the C–O–H–N system, each with nominal mole fraction of H₂O : 0.25, were used for comparative determinations of the solidus of synthetic albite at 4.4 kbar. The fluids were generated by the decomposition of guanidine nitrate CH₄N₂.HNO₃, ammonium oxalate (NH₄)₂C₂O₄.H₂O, and from a 1:2 molar mixture of oxalic acid dihydrate and anhydrous oxalic acid. Hydrogen fugacity during the experiments was not buffered and was found to lie between Ni–NiO–H₂O and MnO–Mn₂O₃–H₂O buffers. Excess H₂ produced by the decomposition of the C–O–H–N solid compounds diffuses out of the sample capsule, resulting in fluids consisting essentially of the species H₂O, CO₂ and N₂. The ternary nature of these fluids, which was predicted by thermodynamic equilibrium calculations, is confirmed by quantitative gas chromatographic analysis of the quenched fluids. Reversals confine the albite solidus between 954°C and 958°C (+2°C) and within experimental limits there is no significant difference between solidus temperatures for each of the three fluid compositions. This suggests that activity coefficients for H₂O are similar in each case and are independent of the CO₂/N₂ ratio in the fluid. These data place an upper bound on the activity coefficient for H₂O at 960°C and 4.4 kbar of approximately 1.8 in H₂O–CO₂–N₂ fluids with the mole fraction of H₂O = 0.25.

Introduction

Holloway and Reese (1974) describe a method which allows the independent variation of P_H₂O, P_CO₂, and f_O₂ during experiments at geologically significant pressures and temperatures. In this method, fluids produced by the decomposition of C–O–H–N solid compounds reach equilibrium at P and T consisting essentially of the species H₂O, CO₂, and N₂. Holloway and Reese evaluated the effects of P, T and f_H₂O on fluid composition by means of equilibrium calculations, but in the absence of any data for activity coefficients, had to assume that all fluid species mixed ideally.

This paper describes the results of an experimental application of the method outlined above. The results yield an estimate of the value of γ_H₂O at 4.4 kbar and 960°C, and also establish the relationship between γ_H₂O and the CO₂/N₂ ratio in the fluid at this P and T. Quantitative analysis gives the equilibrium species composition of quenched C–O–H–N fluids for comparison with theoretical calculations.

Experimental

The fluid-saturated solidus temperatures for synthetic crystalline albite at 4.4 kbar were determined using three different C–O–H–N fluids. The fluids were generated using the method of Holloway and Reese (1974). Table I lists the organic compounds used to generate these fluids and gives the nominal species composition in each case assuming that all excess H₂ is lost by diffusion through the capsule walls so
that only CO₂, H₂O, and N₂ species are present. Each fluid contains X(nom)₄ = 0.25 whereas X(nom)₄ = 0.50, 0.25, and zero respectively.³

The aim of the experiments is to bracket the albite solidus at 4.4 kbar with each of the three fluids. If the solidus temperatures are significantly different, it would mean that γ₄ is dependent on the CO₂/N₂ ratio in the fluid. But if the solidus temperatures are the same within experimental precision, then either γ₄ is essentially independent of the CO₂/N₂ ratio or γ₄ is dependent on fluid composition, but the effect of increasing X(N), is balanced by the effect of decreasing X(CO₂).

Starting Materials

The synthetic crystalline albite used as starting material in the experiments was prepared as a gel following the methods of Hamilton and Henderson (1968), and crystallized hydrothermally. The chemical analysis obtained by X-ray fluorescence analysis (Norris and Hutton, 1969) and by flame photometric methods (Cooper, 1963) gives SiO₂ = 69.10, Al₂O₃ = 18.68, and Na₂O = 11.82.

Experimental Techniques

Experimental runs were carried out in an argon gas media, internally heated, high pressure vessel of 5 cm internal diameter similar to that described by Holloway (1971). Temperature was controlled by a stepless proportional controller and measured with a precision of ±2°C by means of three sheathed chromel-alumel thermocouples in contact with the sample capsule. The accuracy of temperature measurement is believed to lie within ±5°C. Pressures were measured with a Bourdon tube gauge.

The fluid-generating compounds followed by crystalline albite were loaded into Ag-Pd alloy capsules which were sealed by welding. At P and T, H₂O and albite are present in approximate 2:1 molar proportions.

In most cases the unreversed runs were held at P and T for approximately 6 hours. Runs were reversed by holding the charge for 6-7 hours above the solidus at 1050°C, then dropping the temperature to 954°C. A few of the larger albite crystals persisted as relics above the solidus, and acted as nuclei for extensive crystallization at subsolidus temperatures.

Problems associated with solution of albite in H₂O, and vice versa, are believed to be minimal. The activity of H₂O in each of the fluids is considerably less than unity and so the solubility of albite in the fluid phase is reduced considerably (Shettel, 1973). Calculations using the data of Burnham and Jahns (1962) plus the initial fluid/albite ratio show that during the melting experiments there is negligible change in the fluid composition due to solution of H₂O in albite melt.

After removal from the pressure vessel, the sample capsules were weighed to check for leakage. Capsules which did not leak during experiments were usually puffed and escaping gases were audible during opening. When analysis of the quenched fluid was required, the capsule was punctured under vacuum in the analytical system.

All species except H₂O in the quenched fluids were determined by quantitative gas chromatographic analysis. The 2-column gas chromatograph was constructed from parts contained in a Laboratory Equipment Corporation (LECO) carbon analyzer. The chromatograph uses a thermal conductivity bridge for a detector and has the capacity to determine CO₂, propane, butane, and more complex C-O-H gas

---

³ Note that the defining relation for mole fraction will change depending on the fluid considered. For example, in a simple ternary fluid X₄ = n₄/(n₄ + n₁ + n₂) while for a multispecies COHN fluid at P and T, X₄ = n₄/(n₄ + n₁ + n₂ + n₃ + n₄ + n₅ + n₆ + n₇ + n₈ + ... + n₉).
species by means of a Porapak 'Q' column operated at 87°C; it can determine CO, H₂, CH₄, NO, N₂, O₂, and NO₂ by means of a molecular sieve operated at 25°C. Thus, the system is able to detect all major gas species, and many trace species except H₂. Calibration is effected using gases of known composition. The analytical precision (one standard deviation) is about 0.5 percent of the amount present for major species, and about 5 percent for trace species. The amount of H₂O in the quenched fluids was determined by weighing after it had been collected in a dry ice + acetone cold trap. The precision of this method is ±0.0005 gms, which is approximately ±3.5 percent of the amount present. Any NH₃ collected in the cold trap can be detected qualitatively by simple chemical tests.

The nitrogen and carbon contents of albite glasses were determined by quantitative methods (Moore et al, 1970).

Effect of $f_\text{H}_2$ on Fluid Composition

Holloway and Reese (1974) used the results of thermodynamic equilibrium calculations to investigate the relationship between the species composition of C-O-H-N fluids and externally controlled $f_\text{H}_2$. They
showed that the species composition of an equilibrium fluid at $P$ and $T$ did not lie exactly on the $H_2O-CO_2-N_2$ plane of the $C-O-H-N$ tetrahedron. When $X_{H_2O}$ is low (<0.25), this deviation becomes increasingly significant as the external $f_{H_2O}$ increases above that of the MH, OH buffer. Thus, the species compositions of the equilibrium fluids produced by the compounds listed in Table 1 differ slightly from the nominal fluid compositions (also given in Table 1). Of particular importance to the albite melting experiments is the difference ($\delta_{H_2O}$) between the actual mole fraction of $H_2O$ in each of the three fluids and the nominal mole fraction of $H_2O$ (0.250) in the capsule. This is evaluated by means of thermodynamic equilibrium calculations, the results of which are shown graphically in Figure 1.\(^4\) During experiments the ambient $f_{H_2O}$ in the pressure apparatus has been found to lie between NNO, OH and MH, OH. The calculated curves (Fig. 1) reveal that the actual value of $X_{H_2O}$ should be somewhere between 0.250 and 0.254, 0.250 and 0.259, 0.250 and 0.264 for fluids for which the nominal values of $X_{H_2O}$ in the fluid are 0.500, 0.250, and zero, respectively.

Experimental Results and Interpretations

Fluid Analysis

The species composition of the fluid is very sensitive to $X_{H_2O}$; thus reaction during the quench would occur if there was diffusion of $H_2$ into the sample capsule. But $X_{H_2O}$ is believed to remain essentially constant during quenching because the diffusion rate of $H_2$ is relatively slow compared to the quenching time (Makrides and Jewett, 1966), and $f_{H_2O}$ in the pressure vessel is very similar to that in the capsule during the quench. The fluid analyses were complicated by the formation of a water-soluble C-O-H compound during quenching. Heating the quenched fluid to $\sim 350^\circ C$ in a large volume container caused the compound to break down to $H_2O$ and $CO_2$, and it did not reappear as the gases cooled to room temperature.

Analyses of the quenched fluids are presented in Table 1. Fluids produced by the decomposition of the C-O-H-N compounds consist essentially of the species $H_2O$, $CO_2$, and $N_2$, and fluids derived from C-O-H compounds consist essentially of $H_2O$ and $CO_2$. No $NH_3$, $N-O$, $C-H$ or complex C-O-H\(^\#\) gases were detected. Within the limits of analytical uncertainty, the species compositions of the fluids compare very favorably with compositions predicted from the thermodynamic calculations for $f_{H_2O}$ between MH, OH and NNO, OH. Those calculations were made using the program and data described by Holloway and Reese (1974) for $T = 960^\circ C$ and $P = 4.4$ kbar. Table 3 and Appendix II in Holloway and Reese should be consulted for representative minor and trace species.

Solubility of $CO_2$ and $N_2$ in Albite Melt

Quantitative analysis has shown that at $P_t = 4.4$ kbar the solubility of $CO_2$ in albite glass is roughly 0.1 wt percent/kbar $P_{CO_2}$. Thus the mole percent $CO_2$ in the liquid (assuming a molecular weight of 262 for anhydrous liquid albite) ranges from 0.5 to 2.2, depending on $X_{CO_2}$ in the fluid. Rough comparison with the freezing point depression of albite due to dissolved $H_2O$ suggests that the depressant effect of $CO_2$ on the albite solidus will not exceed $-10^\circ C$. Figure 2 illustrates the relationship between the $N_2$ content of albite glass and the partial pressure of $N_2$, and shows that the solubility of $N_2$ in albite glass at 4.4 kbar is negligible.

Melting of Albite

No graphite, nitrides, oxynitrides, or carbonates were observed in the run products. Albite glass can be identified without difficulty in the charge and in grain mounts. In all runs above the solidus, crystals

\[\text{Fig. 2. Solubility of nitrogen in albite glass is illustrated as a function of } P_{N_2}. \text{ Numbers beside each point refer to load pressure (kbar).}\]
and glass were both present, and melting typically occurred on the outer portions of the charge, with the amount of melt produced depending on the duration of the run. Low refractive index isotropic spheres which are occasionally found on the capsule walls in runs both below and above the solidus are believed to be fluid phase precipitates. The results of Shettel (1973) suggest that the solubility of NaAlSi₃O₈ in these H₂O-poor fluids is considerably less than its solubility in pure H₂O fluids.

Figure 3 shows published solidus curves for albite with \( X(\text{nom})_{H_2O} = 1.0, 0.5, \) and zero. Critical runs bracketing the solidus with \( X(\text{nom})_{H_2O} = 0.25 \) at 4.4 kbar lie within the black rectangle which also corresponds to the \( P-T \) field of Figure 4. The results of the critical runs for each of the three fluids are illustrated in Figure 4, and a complete listing of experimental results is contained in Table 2. The solidus temperatures of 957°C, 958°C, and 958°C for fluids with \( X(\text{nom})_{H_2O} = 0.5, 0.25, \) and zero respectively are the same within experimental precision (±2°C).

**Estimate of \( \gamma_{H_2O} \)**

Because the solidus temperatures for the three fluids are identical within experimental precision, one can reasonably conclude that \( \gamma_{H_2O} \) is essentially independent of the \( \text{CO}_2/\text{N}_2 \) ratio in the fluid.

The experiments also yield an estimate of the value of \( \gamma_{H_2O} \) at 960°C and 4.4 kbar. Figure 5 illustrates the relationship between \( a_{H_2O} \) and the temperature of the albite solidus at 4.4 kbar. The solid curve is a second degree polynomial fitted to points taken from published albite solidi with \( X_{H_2O} = 1.0, 0.5, \) and zero (see Fig. 3 for sources). The activity values used in calculating the curve were obtained assuming activity coefficients of unity at \( X_{H_2O} = 1.0 \) and zero, and \( \gamma_{H_2O} = 1.2 \) at \( X_{H_2O} = 0.5 \) (the latter value from personal communication with C. Wayne Burnham, Pennsylvania State University, 1973). The dashed curve is similar, except that \( \gamma_{H_2O} \) at \( X_{H_2O} = 0.5 \) is chosen as unity. In order for the experimentally-determined albite solidus to fall on the solid curve, the value of \( \gamma_{H_2O} \) at \( X_{H_2O} = 0.25 \) must be about 1.8; this implies a significant positive deviation from ideality. However, because of the method of calculation, the estimated value of \( \gamma_{H_2O} \) at \( X_{H_2O} = 0.25 \) is very dependent on the value chosen for \( \gamma_{H_2O} \) at \( X_{H_2O} = 0.5 \). For example: if the experimentally-determined solidus were to lie on the dashed curve, \( \gamma_{H_2O} \) at \( X_{H_2O} = 0.25 \) would be about 1.2. Due to this
uncertainty, as well as the possibility of minor additional freezing-point depression due to dissolved \( N_2 \) and \( CO_2 \), we suggest that the estimate of \( \gamma_{H_2O} = 1.8 \) at \( X_{H_2O} = 0.25 \) be considered an upper bound.

**Acknowledgments**

This research was supported by NSF Grant GA-32442. We are indebted to C. F. Lewis and F. Delles of the Center for Meteorite Studies, Arizona State University, for the carbon and nitrogen analyses. We thank D. R. Waldbaum for suggestions which improved the manuscript, and C. Wayne Burnham for sharing his unpublished information on the activity of \( H_2O \) in \( H_2O-CO_2 \) mixtures.

**References**


Manuscript received, August 1, 1973; accepted for publication, February 15, 1974.